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BASIC FACTS OF GENERAL CHEMISTRY

I

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W. B. SAUNDERS COMPANY

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PREFACE

The author believes that the contents of this small text present the basic facts of general chemistry in a palatable, digestible and assimilable form. The author further believes that the average student—employing an average amount of effort—can master the complete text without auxiliary explanation. These presumptuous beliefs stem from the great care exercised in the preparation of the text, and from the favorable remarks expressed by the author's students concerning his technique of presentation. Every page of the manuscript was read by the author's non-chemist wife. Whenever she experienced the slightest difficulty in comprehension, the wording was altered accordingly. Various sections of the manuscript were also read by students. Their collective degree of comprehension—as ascertained by interrogation—served as a most valuable guide in the writing of those particular sections.

The scope of the text is commensurate with any academic program where a short course in general chemistry is offered or required. Since the bulk of such programs (e.g., nursing, home economics, nutrition, physical education, health, etc.) are either directly or indirectly concerned with the biological sciences (especially physiology), most of the applications have been in that area. The student nurse, for example, will discover that the chemical aspects of pharmacology, physiology and microbiology are presented *in toto*. In no case, however, has the author allowed any segment of the book to be prostituted by specific applications peculiar to a given profession. The nurse, for example, will not be told how to administer ether, and the student of nutrition will not find a table of calories. Such a practice interferes with the logical development of ideas, and destroys the book for all concerned.

The sequence of presentation is of paramount importance in a book of introductory chemistry. To be early or tardy in the introduction of a new idea usually dooms the idea and the galaxy of thoughts which the idea was supposed to have created. For this reason, every attempt has been made to synchronize all facts. The scheme of the book is as follows: Chapters 1 to 5 present the essential ideas and mechanics of inorganic chemistry; Chapters 6 and 7 apply the facts of the foregoing chapters to important elements and their compounds; Chapter 8 demonstrates the value of arithmetic in dealing with chemical problems; Chapter 9 is devoted to the principles and applications of colloidal

chemistry; Chapter 10 presents a synopsis of the cardinal facts of organic chemistry; Chapter 11 presents a synopsis of the chief biochemical reactions in physiology; and Chapter 12 discusses the present status of nuclear chemistry.

It is hoped that instructors will find this small text a refreshing change. The lack of a suitable chemistry in nursing, for example, has long been recognized by the author and his associates. As a matter of fact, this was the prime motive behind this work. Although time is the ultimate judge of any book, the author believes that an improvement has been presented.

The author wishes to acknowledge the assistance of Mrs. Marie E. Litterer in the preparation of the illustrations.

STEWART M. BROOKS

March, 1956

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CHAPTER 1

INTRODUCTION

Matter and energy constitute the universe. Matter is said to be anything which occupies *space* and has *weight*, while energy is probably best defined by saying that it is the *ability to do work*. Just what energy really is seems at present to be beyond even our loftiest of minds. However, all of us are familiar with its common forms and manifestations. The six common forms of energy are: *heat, mechanical, electrical, chemical, light and sound*. From a practical point of view, then, anything which gives us power, and is not capable of occupying space or having weight, is energy—all else is matter. In this work we shall be concerned with the study of matter—*chemistry*. The study of energy is called *physics*.

LAW OF CONSERVATION OF MATTER

Experimentally established by the great French scientist and father of chemistry, Lavoisier, the Law of Conservation of Matter states that *matter is neither created nor destroyed, but may be changed from one form into another*. Before Lavoisier's time this was not appreciated because scientists were misled by the phenomenon of burning. They reasoned that the substance which burns is changed into a weightless state which escapes into the air, never to be returned. By an ingenious experiment Lavoisier removed this fallacy, and made way for future scientists to develop the beautiful science of chemistry. He proved that when a substance burns in air it combines with oxygen and actually becomes heavier, because the substance now has the additional weight of the oxygen. This principle can be readily demonstrated by burning a piece of magnesium ribbon and then weighing the white ash which remains—the ash weighs more than the original ribbon!

LAW OF CONSERVATION OF ENERGY

The Law of Conservation of Energy is identical to the above. It is common experience that energy may change from one form into another form. That the form disappears is true, but the energy which it possessed is of the same magnitude in the new form. When heat is applied to water, and the steam is made to turn a wheel, and the wheel in turn

made to run a generator to produce electricity, we are passing through three forms of energy: heat, mechanical and electrical. Theoretically, the quantity of electrical energy is equal to the quantity of heat energy.

A REVISED CONCEPT

Our atomic age has suggested some drastic changes in fundamental thinking relative to matter and energy. A concert of genius, effort and billion-volt machines has enabled man to look closer at the true "substance" of the earth and the universe. It is now a known fact that matter can be transformed into energy. This was predicted by Einstein in his now famous equation, $E = mc^2$; i.e., energy equals mass (matter) times the speed of light squared; this fact was established by the first atomic blast. Although the Law of Conservation of Matter seems to be somewhat voided by this fact, let us not lose sight of its tremendous value to "everyday chemistry," which is what concerns us here. For all practical purposes, the law stands. It is interesting to note, however, that some scientists believe that energy and matter are one and the same. They look upon matter as being concentrated energy. Although it is not possible to conceive of this in conventional terms, modern mathematics and atomic research allow considerable support. At any rate, this concept gives us a better understanding of what is implied by those scientists who make mention of a "unified theory."

CHANGES IN MATTER

Matter may undergo two kinds of changes: *physical* and *chemical*. Any change which *does not alter* the composition of a substance is called a physical change. The breaking of glass, the melting of ice, and the boiling of water are physical changes because their internal constitution remains the same. Water is water whether it is ice or steam; and glass is glass whether it is in the window or smashed into pieces by a student who should have been studying chemistry. On the other hand, any change which *alters* the composition of a substance is a chemical change. In this type of change one or more new substances are formed from the original substance. The souring of milk, the rusting of iron, the burning of paper, and the explosion of gunpowder are examples of chemical changes. In each instance the internal composition has been altered in such a way that the original substance no longer exists.

CHEMICAL AND PHYSICAL PROPERTIES

The chemist is exact and precise in his description of matter. Once a new substance is discovered he makes a careful study of all its properties. The properties which are ascribed to pure chemical substances

are of two kinds: *chemical* and *physical*. A physical property is a characteristic of a substance which may be ascertained or observed without chemical action; a chemical property is a characteristic which is determined by observing its action, or lack of action, with other substances. To illustrate, let us consider the well-known gas oxygen. Oxygen is colorless, heavier than air, and insoluble in water; these are its physical properties. The fact that it reacts with other substances to support combustion is a chemical property. Since it does burn itself, this would be a chemical property of a negative nature. Any large work on chemistry always contains a detailed account of the physical and chemical properties of important compounds.

STATES OF MATTER

Matter may exist in three states, or forms: *solid*, *liquid* and *gaseous*. A solid is characterized by its definite shape and volume; a liquid by its definite volume and readiness to assume the shape of the receptacle into which it is placed; and a gas by its indefinite shape and volume. Many substances may exist in two or all three states. Such a substance, however, retains the same composition regardless of its state. As pointed out above, water is water whether it is liquid, steam or ice. The change of state is a physical act. It is now known that the three states of matter are merely examples of an energy differential. In the solid condition the molecules (to be discussed later) have little energy and, therefore, possess little motion. This allows for more compactness and accounts for the density of the solid state. In the gaseous state the molecules of a substance have the greatest amount of energy, and are in rapid motion. This accounts for the swift movement and diffusion of the gaseous state. The liquid state is merely an intermediate energy level. The energy differential of the three states is readily appreciated when one compares the amount of energy needed to convert ice and water to steam. Since ice, the solid state, represents a lower energy level than liquid water, it follows that more heat energy must be added to the former than the latter.

KINDS OF MATTER

First of all let us attempt to explain what we mean by the rather awkward term, substance. As may be inferred by those who have read this far, the word has been employed already many times for the want of a better noun. A glance at the dictionary will convince one of its fluid character. Perhaps it is best to say that it is synonymous with the word matter, and used frequently in this text to avoid monotony. To be sure, there are three kinds of matter (or substances): *elements*, *compounds* and *mixtures*.

Elements. *An element is a substance which cannot be decomposed into simpler material by any ordinary chemical means.* (Years ago an element would have been defined simply as a substance which cannot be decomposed into simpler material, with the phrase "by ordinary chemical means" omitted. Subsequently we shall see that this change was caused by our present concept of atomic structure.) The earth and its flora and fauna are constituted by 92 of these elemental substances in an astronomical number of combinations. All things which compose our material world are either elemental in nature or, as is usually the case, composed of a combination of elements. In order that the chemist may conveniently describe the constitution of matter he employs a system of chemical shorthand whereby each element is assigned a *symbol*. The symbol consists of one or two letters of the English or Latin name of the element. The following elements are important to us because they are the principal constituents of our biologic world:

<i>Element*</i>	<i>Symbol</i>
Oxygen	O
Carbon	C
Hydrogen	H
Nitrogen	N
Calcium	Ca
Phosphorus	P
Potassium	K
Sulfur	S
Sodium	Na
Chlorine	Cl
Magnesium	Mg
Iron	Fe
Manganese	Mn
Copper	Cu
Iodine	I

* See Appendix for complete list of elements.

CLASSIFICATION OF THE ELEMENTS. Elements are classified into two general classes: *metals* and *nonmetals*. Chemically, some elements exhibit both metallic and nonmetallic properties; such elements are called *amphoteric* elements. The table below presents the more characteristic properties of metals and nonmetals.

	<i>Metals</i>	<i>Nonmetals</i>
Physical Properties	Lustrous All solids (except mercury) at room temperature Generally high density Good conductors of electricity	Nonlustrous Solids and gases at room temperature Low density Poor conductors
Chemical Properties	Have an affinity for nonmetals; do not chemically combine with each other	Have an affinity for metals; do not combine with each other

Compounds. *A compound is a substance consisting of two or more elements chemically united; that is, combined in such a manner that each constituent element has lost its individual characteristics.* Each compound has its own static personality by virtue of another very basic law of chemistry: the *Law of Definite Proportions*. The Law of Definite Proportions states that when two or more elements chemically combine, they always do so in a *definite proportion* by weight. If this were not true, and elements were as changeable as the weather in the proportion in which they combined with one another, the resulting compound would have variable properties. That this is not the case is most fortunate, for it would mean that when hydrogen and oxygen combine to form water in Moscow it would not necessarily be the same as water formed from a combination of hydrogen and oxygen in the city of New York. The Law of Conservation of Matter and the Law of Definite Proportions, then, render validity to the whole science of chemistry, for without matter's unyielding devotion to these two principles man would be unable to have confidence in his material world. Cane sugar, table salt and water are three common examples of true compounds.

Mixtures. *A mixture is a substance consisting of two or more elements or compounds not chemically combined and in any proportion.* Anything that is not a pure compound or a pure element is a mixture by virtue of deductive reasoning. Air, soil, petroleum, candy and blood are representative examples of mixtures. A mixture may be conveniently differentiated from a compound by reference to the following table.

<i>Mixture</i>	<i>Compound</i>
1. Constituents retain individual properties.	1. Do not retain properties.
2. No definite composition by weight.	2. Definite composition.
3. Can be separated into its constituents by mechanical means.	3. Can be separated only by chemical means.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- _____ matter
- _____ energy
- _____ matter destroyed
- _____ liquid to a gas
- _____ candy
- _____ chemical change
- _____ molecules in rapid motion
- _____ salt
- _____ nitrogen
- _____ poor conductors

Column II

- 1. a gas
- 2. $E = mc^2$
- 3. a mixture
- 4. ordinarily, neither created nor destroyed
- 5. work
- 6. nonmetals
- 7. a compound
- 8. ripening of a banana
- 9. physical change
- 10. an element

CHAPTER 2

STRUCTURE AND BEHAVIOR OF MATTER

What would the “end product” look like if one were to take a piece of matter, say a stone, and by some means break it up into an infinite number of pieces? More specifically, is there a fundamental unit of matter? If so, what is its structure and behavior? Man has pondered such questions for 2000 years. This chapter is concerned with the product of his efforts to supply the answers.

ATOMIC THEORY

In the year 1803, the brilliant deductions of John Dalton presented to man the first unified idea concerning the structure and behavior of matter. He proposed his deductions after deep consideration and appreciation of the two most fundamental laws of chemistry—the laws with which we are already familiar, the Law of Conservation of Matter and the Law of Definite Proportions.

Dalton's deductions, classically referred to as the *Atomic Theory*, make the following assumptions:

1. All matter is composed of very small particles, called atoms.
2. All the atoms of the same element are exactly alike in size, shape and weight, but differ in all respects from the atoms of every other element.
3. Atoms of most elements are able to unite with the atoms of other elements.
4. In all chemical changes atoms do not break up, but act as individual units.

As suggested in this theory, let us adopt the atom as our unit and see if we can refine the thoughts which have already been expressed. A slight glance at the second and third statements will crystallize the rather nebulous definitions which were offered for the element and compound. We said that an element was the simplest type of matter because it could not be broken down into a more simple substance by ordinary means. Although this is a valid definition, we are now able to offer an alternate and more precise description: *An element is a substance made*

up of like atoms. This explains in a very fundamental way why an element is the most elemental substance. A compound, then, may be considered in a similar way: *It is a substance composed of two or more kinds of atoms in a definite proportion by weight.*

The Atomic Theory has *essentially* withstood the test of time. Its most important contribution, however, is the fact that it has served as a stimulus to the fertile minds of the great atomic scientists who followed Dalton. Today we know that although the atom is a practical unit of the universe, there are still smaller particles which constitute the atom. The size of these particles is beyond the grasp of the human mind; that they exist is supported by the labors of our greatest minds in the fields of chemistry, physics and mathematics. The twentieth century concept of the atom is embodied in the *Electron Theory* of matter.

ELECTRON THEORY

This theory holds that the atom is an arrangement of particles not unlike the solar system. It explains and clarifies in an amazing manner what matter really is, and how and why it behaves as it does. The following are the cardinal concepts of this beautiful piece of human reasoning:

1. The atoms of all elements are made up of a characteristic number of positively charged particles called *protons* and negatively charged particles called *electrons*. The proton is about 2000 times as heavy as the electron.

2. The atoms of each element contain the same number of protons as electrons, and therefore are electrically neutral.

3. A dense central portion, called the *nucleus*, contains the protons. Also located in the nucleus are particles called *neutrons*. These particles are electrically neutral and are thought by some to be a union of an electron and proton; their weight is essentially that of the proton.

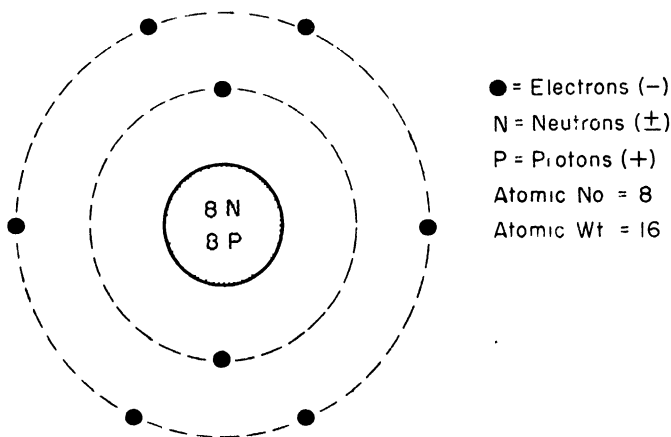
4. Around this nucleus swarm the electrons in a rather definite pattern. The pathways taken by the electrons in their rotation about the nucleus are called *orbits*, or *rings*. The number of rings, or orbits, about the nucleus depends upon the number of electrons.

5. As will be shown, the entire behavior of the atom is dictated by the number and spatial arrangement of these planetary electrons.

Atomic Number.* *The atomic number of an element is equal to the number of planetary electrons about the nucleus of each of its atoms.* Every element has its own characteristic number.

* The atomic number is also equal to the number of protons in the nucleus, and sometimes defined as such.

Atomic Weight. *The atomic weight of an element is equal to the sum of the neutrons and protons in the nucleus of each of its atoms.* A glance at the table of elements, however, will disclose that most elements do not have an *even* atomic weight. This is because an element is usually constituted by two or three varieties of atoms which are alike in every respect save the *number of neutrons* in their nuclei. Thus, the atomic weight of chlorine—35.5—represents the statistical average of its two types of atoms. One type, with 17 protons and 18 *neutrons*, has an atomic weight of 35 (constitutes 75 per cent of chlorine), while the other, with 17 protons and 20 *neutrons*, has an atomic weight of 37



ATOM OF OXYGEN

Fig. 1. A theoretical concept of the atom.

(constitutes 25 per cent of chlorine). Atoms of the same element which differ *only* in respect to their atomic weights are called *isotopes*. Thus, chlorine has 2 isotopes— Cl^{35} and Cl^{37} . The subject of isotopes will be discussed further when we study nuclear chemistry.

Figure 1 illustrates the basic principles of the Electron Theory as they apply to a common element.

VALENCE

A complete and thorough understanding of valence is essential to the understanding of chemistry. The student, therefore, should devote special attention to the following discussion. A little concentration and clear thought at this time will greatly simplify future chapters.

Before we define valence, let us see if we can anticipate its meaning. It was stated under the electron theory that an atom's planetary electrons

rotate about its nucleus in a rather definite pattern. Substantial evidence indicates that *the orbit, or ring, nearest the nucleus (called the first orbit or, more technically, the k orbit) can contain no more than 2 electrons, and the second and third orbits (l and m respectively) no more than 8 electrons each.* The maximal number of electrons permitted in each of the subsequent orbits (for example, n, o, p, etc.) may be 8, 18 or 32. Since many of the common and important elements have an atomic number which does not extend beyond the third, or m, orbit, we shall confine our discussion to the 2-8-8 distribution.*

An illustration at this time will be helpful. The element *argon* has an atomic number of 18. According to what was said above, the electronic pattern about the nucleus of an atom of argon is thus: 2 electrons are in the first orbit; 8 electrons are in the second orbit; and 8 in the third. The electronic configuration for any element with an atomic number less than that of argon (18) may be drawn by simply allotting the maximal number to the respective orbits. If this is done for all elements from hydrogen (atomic number of 1) to argon (atomic number of 18), *only three elements will have an outer orbit with the maximal number of electrons: helium, neon and argon.* The outer orbit of helium (which is really its first and only orbit) has the maximal number of 2; the outer orbit of neon (which is really its second orbit) has the maximal number of 8; and the outer orbit of argon (which is really its third orbit) has the maximal number of 8.

Now let us consider the ability of one element to react with some other element. Of the elements with atomic numbers from 1 through 18, only 3 are not capable of reacting with other elements—*helium, neon and argon* (these elements are said to be *inert*). It is a most interesting fact that each of these elements are constituted by atoms whose *outer orbits contain the maximal number of electrons.* In other words, all elements which are chemically active have *outer orbits which do not have the maximal number of electrons.* The chemist has theorized, therefore, that *elements react with one another in order to obtain an outer ring with the maximal number.* The careful reader will readily perceive the tremendous implication of this statement.

The principal implication is this: If elements react for the purpose of obtaining a maximal number of electrons for their atoms (evidently they are “happiest” in this state), we have an excellent explanation of why—according to Dalton’s Atomic Theory—elements always react in a definite way. For example, sodium (Fig. 2) has an outer orbit containing 1 electron; chlorine has an outer orbit containing 7 electrons. If the single electron of the sodium atom is taken away and given to the

* Atoms with an atomic number greater than 21 may contain up to 18 electrons in the third orbit.

chlorine atom, both atoms will be left with an outer orbit with a maximal number (Fig. 2). In other words, 1 atom of sodium *always* reacts with 1 atom of chlorine to form the compound sodium chloride. If chlorine reacts with aluminum, one atom of aluminum *always* combines (reacts) with 3 atoms of chlorine. This is so because the aluminum atom has 3 electrons in its outer orbit, and must lose these 3 in order to “expose” its

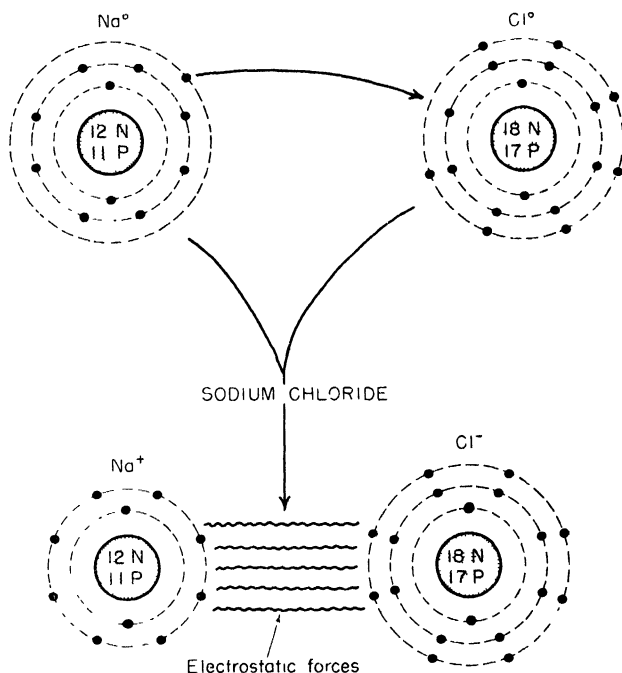


Fig. 2. The formation of sodium chloride by electrovalence.

second ring which has the maximal number of 8. Therefore, 3 atoms of chlorine are called into play because 1 atom of chlorine can accommodate or receive only one electron. Sodium, aluminum and chlorine are examples of elements which react—and thus satisfy their desire for the maximal number of electrons in their outer orbits (usually 8)—by a *gain* or *loss* of electrons. Most elements, however, accomplish the same thing by a *mutual sharing* of electrons. A simple example of mutual sharing is afforded by the reaction between the atoms of hydrogen and oxygen to form water. Figure 3 shows that 2 atoms of hydrogen and 1 atom of oxygen satisfy themselves by coming together and sharing 2 pairs of electrons. In this way oxygen has obtained a maximal number

of 8 (8 is the maximal number of the second orbit), and hydrogen a maximal number of 2 (2 is the maximal number of the first orbit).

At this time we are prepared to receive the definition of valence. Valence is defined as the *number of electrons gained or lost by an atom*;

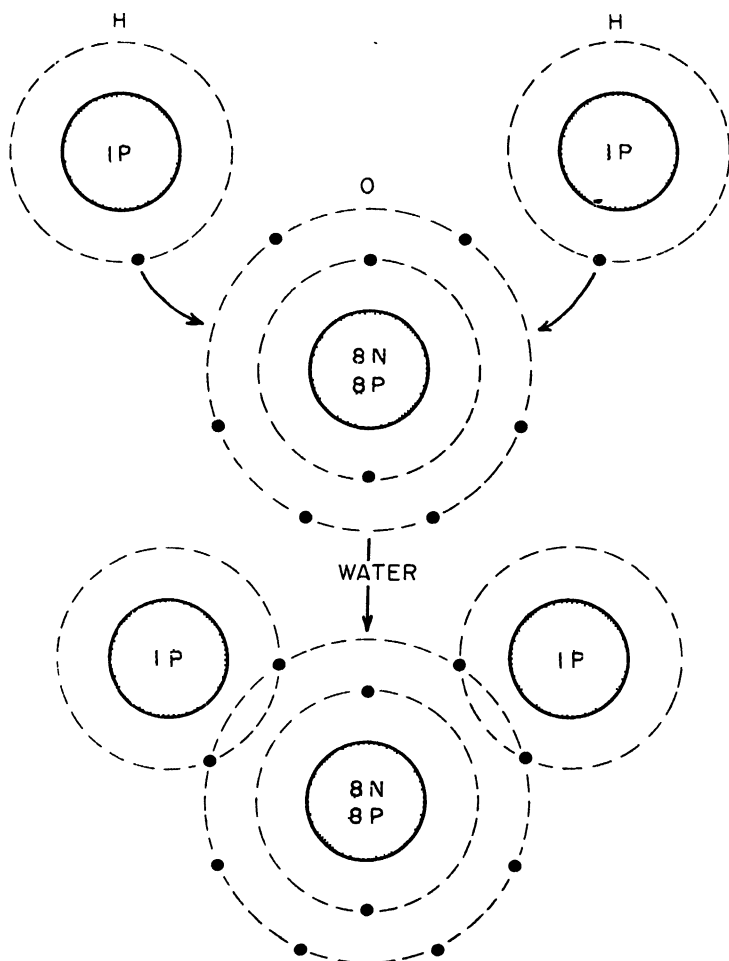


Fig. 3. The formation of water by covalence.

or as the *number of pairs of electrons shared by an atom*. Thus, in the above examples, sodium has a valence of 1 (loses 1 electron); chlorine has a valence of 1 (each atom gains an electron); aluminum has a valence of 3 (each atom loses 3 electrons); oxygen has a valence of 2

(each atom shares 2 pairs of electrons); and hydrogen has a valence of 1 (each atom shares 1 pair of electrons). It should be perfectly clear at this point that the valence of an element is its most important chemical property. By knowing an element's valence we can better understand and predict its chemical behavior. The principal application of valence will be presented in the following chapter. For the present, however, we need to refine our thoughts concerning this important term.

Electrovalence. Valence has been defined as the number of electrons gained or lost by an atom, or the number of pairs of electrons shared by an atom. Elements which gain or lose electrons are said to possess an *electrovalence*; those that share electrons, a *covalence*. It should be pointed out at this time, however, that both types of valence are *numerically* equivalent. Thus, when an element with a valence of 2 (whether covalent or electrovalent) reacts with an element whose valence is 1 (whether covalent or electrovalent), they react in the proportion of 1 atom of the former to 2 atoms of the latter. Since this is so, why do we concern ourselves with the two types of valence? Moreover, how do we know that there are two types of atomic combinations? The answer to the second question will be fully explained in a subsequent chapter. As to why we are interested in the two types of valence, it is because electrovalent compounds and covalent compounds have certain fundamental differences. One difference that may be stated at this time is the following: Electrovalent compounds when dissolved in water permit the solution to carry an electric current; covalent compounds do not. Other differences will be pointed out as we go along.

The formation of an electrovalent compound is represented in Figure 2. When the sodium atom—which is neutral—loses an electron it takes on a charge of plus 1 (Na^+). The chlorine atom which accepts this electron takes on a charge of minus 1 (Cl^-). Now we have 2 *oppositely* charged particles which obey the law of electricity which states that unlike charges attract, and like charges repel.* The Na^+ and Cl^- particles, therefore, are held together by electrostatic forces. X-ray examination of electrovalent compounds thoroughly substantiates the above explanation. A compound such as sodium chloride is visualized as being constituted by a definite pattern of Na^+ and Cl^- particles.

Elements such as sodium which lose electrons during a chemical reaction are said to have a *positive electrovalence*. For sodium this is expressed as Na^+ . Elements which gain electrons are said to have a *negative electrovalence*. For chlorine this is expressed as Cl^- . Similarly, the valence of aluminum is written as Al^{+++} , and read as a plus 3. Of extreme importance is the fact that all true *metals* possess a *positive*

* These charged particles are called ions. Ions will be discussed in a later chapter.

electrovalence; and all true *nonmetals*, a *negative electrovalence*.* From this we can readily see why metals do not chemically react with metals, and why nonmetals do not react with nonmetals. All electrovalent reactions, then, are between metals and nonmetals. The Table of Valences (p. 15) presents the important electrovalent elements.

RADICALS. A radical is defined as a *combination of elements which ordinarily acts as a chemical unit*. The term is presented here because radicals are extremely common in chemistry, and possess an electrovalence. All common radicals with the exception of ammonium (NH_4^+) have a negative electrovalence. Radicals may be considered as "elements." The various radicals and their valences are presented in the Table of Valences (p. 15). (*Radicals never exist in the free state.*)

OXIDATION AND REDUCTION. Throughout chemistry the terms oxidation and reduction are frequently employed. Oxidation when applied to valence (electrovalence) means a *loss of electrons*; reduction when applied to valence means a *gain of electrons*. An element is said to be *oxidized* when it loses electrons, and *reduced* when it gains electrons. In the reaction between sodium and chlorine (Fig. 2) the *sodium* becomes oxidized and the *chlorine* reduced. Unfortunately, these two terms are also used to describe reactions involving oxygen. In this connection, oxidation is defined as *the union of oxygen with some other element*, and reduction as *the removal of oxygen from some other element*. The distinction between the above definitions should be thoroughly understood.

Covalence. As stated above, covalence means a sharing of electrons. When oxygen combines with hydrogen to form water (Fig. 3), each atom of oxygen shares 2 *pairs* of electrons, and each atom of hydrogen shares 1 *pair* of electrons. Therefore, oxygen has a valence of 2, and hydrogen a valence of 1. Carbon, nitrogen, oxygen, phosphorus and sulfur are other common elements which react or combine via covalence. These elements and their valences are presented in the Table of Valences (p. 15).

There are many elements which possess both an electrovalence and covalence. Hydrogen, sulfur and oxygen are common examples. Hydrogen has an electrovalence of 1 and a covalence of 1; oxygen has an electrovalence of 2 and a covalence of 2; and sulfur an electrovalence of 2, and a covalence of 4 or 6.

Multiple Valence. Several elements—both electrovalent and covalent—have more than one *set* valence number. Important common elements of this type include: *mercury, copper, iron, sulfur and nitrogen*. These elements are composed of atoms which are capable of losing,

* The terms "true metal" and "true nonmetal" are used in a chemical sense. Sodium, for example—a "true metal"—is not a typical "metal" physically.

gaining, or sharing more than one *set* number of electrons. Iron (Fe), for example, sometimes loses 2 electrons and becomes Fe^{++} , and sometimes 3, and becomes Fe^{+++} . When the occasion arises, the above and additional information on this subject will be fully discussed.

Table of Common Valences

Electrovalent.

	<i>Metals</i>		<i>Nonmetals</i>
Aluminum	3 (Al^{+++})	Bromine	1 (Br^-)
Barium	2 (Ba^{++})	Chlorine	1 (Cl^-)
Bismuth	3, 5 (Bi^{+++}), (Bi^{++++})	Fluorine	1 (F^-)
Calcium	2 (Ca^{++})	Iodine	1 (I^-)
Copper	1, 2 (Cu^+), (Cu^{++})	Oxygen	2 (O^{--})
Hydrogen	1 (H^+)	Sulfur	2 (S^{--})
Iron	2, 3 (Fe^{++}), (Fe^{+++})		
Lead	2 (Pb^{++})		
Magnesium	2 (Mg^{++})		
Mercury	1, 2 (Hg^+), (Hg^{++})		
Nickel	2 (Ni^{++})		
Potassium	1 (K^+)		
Silver	1 (Ag^+)		
Sodium	1 (Na^+)		
Tin	2, 4 (Sn^{++}), (Sn^{++++})		
Zinc	2 (Zn^{++})		

Radicals

Ammonium	1 (NH_4^+)
Bicarbonate	1 (HCO_3^-)
Carbonate	2 (CO_3^{--})
Chlorate	1 (ClO_3^-)
Hydroxyl	1 (OH^-)
Nitrate	1 (NO_3^-)
Nitrite	1 (NO_2^-)
Phosphate	3 (PO_4^{---})
Sulfate	2 (SO_4^{--})
Sulfite	2 (SO_3^{--})

Covalent:

Carbon	4
Hydrogen	1
Nitrogen	1, 2, 3, 4, 5
Oxygen	2
Phosphorus	3, 5
Sulfur	4, 6

Hydrogen. Hydrogen holds a most unique position among the elements—it is the simplest of them all. An atom of hydrogen is constituted by only 1 proton and 1 electron. Since in a chemical reaction the hydrogen atom loses this 1 electron, it has a valence of a plus 1 (H^+). For this reason, hydrogen—chemically—is considered as a metal. Hydrogen will be discussed in the chapter on metals.

PERIODIC TABLE

In the latter part of the nineteenth century the Russian chemist, Mendeléeff, thought it would be most interesting if he could juggle the elements around in such a manner that some sort of relationship might be shown. To the amazement of the scientific world, and no doubt to himself, Mendeléeff demonstrated that when the elements (omitting hydrogen) were arranged in order of their atomic weights, there was noted a periodic recurrence of similar chemical properties. In general, the "periods" were of the same length—8 elements. Now, if these periods were placed under one another, all of these similar elements fell into vertical columns. Mendeléeff's table, however, later proved to have certain discrepancies which could not be resolved in light of the dictates of the Electron Theory. Moseley's work in England in the early part of this century resulted in a revised Periodic Table (Fig. 4) which obviated the difficulties of the old one. Elements which were obviously out of place in the original table were easily maneuvered into the correct position when Moseley arranged them according to their atomic numbers rather than their atomic weights. The original *Periodic Law*, then, which stated that the properties of the elements are periodic functions of their atomic weights, now reads: *The properties of the elements are periodic functions of their atomic numbers*. The secret of the table will be disclosed if we appreciate the fact that the elements are arranged according to their atomic numbers. Elements of the same vertical column, or *group*, are similar because their atomic numbers are such that the outer orbits of their atoms have the same number of electrons and, hence, the same valence. Thus, the elements lithium, sodium and potassium in Group I (Fig. 4) are alike in their chemistry because each has a valence of 1.

The Periodic Law has proven of incalculable value in the development of chemistry. No doubt its greatest gift to the science has been its suggestions of the existence of certain undiscovered elements, which have subsequently been discovered. In the older tables gaps were present, because often throughout the table there were considerable differences in either the atomic weight or atomic number of neighboring elements. From the physical and chemical properties of the known elements, the "gap elements" were predicted with uncanny accuracy.

From a student's standpoint, the greatest value of the table resides in its simplification and unification of the whole subject of chemistry. If it were not for the system of classification employed in biology, the biologist would have no grasp of the astronomical number of diversified organisms which roam the land, fly the air and swim the sea. He would not live long enough, regardless of his intellect, to study all the forms of

life and draw conclusions. With his marvelous system of classification, however, it is not necessary for the biologist to study all the creatures. It is sufficient, indeed, for him to place thousands of similar organisms together into a single class. And so it is true in chemistry. By an appreciation of the implications of the Periodic Table the student always has at hand a powerful tool to cope with the huge number of chemical substances which constitute the earth. Specifically, if one is familiar with

PERIODIC TABLE																			
GROUPS PERIOD.	O		I		II		III		IV		V		VI		VII		VIII		
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B			
1			I H																
2	2 He		3 Li		4 Be		5 B		6 C		7 N		8 O		9 F				
3	10 Ne		11 Na		12 Mg		13 Al		14 Si		15 P		16 S		17 Cl				
4	18 A		19 K		20 Ca		21 Sc		22 Ti		23 V		24 Cr		25 Mn		26 Fe	27 Co	28 Ni
				29 Cu		30 Zn		31 Ga		32 Ge		33 As		34 Se		35 Br			
5	36 Kr		37 Rb		38 Sr		39 Y		40 Zr		41 Nb		42 Mo		43 Te		44 Ru	45 Rh	46 Pd
				47 Ag		48 Cd		49 In		50 Sn		51 Sb		52 Te		53 I			
6	54 Xe		55 Cs		56 Ba		57-71 RARE EARTHS		72 Hf		73 Ta		74 W		75 Re		76 Os	77 Ir	78 Pt
				79 Au		80 Hg		81 Tl		82 Pb		83 Bi		84 Po		85 At			
7	86 Rn		87 Fr		88 Ra		89 Ac		90 Th		91 Pa		92 * U						

Fig. 4. * Nine artificial elements lie beyond U 92. These are the so-called "transuranium elements": Np 93, Pu 94, Am 95, Cm 96, Bk 97, Cf 98, F 99, Mv 100, Fm 101.

the chemical and physical properties of a group, he is familiar with the chemical and physical properties of its members. At appropriate places throughout the text the properties of these groups will be disclosed by a thorough presentation of representative elements.

A few points concerning the Periodic Table require clarification. The Group number (0-VII) indicates the typical valence of all the elements in that particular group. Group 0 is so designated because—as explained before—these elements have a "full" outer orbit, and do not react with other elements; i.e., they are *inert*. Elements of Group I are constituted by atoms whose outer orbits contain 1 electron; hence they possess a valence of plus 1. Elements of Group VII are constituted by atoms

whose outer orbits contain 7 electrons; hence they have a valence of minus 1. It is evident, therefore, that the true metals are located on the left side of the table (Groups I, II and III), and the true nonmetals on the right side (Groups VI, VII). The elements occupying the central portion of the table (since they contain 4 or 5 electrons in the outer orbits) are covalent. Elements in this area are also *amphoteric*; i.e., they resemble metals in some respects, and nonmetals in other respects.*

It is to be noted that each Group, with the exception of Group 0 and Group VIII, is divided into two *Families*—A and B. The elements of a family are almost *identical* in their chemical behavior, but differ considerably sometimes from the elements of its neighboring family—even though the elements of both have the same valence. The elements of Group I, for example, display a closer relation to each other than they do to the elements of any other Group in the table. Within the Group, however, a finer classification exists; i.e., lithium, sodium and potassium, of Family A, are very similar chemically, but differ considerably (chemically) from copper, silver and gold of Family B.

It is to be also noted that the lengths of the 7 *Periods* vary. Periods 2, 3, and 7 are the so-called “short” Periods—7 or 8 elements in length; 4, 5 and 6 are the so-called “long” Periods—18 or 19 elements in length; and Period 1 contains only 1 element—hydrogen. Suffice it to say that such an arrangement is necessary in order to have similar elements fall into the same Group.

The elements referred to as the *rare-earth metals* (whose atomic numbers range from 57–71) occupy the same position in Group III of the Table. These 15 rare elements are very similar in their chemical properties. They are only of theoretical interest.

In addition to the 92 natural elements, there are 9 *artificial elements* which have been produced in various “atomic machines.” These elements follow uranium (atomic number, 92) in the Table. They will be discussed in the chapter on “Nuclear Chemistry.” At the present time, therefore, there are 101 elements. There is good reason to believe that additional man-made elements are possible.

* Elements of Group VIII slightly resemble the elements in Groups VI and VII.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- _____ like atoms
- _____ unlike atoms in a definite proportion
- _____ a chemical reaction
- _____ atomic number
- _____ atomic weight
- _____ Periodic Table
- _____ of similar chemical properties
- _____ chemically inert
- _____ combining power
- _____ electrostatic forces
- _____ sharing of electrons
- _____ metals
- _____ nonmetals
- _____ an atom gains 2 electrons
- _____ radical

Column II

- 1. covalence
- 2. an element
- 3. an orderly arrangement of the elements
- 4. valence
- 5. a group of atoms which acts as a unit
- 6. a compound
- 7. lose electrons
- 8. member of a Family
- 9. a charge of -2
- 10. equal to protons plus neutrons
- 11. gain electrons
- 12. 8 electrons in outer orbit
- 13. equal to planetary electrons
- 14. when atoms of one element unite with atoms of another
- 15. hold electrovalent compounds together

1. Draw an atom of calcium.
2. Differentiate: valence, electrovalence and covalence.
3. Draw a molecule of magnesium chloride (see Fig. 2).
4. Why are the elements of Group 0 chemically inert?
5. Why are Groups of the Periodic Table divided into Families?

CHAPTER 3

THE MOLECULE, FORMULA, REACTION AND EQUATION

In this chapter we shall become familiar with the tools the chemist employs for expressing the behavior of matter in his test tube. If it were not for his wonderful system of shorthand, the chemist would indeed be seriously handicapped. The rapid growth of chemistry is due in no small part to the highly efficient methods afforded by the formula and equation. The molecule, formula, reaction and equation are intimately related terms.

THE MOLECULE

Although the atom is our true practical unit of chemistry, we must now consider another unit of practical as well as theoretical importance, the molecule. A molecule may be defined as the *smallest particle of a compound that retains the characteristics of the original substance*. For example, if we were to degrade the familiar compound sodium chloride (our common table salt) into smaller and smaller pieces, theoretically we would arrive at a particle, the molecule, which would be constituted by 2 lonely atoms, sodium and chlorine. This is the smallest particle of salt possible, for if it were to be split any further these 2 atoms would be freed from one another, and our compound would then cease to exist.

It has been shown that our common gaseous elements, oxygen, hydrogen, nitrogen, chlorine, and so on, exist in a condition where 2 atoms occur together rather than singly, as is usually the case with elements. Since this is so, we say that these elements are in the molecular condition. A molecule of oxygen, then, would consist of 2 atoms of oxygen.

THE FORMULA

The chemist says that the formula for salt is NaCl ; the formula for water, H_2O ; the formula for sulfuric acid, H_2SO_4 ; and so on. For every known compound the chemist has a formula. What is the meaning and significance of this term? The formula has a definite meaning in chemistry: *It tells us the composition of a molecule*. The Law of

Definite Proportions told us, and still tells us, that when atoms of elements combine to form molecules of a compound they always do so in a definite proportion by weight. Another way of saying the same thing is that the same number of atoms is always involved; hence, a molecule of a compound always has the same number of atoms. Since this is so, it is possible to assign a definite statement to each compound concerning its composition—the *formula*. Therefore, the formula “NaCl” means that in every molecule of our favorite condiment there is 1 atom of sodium and 1 atom of chlorine; the formula “H₂O” means that in every molecule of water on the earth there are 2 atoms of hydrogen and 1 atom of oxygen; and the formula “H₂SO₄” means that in every molecule of sulfuric acid there are 2 atoms of hydrogen, 1 atom of sulfur, and 4 atoms of oxygen.

The next point we should consider is how the chemist knows the kind and number of atoms in the molecule of a certain compound. True, he knows that the number is constant, but this does not indicate the formula. However, the chemist can demonstrate the kinds of atoms in the molecule by the methods of *qualitative analysis*. This is the branch of chemistry which is concerned with the diagnostic chemical and physical properties of elements and compounds. (In future chapters we shall have occasion to study some of the important aspects of this fascinating branch of chemistry.) The number of atoms is ascertained by the methods of *quantitative analysis*. In essence, a quantitative study is carried out by taking a known weight of the compound under investigation, and decomposing it into its constituent elements. The quantity of each element found is then expressed on a percentage basis. The number of atoms of the element can now be obtained by dividing the percentage of the element by its atomic weight. For example, if we were to decompose 9 lbs. of water by some means, such as an electric current, 1 lb. of hydrogen and 8 lbs. of oxygen would be liberated. On a percentage basis, this means that water is composed of 90 per cent oxygen and 10 per cent hydrogen. Now, if we divide these relative weights, i.e., the percentages, by the relative weights of their respective atoms, i.e., their atomic weights, we shall obtain the number of atoms of each element in a molecule of water. Thus, 90 divided by 16, the atomic weight of oxygen, is 5;* 10 divided by 1, the atomic weight of hydrogen, is 10; hence, the ratio of hydrogen atoms to oxygen atoms is 2 to 1, and there are, therefore, 2 atoms of hydrogen and 1 atom of oxygen in every molecule of water.

Fortunately it is not necessary for us to carry out the analysis of every compound to ascertain its formula. This is only necessary when the chemist is dealing with an unknown substance. The formula for any

* Approximately.

compound may be written if we know its constituent elements. This is possible by virtue of a concept with which we are already familiar—valence. The rule is this: *Valences of the elements of a compound must always balance.* The first step is to write down the symbols for the elements present, and next to supply the appropriate number or numbers (called *subscripts*) to the symbols in such a way that the numbers multiplied by the respective valences produce equal products. For example, what is the formula for hydrogen sulfide? Well, we know from the name that hydrogen and sulfur are the constituent elements, so we write down their symbols, H, S. The valence of hydrogen is 1; the valence of sulfur, 2. In this form the valences do not balance, so we must supply the appropriate subscript or subscripts. Just a glance at the problem indicates that by taking 2 atoms of hydrogen to 1 atom of sulfur we have the desired solution, for 2 times the valence of hydrogen, 1, is 2; thus, the correct formula is H_2S . Regardless of the complexity of the compound the general rule applies. If we take another look at the illustration depicting the reaction between sodium and chlorine (Fig. 2), we shall readily see why the rule is true. The illustration makes it quite clear that when atoms lose electrons, other atoms must be present to accept them, and vice versa. But even more important is the fact that only a set number of atoms can play the game, since the outer orbit of an atom must have a set number of electrons. In the case of the sodium-chlorine reaction, the sodium lost 1 electron, so only 1 atom of chlorine, which contains 7 electrons in its outer orbit, was called into play. If chlorine were to react with calcium to form calcium

<i>Compound</i>	<i>Symbol and Valence of Constituent Elements and Radicals</i>	<i>Formula*</i>
Water	H, 1; O, 2	H_2O
Sodium chloride	Na, 1; Cl, 1	NaCl
Carbon dioxide	C, 4; O, 2	CO_2
Sulfuric acid	H, 1; SO_4 , 2	H_2SO_4
Hydrogen chloride	H, 1; Cl, 1	HCl
Calcium hydroxide	Ca, 2; OH, 2	Ca(OH)_2
Calcium chloride	Ca, 2; Cl, 1	CaCl_2
Aluminum sulfate	Al, 3; SO_4 , 2	$\text{Al}_2(\text{SO}_4)_3$
Aluminum chloride	Al, 3; Cl, 1	AlCl_3
Aluminum nitrate	Al, 3; NO_3 , 1	$\text{Al(NO}_3)_3$

* By convention, the positive element in electrovalent compounds is written first; in covalent compounds, the element with the higher valence is written first.

chloride, 2 atoms of chlorine are required, for the calcium atom has 2 electrons to give away, i.e., CaCl_2 .

The rule for writing formulas applies equally to electrovalent and covalent compounds. As we know, there are a few elements which have variable valences, depending upon the nature of the other elements with which they react. Thus, sulfur may have a valence of 2, 4 or 6. This does not present a problem since a little experience and practice with the element concerned indicates which of its valences are involved.

When writing the formula for a compound containing a radical (i.e., SO_4 , CO_3 , NO_3 , etc.), it is only necessary to remember that the radical acts as a chemical unit, and has a characteristic valence just as the element. For example, the formula for aluminum nitrate is $\text{Al}(\text{NO}_3)_3$. Since the NO_3 radical has a valence of 1, 3 of them must be present to balance the valence of aluminum which is 3.

The table on page 22 presents some common compounds and their formulas. The formula in each case may be confirmed by applying the rule and technique presented above.

THE REACTION

A great deal has been said about the interaction of atoms; i.e., we have concerned ourselves with the theoretical aspects of chemical activity. Now is the time and place for us to consider activity on a larger scale, i.e., the reaction in the laboratory. But let us never lose sight of the fact that what happens in the test tube is merely an amplification of atomic phenomena.

A *chemical reaction* occurs when two or more substances react with one another to produce new substances. The chemical changes mentioned earlier in the text are now seen to be the result of chemical reactions. Thus, the burning of paper is a chemical change because the elements of the paper—carbon, hydrogen and oxygen—react with the oxygen in the air to form the new substances, carbon dioxide and water.

Most chemical reactions release energy in the form of heat—*exothermic reactions*. Energy in the form of light and electricity* is released by a few reactions. However, even in these cases heat is usually present. A chemical reaction may liberate its energy gradually, as do those reactions within our bodies, or with explosive violence as when we pull the trigger of a gun. There are some reactions that will not occur unless energy is supplied either in the form of heat, light or

* A battery is the best example. A battery is made by placing two unlike metals (electrodes) in an electrolyte solution. When strips of copper and zinc are placed in a solution of sulfuric acid, and the strips connected to a voltmeter, a voltage is shown.

electricity. Reactions which require heat in order to take place are called *endothermic* reactions.

THE EQUATION

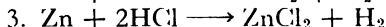
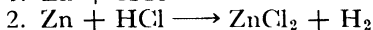
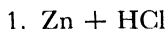
What happens in the test tube, i.e., the chemical reaction, is succinctly described and explained by the *chemical equation*. The following steps present the manner in which an equation is written:

1. Write the symbol or formula for each of the substances participating in the reaction to the left of an arrow.

2. In a similar manner express the products formed on the right side of the arrow.

3. Balance the equation by placing appropriate numbers (called *coefficients*) before the symbols or formulas in such a way that the number of atoms of each element is the same on both sides of the equation.

Let us see how the above steps apply to a specific reaction, e.g., the reaction between zinc and hydrochloric acid to form zinc chloride and hydrogen. The equation is written thus:



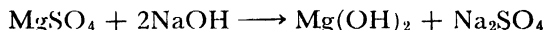
Our complete balanced equation for the reaction between zinc and hydrochloric acid reads: 1 atom of zinc plus 2 molecules of hydrochloric acid yield 1 molecule of zinc chloride plus 1 molecule of hydrogen.

In order that we may be able to balance correctly most equations in general chemistry the following points are important to remember:

1. The subscripts of the formulas must *never* be tampered with when balancing. Remember what the Law of Definite Proportions says: The composition of a compound is constant.

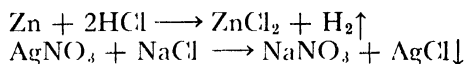
2. When dealing with our common gaseous elements whose molecules contain 2 atoms (H_2 , O_2 , N_2 , etc.), they should be written as such in the equation, and not as their symbols (H , O , N , etc.).

3. During a chemical change radicals usually remain intact and are, therefore, treated as chemical units. For example, in the reaction between magnesium sulfate (MgSO_4) and sodium hydroxide (NaOH), the sulfate radical, SO_4 , and the hydroxyl radical, OH , merely change partners, thus:



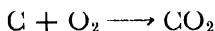
4. Although an equation is not incorrect without them, arrows are used to indicate when a product is a gas ($\uparrow$), and when a product

formed is insoluble ($\downarrow$). An insoluble product formed as a result of a chemical reaction between solutions is called a *precipitate*. The following are illustrative equations:

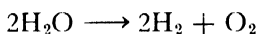


Types of Reactions. In science we are always classifying in order to facilitate the learning process. Although there are countless chemical reactions, all may be grouped into four types. The types of reactions and illustrative equations are as follows:

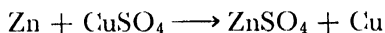
1. **DIRECT COMBINATION.** Two or more elements or compounds react to form a more complex substance; also called *synthesis*.



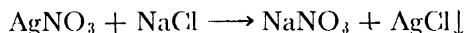
2. **DECOMPOSITION.** A reaction in which a compound is broken up into its constituent elements or into simpler compounds; also called *analysis*.



3. **SINGLE REPLACEMENT OR SUBSTITUTION.** A reaction in which a free element replaces a combined element.



4. **DOUBLE REPLACEMENT.** A reaction in which the elements of the reacting compounds change partners. This is probably the most common type of chemical reaction.



QUESTIONS

- Write the formulas for the following compounds: potassium chloride, ammonium sulfate, sodium hydroxide, aluminum carbonate, nitrogen trioxide, calcium bicarbonate, lead chloride, zinc sulfate, sodium fluoride and magnesium phosphate.
- Write the equations for the following reactions:
 - Magnesium hydroxide + hydrochloric acid $\longrightarrow$ magnesium chloride + water
 - Silver nitrate + potassium phosphate $\longrightarrow$ potassium nitrate + silver phosphate (insoluble)
 - Carbon monoxide (CO) + oxygen $\longrightarrow$ carbon dioxide
 - When calcium bicarbonate is heated, calcium carbonate, carbon dioxide and water are formed.
 - When sodium bicarbonate is taken into the stomach, it reacts with hydrochloric acid to form sodium chloride, carbon dioxide and water.

CHAPTER 4

IONS

Relatively speaking, we have come a long way in our understanding of matter since Chapter 1. There is still, however, one more concept to assimilate before we have an incipient working knowledge of chemistry. Strangely enough, this concept may be expressed in one single, simple and innocuous word—the *ion*. It is fair to say that the chemist would never have mastered the true nature of the chemical reaction without this word, and what it implies and explains. Although “the ion” antedates the Electron Theory, it was not discussed before because we were not prepared to appreciate its meaning and applications. In this chapter we shall discuss the ion, and those basic points of chemistry which are explained “ionically.”

THE IONIZATION THEORY

It has been known for a long time that solutions of certain compounds conduct an electric current and that others do not. Figure 5 shows the apparatus which is employed to tell whether a solution does

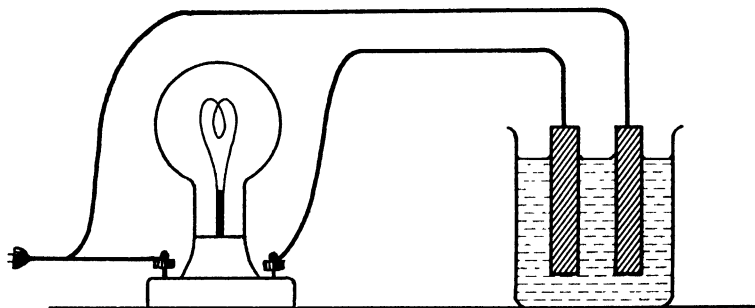


Fig. 5. Apparatus employed to test the ability of a solution to carry a current. When the bulb lights it shows that a current has passed through the solution.

or does not conduct an electric current. Compounds in solution which allow a current to pass are called *electrolytes*; those which do not are referred to as *nonelectrolytes*. How can we account for this fact? What is the fundamental difference between these two types of compounds? The answer to these questions—and many others—was presented in the

middle of the nineteenth century by the Swedish chemist, Svante Arrhenius, in a monumental piece of work—the *Ionization Theory*. The Ionization Theory, also called the *Theory of Electrolytic Dissociation*, is a rather lengthy piece of work, and well fortified with mathematics. The essence of the theory, though, can be conveniently presented in a manner which is readily intelligible. The following are the cardinal points of the theory:

1. Acids, bases and salts when dissolved in water dissociate (*ionize*) into ions.

2. An ion is an atom or radical with an *electric charge*.

3. *Metallic* ions carry *positive charges*, while *nonmetallic ions* carry *negative charges*.

4. The solution is electrically *neutral* because the number of positive ions is *equal* to the number of negative ions.

5. When an electric current is passed through the solution, the positive ions, called *cations*, travel toward the negative electrode (*cathode*), while the negative ions, called *anions*, travel toward the positive pole (*anode*).

Arrhenius looked upon the ion as the most fundamental particle. Since then the Electron Theory has proved otherwise, as we know. Arrhenius' marvelous reasoning, however, is not voided in the least by the Electron Theory of matter. Instead, the Electron Theory explains the Ionization Theory, and vice versa; there is perfect agreement between these two theories. Let us look more closely at the Theory of Ionization, and see how easy it is to understand what it says in the light of what we already know.

There are four kinds of compounds in chemistry, excluding the compounds of carbon: *acids, bases, salts and oxides*. These four kinds of compounds will be adequately treated in the next chapter, but for the moment let us consider acids, bases and salts in relation to the above theory. All acids, bases and salts are electrolytes; this may be easily demonstrated by the conductivity experiment (Fig. 5). The reason they conduct a current is offered by the first statement of the Ionization Theory which says that these compounds ionize (dissociate) into charged particles called ions. The remaining statements of the theory tell how these ions behave.

But let us go further, and see why these compounds do furnish ions. From our work with valence we know that there are two ways atoms combine—*covalence* and *electrovalence*.* Since we are looking for charged particles, i.e., ions, we need not bother with covalent compounds, for we said that in this type of combination atoms share elec-

* An electrovalent compound is often referred to as a *polar* compound; a covalent compound, *nonpolar*.

trons; thus, it is the electrovalent compound which holds the secret. Figure 6 shows very clearly what happens when an electrolyte dissolves in water. Once again our old friend sodium chloride (a salt) has been chosen. When a molecule of NaCl comes in contact with water, the electrostatic forces which hold the sodium atom to the chlorine atom are broken, and the atoms are freed from one another. But, it is to be noted that after they part they are no longer atoms—they are ions; the sodium has one less electron, and the chlorine one more electron than their

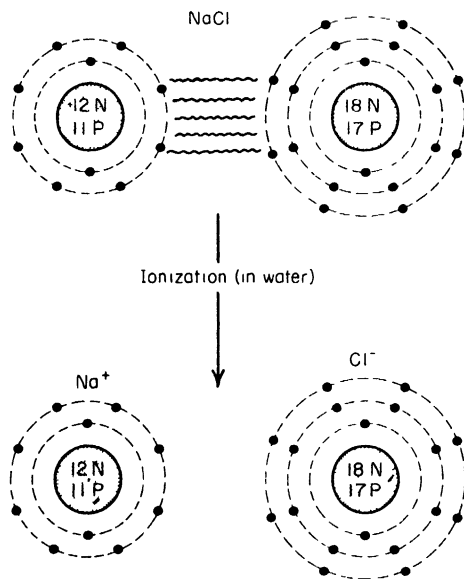
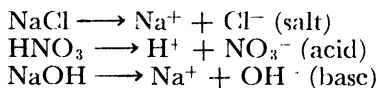


Fig. 6. Ionization of sodium chloride.

respective atoms (see Fig. 2). As a result, the sodium ion has a positive charge of 1 (Na^+), and the chlorine ion a minus charge of 1 (Cl^-). All electrolytes behave in this manner, i.e., all acids, salts and bases. To represent what happens when a compound ionizes, the following ionic equations are illustrative:



Let us now define acids, bases and salts on a basis of ionization. *An acid is a compound which in solution furnishes hydrogen ions (H^+); a base, hydroxyl ions (OH^-); and a salt, metallic and nonmetallic ions e.g., sodium chloride.*

Electrolysis. Electrolysis is defined as the *decomposition of a compound by means of an electric current*. It may correctly be inferred that only electrovalent compounds—electrolytes—are able to be decomposed by this means. Figure 7 illustrates the electrolysis of copper

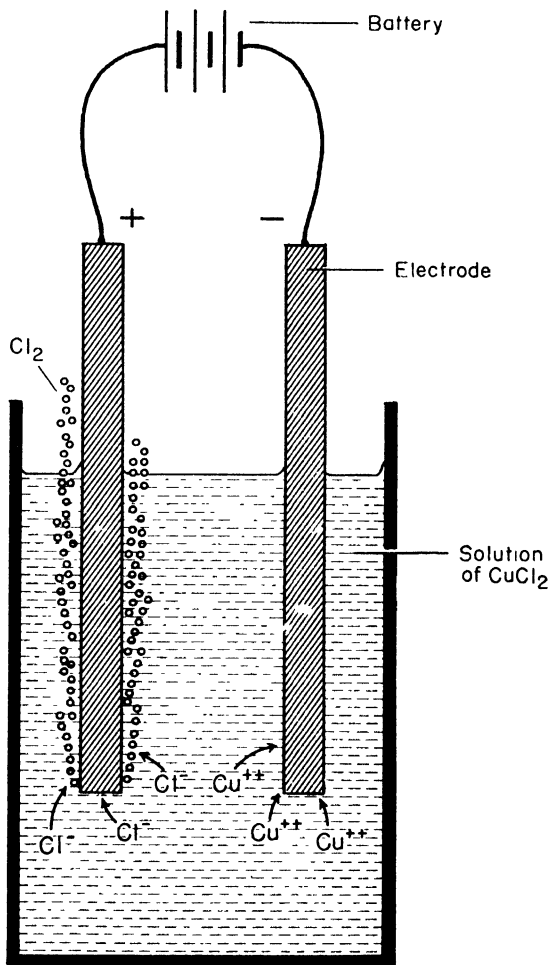


Fig. 7. Electrolysis of CuCl_2 .

chloride. When current is applied, the copper ions (Cu^{++}) migrate toward the cathode, and the chlorine ions (Cl^-) toward the anode. At the anode the chlorine ion gives up 1 electron, and becomes an atom. The electrons thus taken by the anode travel through the wire (a current,

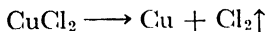
by the way, is defined as a flow of electrons), and accumulate at the cathode. At the cathode the copper ion takes on 2 electrons, and becomes an atom of copper. The whole process may be illustrated by the following ionic equations:

1. $\text{CuCl}_2 \longrightarrow \text{Cu}^{++} + 2\text{Cl}^-$ (ionization)
2. $\text{Cu}^{++} + 2e \longrightarrow \text{Cu}^0$ (cathode)*
3. $\text{Cl}^- - 1e \longrightarrow \text{Cl}^0$ (anode)

* a. e = electron.

b. A degree sign (Cu^0) at the upper right of a symbol indicates neutrality, i.e., an atom.

The electrolysis of CuCl_2 is an example of decomposition, and the equation may be written thus:



Unless ionic equations are specified, the regular equation is satisfactory. The products of the reaction, i.e., copper and chlorine, are formed at the cathode and anode respectively. When this experiment is carried out in the laboratory, bubbles of chlorine gas are seen rising from the anode; the cathode becomes coated with copper.

Electrolysis tells and explains many chemical facts. We should especially note that the number of electrons which the ions gain or lose is equal to their valence. For example, copper has a valence of 2, and gains 2 electrons; chlorine has a valence of 1, and loses 1 electron. *Further let us note that at the cathode an ion becomes reduced, and at the anode, oxidized.* Electrolysis is an important procedure in chemistry. We shall have occasion later on to discuss it in connection with the electroplating and refining of metals, and the manufacture of many important substances.

REACTIONS IN SOLUTION

When we stop to realize that most chemical reactions occur in an aqueous medium, the importance of ions would seem to require no further proof. Indeed, protoplasm is nothing more than water vitalized with certain elements and compounds in the ionic condition. Reactions in solution and reactions in general are beautifully explained via the ion.

In the last chapter a few remarks were presented concerning the chemical reaction. What was not said at that time is implied by this question: How do we know if chemical X will react with chemical Y? This is an extremely important question because we and the chemist are ultimately interested in getting reactions "to go." Figure 8 supplies the answer in speedy fashion. If chemical AB and chemical CD are dissolved in water, four kinds of ions will be present in solution: A^+ , B^- , C^+

and D^- . Now, these ions are free to move about the solution, and there is every possibility for ion A^+ to come in contact with ion D^- to form AD ; and for ion C^+ and ion B^- to form BC . It is to be noted, however, that our "products," AD and BC , ionize as soon as they are formed to A^+ , B^- , C^+ and D^- , and there is, therefore, every possibility that these ions may combine and form AB and CD —our starting chemicals! If, on the other hand, the products AD and BC were in some way not able

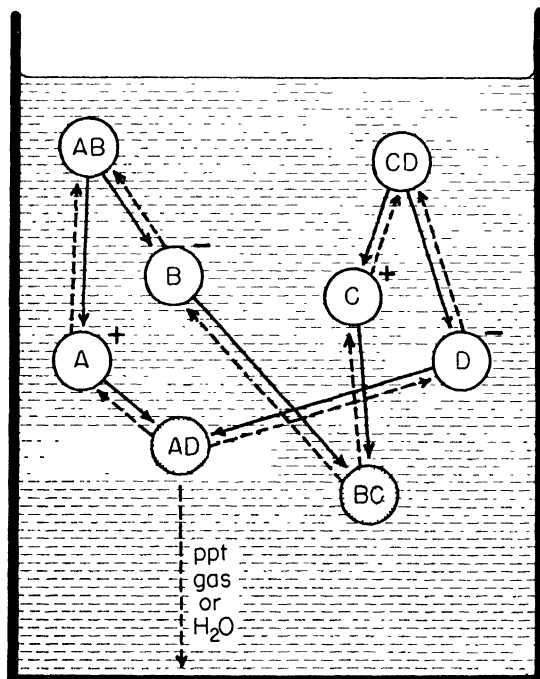


Fig. 8. Reactions in solution (See text.)

to ionize, the starting chemical compounds would not be re-formed. There are three circumstances under which the products will not react to re-form the original compounds:

1. When one of the products formed is insoluble.
2. When one of the products formed is a gas.
3. When water is formed.

When a product is insoluble* or a gas, it is taken from the "field of action," i.e., the solution; when water is formed, it ionizes to such a low extent that the reaction cannot go in the reverse. When the products of a

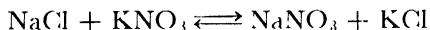
* See "Rules of Solubility," Appendix.

reaction are unable to react to form the original compounds, the reaction is said to be *irreversible*; when they do react to form the original products, the reaction is said to be *reversible*. From a practical point of view, the reversible reaction is no reaction at all—nothing happens. It is the irreversible type which allows us to form new substances. Let us illustrate the reversible and irreversible reactions with specific examples.

Reversible Reactions. If we add a solution of sodium chloride (NaCl) to a solution of potassium nitrate (KNO_3), the following equation may be written:

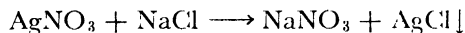


Now, the products NaNO₃ and KCl are soluble compounds and ionize readily. Soon, therefore, after the solutions have been mixed, the products are reacting to form the original substances as fast as they are being formed themselves. Actually, it is a dynamic state with reactions taking place in both directions. This reaction, then, and all reversible reactions are written thus:



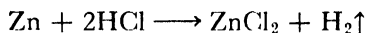
More scientifically, we say that in a reversible reaction a state of *dynamic equilibrium* exists; i.e., the speed of the forward reaction is equal to the speed of the reverse reaction. Later on we shall have several occasions to utilize the concept of reversibility or equilibrium.

Irreversible Reactions. Let us now add a solution of sodium chloride (NaCl) to a solution of silver nitrate (AgNO_3). When these two colorless, clear solutions are mixed, it is instantly perceivable that a chemical reaction has taken place—a beautiful white precipitate forms. The reaction is written thus:



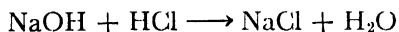
The white precipitate is silver chloride, and the reaction is irreversible because this compound, being insoluble, is not able to ionize and react with the sodium nitrate (NaNO_3). Note that in an irreversible reaction, only the forward arrow is used.

Now let us perform another experiment. If we add zinc (Zn) to a solution of hydrochloric acid (HCl) a reaction takes place instantly: a powerful effervescence ensues; hydrogen gas is liberated. The reaction is as follows:



The reaction is an irreversible one because a gas is formed. At the end of the reaction, only zinc chloride (ZnCl_2) remains.

For our last example and type of irreversible reaction, let us add a solution of sodium hydroxide (NaOH) to a solution of hydrochloric acid (HCl). A reaction is evident because a considerable amount of heat is liberated. Also, if we evaporate the reacting mixture, only salt remains. The reaction is represented thus:



This reaction is irreversible because a nonionizable compound is formed—water.

Let us remember, then, that a reaction goes to completion—i.e., all the original substances are consumed to form new products—when one of the products formed is a *gas, precipitate or water*. It is just as important, however, to appreciate and remember why this is true.

RATE OF REACTION

By now we should have a fair idea as to what a chemical reaction really is. At this point a few words must be added concerning those outside forces which affect the rate of a reaction. By the rate of a reaction we mean the speed at which a reaction takes place. For example, when powder explodes within a shell, its rate of reaction is tremendously greater than the rusting of iron. Below are presented factors which affect the rate of chemical activity.

Nature of Reacting Substances. Obviously, different substances react at different rates. One point in particular is always true: The speed of reaction between electrovalent compounds greatly exceeds the speed of reaction between covalent compounds. In other words, ions react with one another faster than atoms. This explains why substances in solution usually react at once, as opposed to the slow reactions in the dry state. As a matter of fact, reactions between electrovalent compounds in solution need little or no help from the outside; it is the covalent compound which must be prodded. In the dry state, however, even electrovalent compounds require some energy to react, for in this condition the ions are not as free as in solution.

Temperature. A rise in temperature greatly increases the rate of a reaction. Roughly speaking, a rise of 10° C. about doubles the rate. Therefore, a reaction proceeding at a certain rate at 0° C. will go twice as fast at 10° C., and four times as fast at 20° C. When the temperature is lowered, chemical activity is decreased. Refrigeration is nothing more than a method to retard chemical reactions within foods.

The reason why an increase in temperature speeds a reaction is easy to understand. When substances are heated their molecules become more energetic; hence, they collide with one another more frequently, and strike with greater force. In this manner, more molecules of the

reacting substances are given an opportunity to react. As a matter of fact, every reaction of covalent substances has a "critical temperature," below which the molecules of the reacting substances do not have sufficient frequency of collision or impact to react with one another.

Catalysis. Catalysis is a very frequent term in chemistry. We shall employ this word many times before the end of the text. A catalytic agent is defined as an agent which *alters a chemical reaction without itself being changed*. There are many substances which react with difficulty, or not at all, even at high temperatures and under other favorable conditions. If a catalytic agent is added, the reaction will go along smoothly, and usually at a much lower temperature. Another amazing thing about catalysts is that they are effective in very small quantities; in many cases just a *trace* will enable a chemical reaction to take place between several pounds of reacting substances. Catalysts are also of diverse nature; some are simple compounds (usually metals or oxides), and many are complex carbon compounds of natural origin.

Catalysis, then, is certainly to be considered as a factor which affects the rate or speed of a reaction. The chemist employs catalysts frequently in the laboratory and industry to make substances react, and occasionally to retard chemical activity. The preparation of oxygen will serve to illustrate the importance of catalysis. Oxygen may be prepared by strongly heating potassium chlorate (KClO_3) in a test tube. The reaction does not proceed easily, however, and the yield of oxygen is low. On the other hand, if we thoroughly mix a little manganese dioxide (MnO_2) with the potassium chlorate, and then apply heat, the reaction takes place readily and the yield of oxygen is good.

Catalysis is so important that the chemist considers it a subject by itself. Just how a catalyst performs its duties is at the present a moot question. Since a catalytic agent is highly specific, there is perhaps something about its physical and chemical properties which bring the reacting substances into closer molecular and atomic proximity. There is evidence that a catalyst may in some reactions act as an intermediate. In any case, the catalyst remains unchanged at the end of the reaction. This is most fortunate, because chemistry, whether it is concerned with the laboratory, industry, or the tissues of our bodies, strives for economy.

Concentration. The effect of concentration upon a given reaction is succinctly stated by the *Law of Mass Action*. This law states that the *speed of a chemical reaction is directly proportional to the concentration of the reacting substances*. The explanation of this basic and important principle is intuitive. Hypothetically, let us say that substance A reacts with substance B to form C. Further, let us suppose that 1 atom of A and 1 atom of B are placed in a beaker of water. In another beaker let us place 2 atoms of A and 1 atom of B. The question is this: In which

beaker are the atoms more likely to meet and react to form C? The answer is almost too obvious: the second beaker. Concentration, therefore, determines the likelihood of atomic interaction—or speed of reaction.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- ___ electrolytes
- ___ do not form ions
- ___ ions
- ___ anion
- ___ pole
- ___ electrostatic forces broken
- ___ decomposition
- ___ concentration
- ___ usually enhances a reaction
- ___ catalyst

Column II

- 1. charged atoms
- 2. electrolysis
- 3. electrovalent compounds
- 4. mass action
- 5. alters a reaction
- 6. ionization
- 7. heat
- 8. cathode
- 9. a negative ion
- 10. covalent compounds

1. Draw a diagram to illustrate what happens when an electric current is passed through a solution of gold chloride.
2. A physician asked a pharmacist if it is possible to compound a liquid prescription containing potassium chloride and zinc sulfate without a reaction. What do you think he said?
3. Why are reactions in which water is formed irreversible?
4. Name the factors which influence the speed of a reaction. Give an example of each.
5. A man was electrocuted by using a soda-acid fire extinguisher (contains H_2SO_4 and NaHCO_3) on an electrical fire. Explain.

CHAPTER 5

OXIDES, ACIDS, BASES AND SALTS

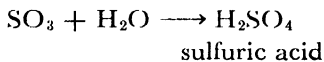
The number of compounds known to the chemist is close to a million, with the list growing rapidly as new synthetic substances are added. As pointed out before, the chemist must employ measures of classification analogous to those of the biologist in order to cope with this bewildering figure. Chemistry is divided into two great areas of study—*organic* and *inorganic*. Inorganic chemistry is the study of all the elements other than carbon; the study of carbon and its compounds is relegated to *organic chemistry*. The reason why carbon is considered as a separate area of study is because of its strange property of combining with itself. This property is responsible for the huge number of carbon compounds. Organic chemistry—one of the brightest pebbles on the beach of science—will be studied after we have passed through the elements of our inorganic world.

There are four classes of inorganic compounds: *oxides, acids, bases* and *salts*. Once we have a working knowledge of each class, our study of chemistry will be in clear focus. It is the purpose of this chapter to tell us the principal points of interest of the oxide, acid, base and salt.

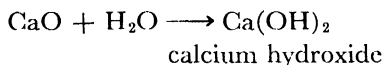
OXIDES

An oxide is a compound containing oxygen with another element. Oxygen combines with metals to form metallic oxides, and nonmetals to form nonmetallic oxides. The following are some important oxides: water (H_2O); carbon dioxide (CO_2); carbon monoxide (CO); calcium oxide (quicklime) (CaO); and iron oxide (rust) (Fe_2O_3). Oxides are prepared by burning or heating an element in air.

Acid Anhydride. *An acid anhydride is a nonmetallic oxide which reacts with water to form an acid.* There is an acid anhydride for most inorganic acids. For example, sulfur trioxide is the acid anhydride of sulfuric acid:



Basic Anhydride. *A basic anhydride is a metallic oxide which reacts with water to form a base or hydroxide.* Calcium oxide is thus the basic anhydride of calcium hydroxide:



Nomenclature. The name of an oxide is derived from the name of the element, followed by the word oxide. In cases where an element has more than one valence and forms a series of oxides, they are distinguished from each other by the prefixes mon-, di-, tri-, tetra-, and so on. The following table illustrates the method of naming:

<i>Oxide</i>	<i>Formula</i>
Calcium oxide	CaO
Magnesium oxide	MgO
Zinc oxide	ZnO
Carbon monoxide	CO
Carbon dioxide	CO ₂
Phosphorus trioxide	P ₂ O ₃
Phosphorus pentoxide	P ₂ O ₅

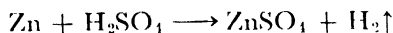
ACIDS

An acid is best defined as a compound which furnishes *hydrogen ions* (H^+).^{*} If we remember that an acid is an acid because of the hydrogen ion we will never be confused; it is the H^+ ion which endows the acid with its characteristic chemical properties. The hydrogen of acids is combined with either one or more nonmetallic elements or a radical.

Properties. **TASTE.** All acids have a sour taste. The sour taste of lemons, grapes and rhubarb is due to the acid they contain.

ACTION ON INDICATORS. Certain dyes, called *indicators*, undergo a color change when exposed to an acid medium. The most popular indicator is litmus. Litmus turns from *blue* to *red* in the presence of acid. Another indicator commonly employed is *methyl orange*. Methyl orange turns from *orange* to *red* in the presence of acid.

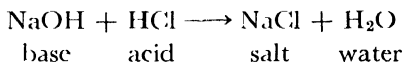
ACTION ON METALS. Most metals (copper, mercury, silver, platinum and gold are exceptions) react with acids to form hydrogen and a salt:



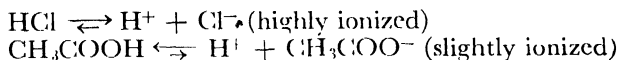
In this reaction zinc displaces the hydrogen from sulfuric acid, and forms the salt, zinc sulfate.

^{*} According to the modern concept (the *Brønsted Theory*), an acid is defined as a *donor of protons*. Actually, for practical purposes, a proton is equivalent to the hydrogen ion. Also, in water solutions, hydrogen ions do not exist as such, but as the *hydronium* ion, H_3O^+ ; i.e., the hydrogen ion is carried by a water molecule. However, the chemist still employs the term " H^+ ," but understands that it is H_3O^+ .

ACTION WITH BASES. Acids react with bases (metallic hydroxides) to form salts and water. This reaction, called *neutralization*, will be more fully appreciated later on in the chapter. The following is illustrative:

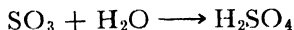


STRONG AND WEAK ACIDS. It is important to understand that acids differ in the degree to which they exhibit the above properties. Acids are, therefore, said to be *strong* or *weak*. Our conductivity experiment (Fig. 5) is the key to why an acid is strong or weak: *Strong acids are good electrolytes; weak acids are poor electrolytes*. This means that strong acids are highly ionized, and furnish a high concentration of H^+ ions, while the weak acids are slightly ionized, and produce few H^+ ions. The ionic equations for hydrochloric acid (HCl), a strong acid, and acetic acid (CH_3COOH), a weak acid, are written to indicate the degree of ionization:

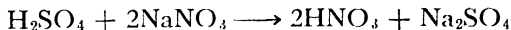


Preparation. The following are the two common methods used in preparing acids:

1. ACID ANHYDRIDE PLUS WATER.



2. SULFURIC ACID PLUS A SALT. This is the method most applicable to the laboratory. In this procedure, a salt of the desired acid is heated with sulfuric acid. The preparation of nitric acid is illustrative:



Nomenclature. A *binary* acid is composed of only two elements, i.e., *hydrogen and some nonmetal*. Binary acids are named by using the stem of the nonmetal with the prefix *hydro-* and the suffix *-ic*. Thus, the acid consisting of hydrogen and chlorine is called *hydrochloric acid*; that consisting of hydrogen and bromine, *hydrobromic*; that consisting of hydrogen and iodine, *hydriodic*.

A *ternary* acid is composed of three elements: *hydrogen, a nonmetal, and usually oxygen*. Three such elements are usually able to combine to produce several acids, i.e., a series. If only two acids are formed, the naming is simple: We use the suffix *-ic* for the acid containing the more oxygen, and *-ous* for the other. In cases where more than two acids are produced, we must supplement our suffixes with suitable

prefixes. For the acid containing the most oxygen, we use the prefix *per*-; for the acid containing the least oxygen, we introduce the prefix *hypo*-. The following table illustrates the rules:

<i>Acids of Chlorine</i>	<i>Formulas</i>	<i>Acids of Sulfur</i>	<i>Formulas</i>
Hydrochloric acid	HCl	Hydrosulfuric acid	H ₂ S
Hypochlorous acid	HClO	Hyposulfurous acid	H ₂ SO ₂
Chlorous acid	HClO ₂	Sulfurous acid	H ₂ SO ₃
Chloric acid	HClO ₃	Sulfuric acid	H ₂ SO ₄
Perchloric acid	HClO ₄	Persulfuric acid	H ₂ SO ₅

Let us not be alarmed by the above "chemical grammar." The rules were intended to show that the chemist employs a definite system in naming his compounds. With practice we shall easily add these rules to our working knowledge of chemistry. Moreover, the number of important inorganic acids are relatively few, and easy to remember. The following acids and their formulas should be memorized:

<i>Acid</i>	<i>Formula</i>
Hydrochloric acid	HCl
Sulfuric acid	H ₂ SO ₄
Nitric acid	HNO ₃
Phosphoric acid	H ₃ PO ₄

BASES

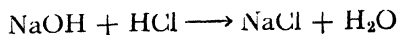
A base is a compound of a metallic element with one or more *hydroxyl (OH) groups*. A base is best defined, however, as a compound whose water solution contains hydroxyl ions (OH⁻).^{*} Let us remember that a base is a base because of the hydroxyl ion. for it is the OH⁻ ion which endows the base with its characteristic chemical properties.

Properties. TASTE. Bases have a bitter taste.

ACTION ON INDICATORS. Bases act opposite to acids on indicators. Bases turn litmus from *red to blue*, and methyl orange from *orange to yellow*. Another important indicator for bases is *phenolphthalein*. This indicator is turned *red in a basic medium*, and remains *colorless in an acid medium*.

ACTION WITH ACIDS. Bases neutralize acids, forming salts and water. This reaction is called *neutralization*. The following is illustrative:

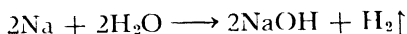
^{*} According to the modern concept (*the Brönsted Theory*), a base is defined as *an acceptor of protons*. Certain substances, therefore, other than hydroxides may be technically considered bases. For all practical purposes, however, the above definition is entirely satisfactory.



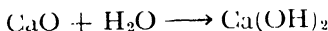
STRONG AND WEAK BASES. The strength of a base depends upon the degree of ionization.

Preparation. There are four simple and common methods of preparing bases:

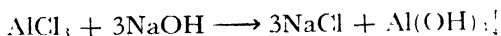
1. **ACTION OF AN ACTIVE METAL WITH WATER.** When sodium or potassium is dropped in water an explosive reaction takes place, with the formation of the hydroxide and hydrogen:



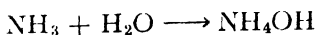
2. **ACTION OF A BASIC ANHYDRIDE WITH WATER:**



3. **ACTION BETWEEN A SALT AND ANOTHER BASE:**



4. **AMMONIA AND WATER.** Ammonia reacts with water to form the important base, ammonium hydroxide:



Nomenclature. The name of a base is derived from the name of the element, followed by the word hydroxide. The following important bases and their formulas should be memorized:

<i>Hydroxide</i>	<i>Formula</i>
Sodium hydroxide	NaOH
Potassium hydroxide	KOH
Ammonium hydroxide	NH_4OH
Calcium hydroxide	$\text{Ca}(\text{OH})_2$

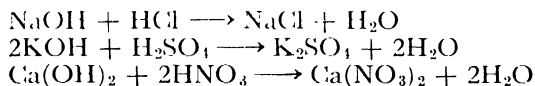
SALTS

Salts are compounds which result from the substitution of a metal for hydrogen in an acid. A salt is also defined as a compound consisting of a metal with a nonmetal or an acid radical. Salts far outnumber acids and bases and it is, therefore, most important that we have a good understanding of their properties, methods of preparation and nomenclature. Salts have a wide variety of characteristics. Those

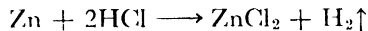
containing a common element, however, usually have similar chemical and physical properties. As a general rule, salts are white *crystalline* solids with a "salty" taste. When in solution, all salts are 100 per cent ionized.*

Preparation. Salts are prepared in many ways. The following methods of preparation are suggested because of their fundamental nature:

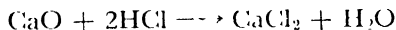
1. **NEUTRALIZATION.** We have already encountered this term twice before. Neutralization is the reaction between an acid and a base, forming a salt and water. Neutralization is also defined as the union of the hydrogen (H^+) and the hydroxyl ion (OH^-) to form water. (We shall do well to remember that the reason a neutralization reaction goes to completion is because water does not ionize.) The following are neutralization reactions:



2. ACTION OF AN ACID ON A METAL:



3. ACTION OF AN ACID ON A METALLIC OXIDE:



4. DIRECT UNION OF METALLIC AND NONMETALLIC ELEMENTS:



Nomenclature. No difficulty will be experienced in the naming of salts if we recall the nomenclature of the acids. Salts derived from a ternary acid are named by stating the metal and following it with a word having a characteristic suffix. If the name of the acid ends in *-ic*, the suffix for its salt is *-ate*; if the acid ends in *-ous*, the suffix is *-ite*. If the name of the ternary acid has a prefix, such as *hypo-* or *per-*, that prefix is made the prefix of the salt. Salts of binary acids are easy to name: the name of the metal is followed by a word having the suffix *-ide*. The table below illustrates the method of naming the sodium salts of the chlorine acids.

* Salts, as a matter of fact, do not need water to ionize, for a fused salt is able to carry a current.

<i>Acid</i>	<i>Formula</i>	<i>Salt</i>	<i>Formula</i>
Hydrochloric acid	HCl	Sodium chloride	NaCl
Hypochlorous acid	HClO	Sodium hypochlorite	NaClO
Chlorous acid	HClO ₂	Sodium chlorite	NaClO ₂
Chloric acid	HClO ₃	Sodium chlorate	NaClO ₃
Perchloric acid	HClO ₄	Sodium perchlorate	NaClO ₄

Types of Salts. **ACID SALTS.** Let us consider the neutralization reaction between NaOH and H₂SO₄. In this reaction there are two possibilities:



or



Thus, acids with more than one replaceable hydrogen atom may form more than one salt. Salts of *polybasic acids* (acids containing more than 1 atom of hydrogen) containing 1 or more atoms of hydrogen are called *acid salts*. Many times acid salts are improperly named. We will experience no confusion in naming an acid salt if we employ the proper prefixes. Thus, the sodium salts of phosphoric acid may be called *trisodium phosphate*, Na₃PO₄; *disodium hydrogen phosphate*, Na₂HPO₄; and *monosodium hydrogen sulfate*, NaH₂PO₄. It is common practice to use the prefix, bi-, to name an acid salt of a *dibasic acid*, e.g., H₂CO₃ and H₂SO₄. Thus, Na₂SO₄ is called *sodium sulfate*, and its acid salt, NaHSO₄, *sodium bisulfate*.

NORMAL SALTS. A normal salt is a salt which does not contain hydrogen. Thus, in the above illustrations Na₃PO₄ and Na₂SO₄ are normal salts.

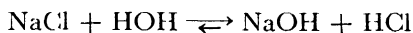
DOUBLE SALTS. A double salt is a compound containing two metals combined with one acid radical. Our common *alum*, KAl(SO₄)₂, is a good example. This compound is called *potassium aluminum sulfate*. A large number of our mineral substances are double salts.

Hydrolysis

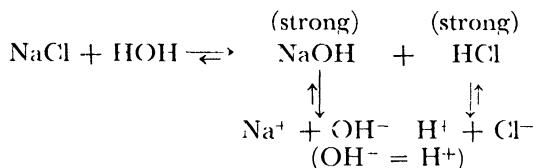
Let us prepare a solution of sodium chloride (NaCl), a solution of aluminum chloride (AlCl₃) and a solution of sodium carbonate (Na₂CO₃). If these solutions are now tested with litmus, we shall discover that only the sodium chloride "behaves like a salt," i.e., reacts neutral. The solution of aluminum chloride is acidic, and the sodium carbonate solution is basic in reaction. Since an acid is associated with the H⁺ ion, and a base with the OH⁻ ion, how do we account for the results? The answer to this question is *hydrolysis*. Hydrolysis is defined

as the *reaction between a salt and water producing an acid and a base*.^{*} If the acid and base produced are both strong, the solution is neutral; if the acid is stronger than the base, the solution is acidic; and if the base is stronger than the acid, the solution is basic.[†] This explanation is entirely satisfactory, but it will help us to remember and appreciate hydrolysis better if we study the mechanism of the reaction.

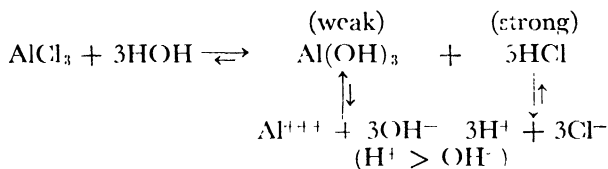
It was stated before that water does not appreciably ionize. However, the few ions which are formed are sufficient to react with a salt. Since water ionizes into H^+ ions and OH^- ions, let us write its formula as HOH. The following reversible reaction takes place in solution:



Note that this reaction is reversible because the products are neither insoluble, gaseous nor nonionized. In other words, if the water were to be evaporated from the solution, sodium chloride would remain. Now, both the base (NaOH) and the acid (HCl) are strong electrolytes; i.e., they are highly ionized. The overall picture, then, is that there are as many H^+ ions as OH^- ions; hence, the solution is neutral. The following reaction is more complete:



The following hydrolysis reaction accounts for the acidity of aluminum chloride:

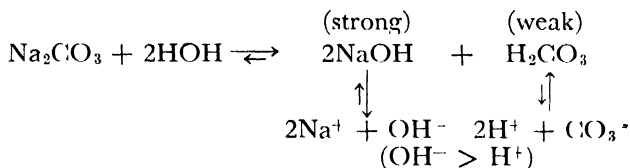


The products, aluminum hydroxide and hydrochloric acid, do not ionize to the same extent. Since HCl is a strong acid, it furnishes more ions than does the weak base, aluminum hydroxide; thus, the H^+ ions outnumber the OH^- ions, and our solution is acid in reaction.

^{*} In a more general sense hydrolysis may be accurately applied to any reaction in which a substance is chemically altered by water.

[†] H_2SO_4 , HCl and HNO_3 are strong acids; NaOH and KOH are strong bases. All other acids and bases may be considered weak.

For the hydrolysis of sodium carbonate solution we have:



This solution is basic because the OH^- ions exceed the H^+ ions.

Hydrolysis is of great practical concern in and out of the laboratory. Anyone who employs chemistry in any form usually must know if a solution is acidic, basic or neutral. From a theoretical point of view, an understanding of hydrolysis is essential.

HYDROGEN ION CONCENTRATION (pH)

The aphorism that big things come in little packages is thoroughly substantiated by the expression *pH*. *pH* is of paramount interest not only to the chemist, but also to anyone who employs the disciplines of chemistry in any form. The value of *pH* arises from the fact that this term is an *exact* and easy way to express the "reaction" of a solution—i.e., the degree to which it is *acidic* or *basic*. There is scarcely a substance which is immune from the influence of a solution with which it comes in contact. Moreover, many substances are inhibited or destroyed by extremely slight changes in acidity or basicity. Of these substances, protoplasm—or life itself—heads the list; death results when the point of optimum performance of the blood shifts ever so slightly in relation to its acid or base content.

In a liter of pure water the hydrogen ions (H^+) weigh 0.0000001 gram. *Since water is neutral*, there are as many hydroxyl ions (OH^-) as hydrogen ions and, therefore, the concentration of hydroxyl ions in a liter of water is the same, or 0.0000001 gram per liter. *In any solution which is not neutral, therefore, the concentrations of the hydrogen ions and the hydroxyl ions will not be equal. A neutral solution has a pH of 7 (pH 7)—the number 7 standing for the number of places to the right of the decimal point in 0.0000001.* A solution with an H^+ concentration of 0.00000001 will have a *pH* 8. Thus, the higher the *pH* the less the acidity—or the greater the basicity. The *pH* range extends from 0 (pure acid) to 14 (pure base) (see Fig. 9). A *pH* of 7.5 would indicate that a solution is very slightly alkaline; a *pH* of 6.9 would be on the "acid side of neutral." The *pH* of the blood is between 7.35 and 7.4; a slight change (± 0.5) either way is incompatible with life.

Since the *pH* of a solution is one of its most important characteristics, several methods have been devised to measure it, the most accurate

method involving the use of special "*pH* meters." Commonly, however, dye indicators are employed, e.g., litmus, methyl orange and phenolphthalein. Because these substances do not change color at an *exact pH*, they are employed only in those cases where the exact *pH* is not required. Litmus, for example, is of value only in so far as it can tell whether a solution is "fairly acid" or "fairly basic." It is possible to

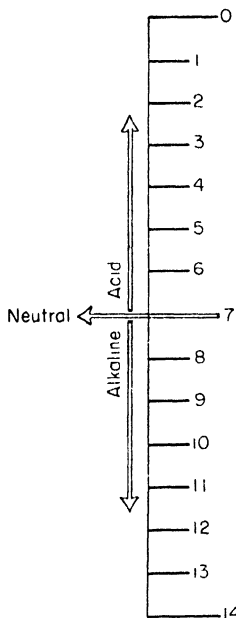


Fig. 9. The *pH* range. (See text.)

buy "*pH* paper" which affords some degree of accuracy. Weakly acidic or basic solutions which do not cause litmus paper to change may be detected by "*pH* paper." The test is carried out by wetting the paper, and then matching the color against a set of standards.

QUESTIONS

1. What is the chemical name of N_2O_3 ?
2. Sulfur dioxide reacts with water to form sulfurous acid. Write the equation.
3. What is the basic anhydride of calcium hydroxide? Write the equation for the reaction between this oxide and water.
4. Write the equation for the reaction between phosphoric acid and potassium hydroxide.
5. Write the equation for the reaction between aluminum and sulfuric acid.
6. What is the chemical name of $\text{Al}(\text{OH})_3$?
7. Name the salts of the following acids: H_3PO_4 , HCl , H_2SO_4 , H_2SO_3 , HNO_3 and HNO_2 .

8. What are the acceptable names of $\text{Ca}(\text{HCO}_3)_2$, KHSO_3 , Na_2HPO_4 , HClO and KCl ?
9. Milk of magnesia is a popular agent used to neutralize excess acidity in the stomach. Write the equation which explains this activity.
10. On a basis of hydrolysis explain (using equations) why a salt such as K_2CO_3 would irritate the stomach.
11. On a basis of hydrolysis explain (using equations) why NH_4Cl is acidic in solution.
12. Fungi grow best at pH 5, while bacteria grow best at pH 7. What is the chemical significance of this statement?
13. Five hundred cubic centimeters of a certain solution contain .0005 gm. of H^+ ions. What is the pH of this solution? (1 liter = 1000 cc.)
14. If some KCl were dissolved in pure distilled water, what would be its pH ?
15. The pH of distilled water is slightly (usually) on the acid side. Offer an explanation.

CHAPTER 6

THE NONMETALS

The preceding chapters were devoted to the development of ideas. A discussion of the elements and their compounds was deferred until now for the sake of continuity. Although new terms and ideas will be presented in future chapters, the basic facts of inorganic chemistry have been stated. Now we are prepared and ready to familiarize ourselves with the important elements and their compounds.

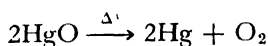
In this chapter we shall study the important nonmetals and their compounds; in the following chapter, the metals and their compounds. We should closely correlate this study with the position of the elements in the Periodic Table (Fig. 4). As pointed out before, the Periodic Table lessens our work in chemistry by affording us an easy and applicable system of classification. Briefly, let us review the general arrangement and structure of the table. The vertical columns are called *groups* and the horizontal divisions, *periods*. Elements of the same group are similar in their chemistry; therefore, if we are familiar with the chemistry of one, we know a great deal about the chemistry of the other elements of the group. This applies beautifully to the first 16 elements, but does not strictly hold throughout the table. For example, the elements copper, silver and gold of Group I bear little relation to lithium, sodium and potassium. Thus, in the same group we may have subgroups; these subgroups are called *families*. In the above example, copper, silver and gold belong to one family (Family B in the table), and lithium, sodium and potassium another (Family A). Each group has its characteristic valence. Since some elements exhibit more than one valence, the valence indicated above each group is the one which is most common to the elements of that group. It is to be recalled also that elements of Group I are true metals, and those of Group VII, true nonmetals. As we pass toward the middle of the table from either side, the elements become somewhat ambiguous in nature. Elements of Group VIII are metallic in their physical properties and variable in their chemical properties. The elements of Group 0 are the so-called inert gases; since their outer orbits are filled, they do not react with other elements.

OXYGEN

Oxygen is the most abundant element. It occurs in the free state in the atmosphere at a concentration of about 21 per cent, and in the combined state, e.g., water, quartz, clay and limestone, it constitutes 50 per cent of the earth's crust. The credit for the discovery of oxygen is given to Joseph Priestley, an English clergyman. Priestley prepared the gas in 1774 by heating mercuric oxide (HgO).

Preparation. Oxygen may be prepared in several ways. The following two methods are most applicable to the laboratory:

1. DECOMPOSITION OF MERCURIC OXIDE:



* Delta (Δ) means heat.

2. DECOMPOSITION OF POTASSIUM CHLORATE. This is the most common method. In this method a mixture of potassium chlorate

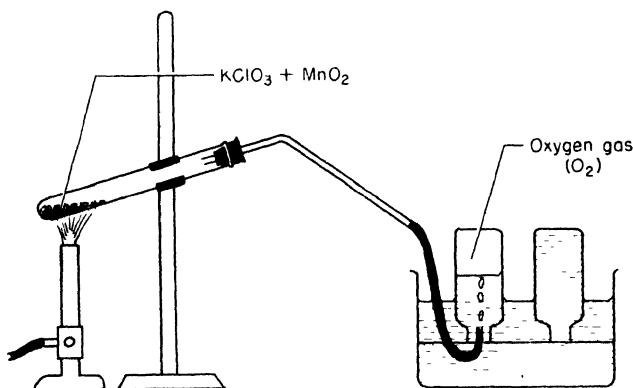
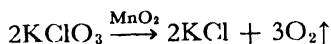


Fig. 10. Preparation of oxygen.

(KClO_3) and manganese dioxide (MnO_2) is gently heated. Since the gas is insoluble in water, it is collected by the method shown in Figure 10.



In this reaction manganese dioxide acts as a catalyst.

Commercially, oxygen is prepared by the following two methods:

1. ELECTROLYSIS OF WATER. When an electric current is passed through water (a little H_2SO_4 is added to make the water conductive),

it is decomposed into oxygen and hydrogen. The hydrogen is collected over the cathode, and the oxygen over the anode:



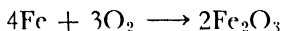
2. **LIQUID AIR.** When air is subjected to extremely high pressures and low temperatures, it is converted into a liquid. At room temperature liquid air boils away. Since nitrogen has a lower boiling point than oxygen, it escapes first, leaving pure oxygen.

Physical Properties. Oxygen is a colorless, odorless and tasteless gas. The gas is slightly soluble in water, 100 cc.* of water at 0° C. dissolving 4 cc. of the gas at atmospheric pressure. Oxygen is slightly heavier than air.

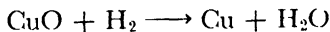
Chemical Properties. Oxygen combines with most of the elements—nonmetals as well as metals—to form oxides. This process is called *oxidation*. Let us recall another definition of this term: Oxidation is the loss of electrons. When we think of oxidation another term suggests itself—*reduction*. Reduction is the opposite of oxidation; it likewise has two definitions: Reduction is defined as the gain of electrons, or as the loss of oxygen. Oxidation and reduction, then, may or may not involve oxygen.

An agent which brings about the oxidation of another substance is called an *oxidizing agent*; one that reduces another substance is called a *reducing agent*. These agents may or may not involve oxygen. For the moment we are concerned with oxidation and reduction and their agents as they apply to oxygen. The following reactions illustrate oxidation and reduction:

OXIDATION:



REDUCTION:



In these reactions the following points are to be noted:

1. Iron (Fe) is being *oxidized* by oxygen; i.e., oxygen is the *oxidizing agent*.

2. Copper oxide is being *reduced* by hydrogen; i.e., hydrogen is the *reducing agent*.

3. Further, note that when one substance is oxidized another substance is reduced, and vice versa. Thus, while the CuO is being reduced, the hydrogen is being oxidized.

* cc. = cubic centimeter.

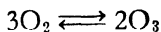
Oxidation is said to be *slow* or *rapid*. The rusting of iron and the "burning" of sugar within our tissues are examples of slow oxidation. Rapid oxidation, or *combustion*, is synonymous with burning. In contrast to slow oxidation, rapid oxidation causes light and heat to be emitted. *Spontaneous combustion*, however, testifies to the fact that heat is liberated during slow oxidation. If oily rags are placed in a dark warm room with poor ventilation, the heat which accumulates from the oxidation of the oil will reach an intensity sufficient for the rags to burn. This brings up another important point—*kindling temperature*. The kindling temperature is defined as the temperature to which a substance must be heated in order to burn. The more combustible a substance is, the lower is its kindling temperature.

Strangely enough, oxygen does not burn—it supports burning. This is not a paradox, however, when we realize that burning, i.e., the liberation of heat and light, is merely the manifestation of a chemical union between oxygen and some other element.

Uses. Oxygen is placed into steel cylinders under pressure. It is employed extensively in medicine in cases of respiratory embarrassment. In industry oxygen is widely used to produce high temperatures for welding and cutting. The oxyhydrogen torch and oxyacetylene torch reach temperatures as high as 4000°C .

Ozone. Several elements, e.g., oxygen, phosphorus, sulfur and carbon, exist in two or more forms. Although their properties are essentially the same, they do have individual characteristics. One form is always more stable and common than the others. These forms of the same element are called *allotropic* forms.

Ozone—written O_3 —is the allotropic modification of oxygen. Ozone is a colorless gas possessing a garlic-like odor; liquid ozone is dark blue. Ozone may be readily prepared by passing a *powerful spark through air or oxygen*. The reaction is as follows:



Chemically, ozone is a *much more powerful oxidizing agent than oxygen*. For this reason, ozone is often used where an oxidizing agent is indicated. In the form of ozonized air—produced by a silent electric discharge—it has been used to sterilize, bleach and remove objectionable odors.

WATER

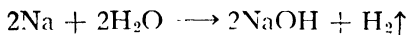
Water—the principal compound of oxygen—is our most familiar, most abundant, most useful and most interesting chemical compound. Water not only covers most of the earth's surface, but is also the *prin-*

cipal constituent of its plants and animals: Cucumbers and tomatoes are about 95 per cent water; the human body is about 70 per cent water. Water is without question the marvel of the earth, and perhaps the universe. Water is a marvel to the chemist because of its multitude of useful and unique properties, in conjunction with the fact that it is one of the earth's simplest substances— H_2O .*

Physical Properties. Water is a tasteless and colorless liquid. At standard pressure (1 atmosphere or 14.7 lbs. per sq. in.), water freezes at 0°C . (32°F .) and boils at 100°C . (212°F .). Water has the peculiar property of expanding when it cools from 4° to 0°C ., and while it freezes. At 4°C . water has its greatest density: 1 cc. weighs 1 gm. Above or below this temperature 1 cc. weighs less (very slightly of course) than 1 gm.

Chemical Properties. Although water displays extreme stability when subjected to high temperatures (it may be heated to 1000°C . before any decomposition takes place), it does react with several chemical substances to produce important products.

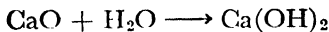
1. ACTION WITH METALS. Water reacts with the active metals such as potassium, sodium, calcium and iron. In this action part or all of the hydrogen is replaced. Sodium, for example, reacts with water to produce sodium hydroxide and hydrogen, thus:



2. ACTION WITH ACID ANHYDRIDES. It was pointed out before that nonmetallic oxides, or acid anhydrides, react with water to produce an acid:



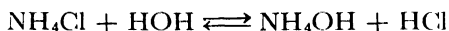
3. ACTION WITH BASIC ANHYDRIDES. Water reacts with metallic oxides, or basic anhydrides, to produce bases or hydroxides, thus:



4. HYDROLYSIS. As we already know, salts in solution render the solution acidic, basic or neutral, depending on the products formed in the equilibrium reaction between the salt and water (hydrolysis). A

* An isotope of hydrogen called *deuterium* (with an atomic weight of 2) combines with oxygen to form "heavy water"— D_2O (discovered by Urey in 1932). Ordinary water contains heavy water in a proportion of about 1 part in 6000. Heavy water *differs significantly* from ordinary water in its physical, chemical and physiologic properties. At the present time large amounts of heavy water are used in atomic plants to absorb fast neutrons, and thus reduce radiation hazards to personnel.

solution of ammonium chloride, for example, is acidic because the hydrochloric acid formed is a stronger acid than the ammonium hydroxide formed is a base:



5. **ELECTROLYSIS.** Water is decomposed by an electric current into its constituent elements: hydrogen and oxygen.

6. **WATER OF CRYSTALLIZATION.** A characteristic property of most salts is that they possess a crystalline structure. If certain crystalline salts are heated they change to a shapeless or amorphous mass. It will be discovered during the course of heating that water is driven off. This water, called the *water of crystallization*, or *water of hydration*, is an essential constituent in the structure of the crystal. The powder remaining after the water of crystallization has been removed is referred to as the *anhydrous* form of the compound. The term *hydrous* is applied to the crystalline form. Many substances contain water, but in a *mechanical* way and, therefore, in varying amounts. The following are examples of salts which have the hydrous and anhydrous forms:

Salt	Anhydrous Form or Anhydrate	Hydrous Form or Hydrate
Copper sulfate	CuSO_4	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Sodium carbonate	Na_2CO_3	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Calcium chloride	CaCl_2	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
Magnesium sulfate	MgSO_4	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Many hydrous salts lose water when merely exposed to the air. Such substances are said to be *efflorescent*. Crystals of washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) on standing in air lose their water of crystallization and crumble to a white powder. Efflorescence, therefore, has an economic as well as a chemical meaning; namely, that when a hydrous salt is purchased, you are purchasing a certain amount of water. Two other terms come to mind when efflorescence is mentioned: *deliquescent* and *hygroscopic*. A hygroscopic substance is one which absorbs moisture from the air. A deliquescent substance is one which absorbs sufficient water from the air to *dissolve itself*. Calcium chloride, for example, is so deliquescent that a crystal liquefies soon after being exposed to the atmosphere.

Purification. In order to make water fit for human consumption it is treated physically and chemically to remove any harmful foreign matter. In addition, water should be clear and palatable. The following table summarizes the methods commonly employed.

Methods of Water Purification*

Aeration .	The process of oxidizing organic material in the water (by the oxygen in the air), thus depriving bacteria of their food. Aeration is usually accomplished by spraying the water into the air through fountains, or by passing the water over tile or rocks.
Boiling .	A simple method for destroying microorganisms in water.
Chlorination . .	Carried out by adding chlorine gas to water (1 to 1,000,000 concentration). Destroys pathogenic bacteria.
Distillation	Used to prepare chemically pure water, i.e., water free from dissolved solids.
Filtration .	Used to remove suspended matter in the water (e.g., passing through sand).
Sedimentation . . .	Allowing water to stand to facilitate settling out of particles. This is often hastened by adding chemicals which form an insoluble gelatinous precipitate (called a <i>coagulum</i>). The coagulum in settling enmeshes the suspended particles.

* In practice, usually two or three of the above methods are used together in the purification of a community's water supply.

In the laboratory *distilled water* must be used. Distilled water is completely free of any dissolved substance. Since most chemical reactions are carried out in an aqueous medium, it is essential that the "unknown substances"—mineral salts—of tap water are not present to interfere

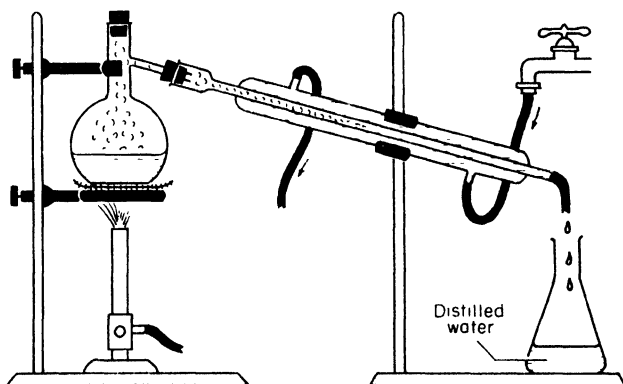


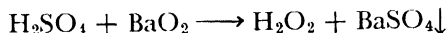
Fig. 11. Distillation apparatus.

with the natural course of the reaction. Distilled water is prepared in the laboratory by the apparatus shown in Figure 11. The process of *distillation* consists of *evaporation* (i.e., converting the liquid to the gaseous state) and *condensation* (i.e., converting the gaseous to the liquid state). Distillation is not only the best way to purify water chemically, but also any liquid substance.

HYDROGEN PEROXIDE (H_2O_2)

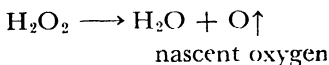
Oxygen forms two oxides with hydrogen: *hydrogen monoxide* (water); and *hydrogen dioxide* or, more commonly, *hydrogen peroxide*. The latter compound does not obey the law of valence.

Preparation. Hydrogen peroxide is prepared by the reaction between dilute sulfuric acid and barium peroxide, thus:

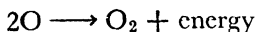


The above reaction goes to completion because barium sulfate is insoluble. Hydrogen peroxide is recovered from the reaction by filtration.

Properties. Pure hydrogen peroxide is a clear, syrupy liquid about one and one-half times as heavy as water. Since it holds its "excess" oxygen very loosely, it is a powerful oxidizing agent. In fact, it is so unstable that it readily explodes when exposed to heat or light. Hydrogen peroxide decomposes according to the following equation:



Uses. As pointed out before, the nascent state of a gas—i.e., the state in which the atoms of a gas are set free, and before they combine to form molecules—is highly active chemically. This activity is probably explained by the energy released when the atoms unite, thus:



For this reason, hydrogen peroxide possesses antiseptic and bleaching actions. Its bleaching action, however, is confined to those pigments which are decolorized by oxidation. Hydrogen peroxide is sold in the pharmacy as a 3 per cent solution of the pure compound in water. Obviously, aging and heat will attenuate its action. At best, hydrogen peroxide is only mildly antiseptic. The effervescence produced (escape of oxygen) when hydrogen peroxide is applied to a wound is no doubt more important than its inherent antiseptic action. The effervescence aids in loosening tissue debris, and thereby facilitates cleansing.

SOLUTIONS

The solution is one of the most practical tools in chemistry. A knowledge of the principles of solutions is essential to anyone who employs chemicals. *A true solution is an homogeneous liquid mixture of two or more substances whose particles are of molecular or atomic size.* The *solute* refers to the substance which goes into solution; it may be either a solid, liquid or gas. The *solvent* is the substance (usually water)

which dissolves the solute. When two liquids mix in all proportions, thus forming a true solution, they are said to be *miscible*, e.g., alcohol and water. Nonmiscible, or *immiscible*, liquids do not mix, e.g., oil and water. The terms *suspension* and *emulsion* should be differentiated from solution or true solution. A suspension is a mixture of a solid and a liquid in which the particles settle out on standing, e.g., sand in water. An emulsion is a mixture of two or more immiscible liquids which separate slowly, e.g., milk.

Kinds of Solutions. A general and easy way to classify solutions is on a basis of the proportion of solute to solvent. Later on we shall learn more precise ways to express a solution's concentration.

1. A *dilute solution* is one which contains a small amount of solute in relation to the solvent.

2. A *concentrated solution* is one which contains a large amount of solute in relation to the solvent.

3. An *unsaturated solution* is one which is capable of dissolving more solute under the same conditions of temperature and pressure.

4. A *saturated solution* is one which contains all the solute it can normally dissolve at a given temperature and pressure.

5. A *supersaturated solution* is of little practical importance, but of some interest. This type of solution may be easily demonstrated in the laboratory by using a chemical called sodium thiosulfate (hypo). If a saturated solution of hypo (at a given temperature) is heated, additional solute can be dissolved. This is common experience. Now, if this solution is carefully cooled to the original temperature, the hypo which was dissolved over and above the saturation point remains in solution. Such a solution is said to be supersaturated. This condition is extremely unstable. If a minute crystal of hypo is added (or if the vessel is shaken) the excess solute will crystallize out, leaving a saturated solution.

Preparation of Solutions. The speed with which a solid goes into solution is usually increased by *pulverization*, *agitation* (e.g., stirring) and *heating*. An increase in the temperature of the solvent *decreases* the solubility of gases. An increase in pressure, however, *increases* the solubility of a gas. Soda water, for example, contains dissolved carbon dioxide which is put in solution and kept there by pressure. The effervescence (escape of gas) seen when a bottle of pop is opened is due to the release of pressure. Pressure has very little effect on the solubility of solids. The miscibility of liquids is not significantly altered by temperature or pressure.

Colligative Properties. Solutions have certain properties which are related to the concentration of the solute. These properties—*viz.*, *freezing point*, *boiling point* and *osmotic pressure*—are known as *colligative properties* of the solution.

FREEZING POINT. Water, which freezes at 0° C. in the pure state, freezes at a lower temperature when it contains a dissolved substance. This applies to all solutions. *The freezing point of a solution is lower than that of the solvent*, and the degree of depression is proportional to the concentration of the solute.

BOILING POINT. The boiling point of a solution is *higher* than that of its solvent, the degree of elevation being proportional to the concentration of the solute.

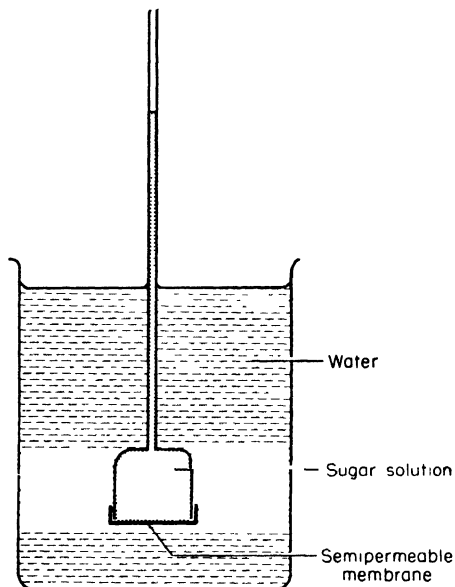


Fig. 12. A demonstration of osmosis.

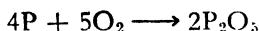
OSMOTIC PRESSURE. Before we can appreciate what is meant by a solution's osmotic pressure, we must understand the term *osmosis*. Osmosis may be simply and adequately explained by use of the apparatus shown in Figure 12. This apparatus consists of a thistle tube to the lower end of which is attached a parchment membrane. Within the tube is a solution of sugar in water. The parchment serves as a *semi-permeable membrane*. A semipermeable membrane is a membrane which permits solvent molecules to pass (water), but not solute molecules (sugar). Since the concentration of water outside the tube is greater than it is inside, water will diffuse from *outside* to *inside* in an attempt to equalize these concentrations. This "migration" from outside to inside is evidenced by the rising of the water in the glass tube. The

water will stop rising when the hydrostatic pressure is sufficient to prevent further passage of solvent molecules. *Osmosis, then, is the diffusion which proceeds through a semipermeable membrane, separating two solutions, with the principal flow toward the denser solution. Osmotic pressure* refers to the "pull" the denser solution has on the less dense solution. It is important to remember that osmosis occurs whenever two miscible solutions—*without regard to the nature of the solutes*—are separated by a semipermeable membrane. Living cells have semipermeable membranes, and depend for much of their activity upon osmosis. In our study of biochemistry we shall have many occasions to employ this term.

NITROGEN AND ITS COMPOUNDS

Nitrogen is the most abundant element of the atmosphere: It constitutes about 78 per cent of the air by volume. In the combined state it occurs in a number of compounds, both organic and inorganic. The chief inorganic forms of nitrogen are mineral nitrates, specifically, sodium nitrate (Chile saltpeter). Organically, nitrogen is the characteristic constituent of proteins and, therefore, is present in the protoplasm of all plants and animals. Presently we shall see that nitrogen is just as vital to our existence as oxygen.

Preparation. REMOVAL OF OXYGEN FROM AIR. This is an excellent way to prepare nitrogen in the laboratory. The easiest manner in which we can remove oxygen from the air is to place a piece of phosphorus in an enclosed volume of air. The phosphorus reacts readily with the oxygen to form phosphorus pentoxide, a solid; the gas remaining is almost pure nitrogen:



LIQUID AIR. This is the commercial method of preparation. Air is first reduced to a liquid by high pressures and low temperatures. When the pressure on the liquid is released the nitrogen readily escapes. The escaping nitrogen can then be liquefied and placed into steel cylinders under pressure.

Physical Properties. Nitrogen is a colorless, tasteless and odorless gas. It is slightly lighter than air, and slightly soluble in water.

Chemical Properties. Chemically, nitrogen is not a very active substance. Nitrogen does not burn, support combustion, or react readily with other elements. It does under extreme conditions combine with oxygen to form oxides, and with hydrogen to form ammonia.

The Atmosphere. Something should be said about the gaseous sea within which we live—the air. Minute traces of air are probably to be found at a distance as high as 2000 miles above the earth. The bulk of

the air, however, lies within a range of five miles above the earth. At sea level air exerts a pressure of 14.7 pounds per square inch. Since the composition of air is not exactly constant, and since its constituents exert their individual characteristics, *air is certainly a mixture and not a compound*. The average composition of dry air is as follows:

Nitrogen	78 %
Oxygen	21 %
Carbon dioxide	04 %
Argon	96 %
Neon	} traces
Helium	
Krypton	
Xenon	
Hydrogen	
Ozone	

The Nitrogen Cycle. In nature, nitrogen is necessary for life. A complex relationship exists between the plant and animal worlds relative to this element. Essentially, this is a reciprocal agreement whereby the plants feed the animals and the animals, in turn, aid in maintaining the plants. The free nitrogen of the air, strangely enough, is not available to plants and must, therefore, be converted into a usable form. The related chemical events, involving the free nitrogen of the air and its compounds in protoplasm and in the earth's soil, constitute the so-called *nitrogen cycle*.

Briefly, the cycle may be described thus: A variety of microorganisms in the soil bring about the *decay* or *putrefaction* of organic matter, i.e., material derived from dead plants and animals and animal wastes. As a result of this microbial action, *ammonia* is liberated. Another group of microorganisms, called *nitrifying bacteria*, convert this ammonia into *soluble nitrate salts*, e.g., sodium nitrate. Plants absorb these nitrates into their roots and utilize them to manufacture proteins for protoplasm. The animal world obtains its proteins by consuming plants. In time plants and animals die and add their nitrogen to the soil in the form of nitrates. The above situation is somewhat complicated by the fact that another group of bacteria, called *denitrifying bacteria*, act upon nitrates to form nitrogen gas, which escapes to the air. If there were not some mechanism, therefore, whereby this lost nitrogen could be returned to the soil, the earth would become depleted of its nitrates—and life. A strange group of bacteria, called *nitrogen-fixing* bacteria, are able to convert, directly, atmospheric nitrogen into bacterial protoplasm. Since these organisms live a symbiotic* life on the roots of certain plants

* A biologic term which means living together for mutual benefit.

(e.g., alfalfa and clover), they share their proteins or protoplasm with the plant. The return of nitrogen to the soil by the nitrogen-fixing bacteria completes the cycle. Figure 13 presents the above facts in a diagrammatic manner.

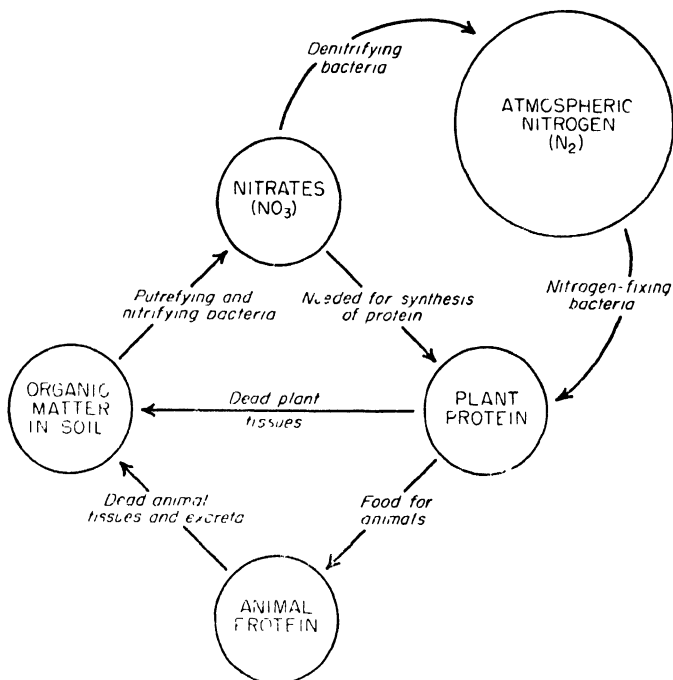
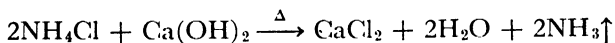
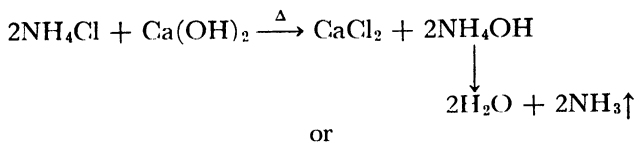


Fig. 13. Nitrogen cycle.

Ammonia (NH₃)

Ammonia, a gaseous compound of nitrogen and hydrogen, is probably the most important compound of nitrogen—certainly the most popular. It is present in minute quantities in the air as a result of the decomposition of plant and animal matter. The characteristic odor of decaying manure is due in no small part to the ammonia being liberated.

Laboratory Preparation. In the laboratory ammonia is conveniently prepared by heating a mixture of ammonium chloride (NH₄Cl) and calcium hydroxide (Ca(OH)₂). These two compounds react (double decomposition) to form ammonium hydroxide (NH₄OH) which, being unstable, decomposes into ammonia gas and water. The ammonia, being lighter than air, is collected by upward displacement (Fig. 14). The reaction is as follows:



Commercial Preparation. Ammonia is prepared commercially in vast quantities chiefly by three processes: *destructive distillation* of soft coal, i.e., heating coal out of contact with air, the *Cyanamide Process*, and the *Haber Process*. The Haber Process heralded an era of synthetic chemistry. From a practical and theoretical point of view, this process is

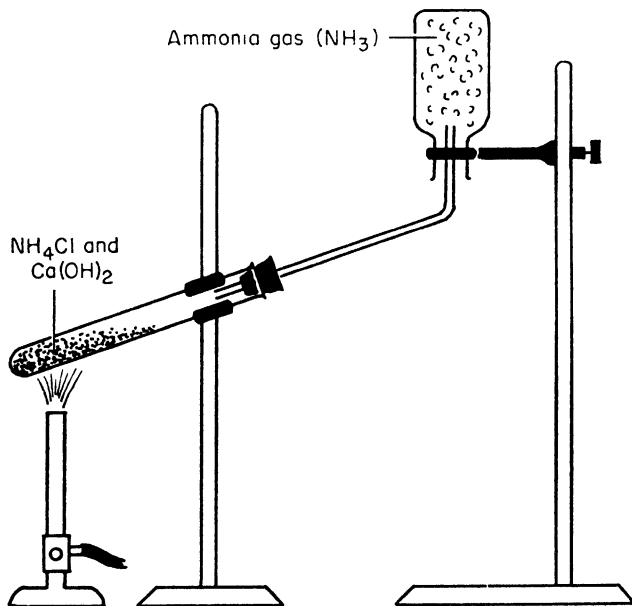
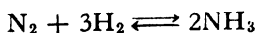


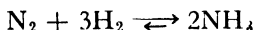
Fig. 14. Preparation of ammonia gas.

of paramount interest to us. The Haber Process employs nitrogen from liquid air, and hydrogen from the electrolysis of water. These elements are made to combine as follows:



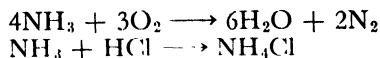
This is a most interesting situation. It was stated before that we do not receive yields from reversible reactions. However, it was also

pointed out that reversible equations may be rendered "productive" by the application of certain principles. As the equation stands, it is true—nothing does happen. If we increase the *temperature* and the *pressure*, however, ammonia is formed. The increase in pressure is especially important. In this equation—and in all equations involving gases—the reaction may be stated in terms of volumes, thus: 1 volume of nitrogen reacts with 3 volumes of hydrogen to produce 2 volumes of ammonia. In other words, the volume of the ammonia is one-half the total volume of the reactants. This is the reason an increase in pressure favors the formation of ammonia. Perhaps we can understand this effect of pressure more effectively if we recall what happens when a piece of ice is squeezed in the hand: The ice melts in a shorter period of time than if the ice is simply held in the hand. Since the volume of the ice exceeds the volume of the water, an analogy is evident: *Pressure favors the formation of a product whose volume is less than the volume of the original substances.* In a general sort of way this makes sense, because when a "system," having been subjected to pressure, assumes a smaller volume, it is "absorbing" or "undoing" the pressure so as to relieve the stress. This effect of pressure is a special case of one of the most important generalizations of chemistry and physics, first stated by Le Chatelier in 1887. *Le Chatelier's Principle* is stated as follows: *If a stress is applied to a system in equilibrium, the position of the equilibrium will shift in such a direction as to diminish the applied stress.* The Law of Mass Action (p. 34) is another special case of this principle. Thus, by applying Le Chatelier's Principle, many "worthless equilibria" are made important industrial processes. Under the favorable conditions of the Haber Process, then, the above equation becomes:



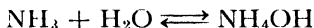
Physical Properties. Ammonia is a colorless gas, having a strong pungent odor. It is approximately one-half times as heavy as air. Ammonia liquefies easily. One of the outstanding characteristics of ammonia is its extreme solubility in water: *One volume of water dissolves 700 volumes of ammonia.*

Chemical Properties. Ammonia burns in pure oxygen to form water and nitrogen; it reacts directly with acids forming *ammonium* salts:



ammonium chloride

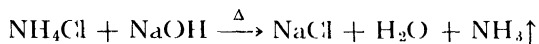
Another important property of ammonia is its reaction with water, forming ammonium hydroxide:



Ammonium hydroxide, as might be inferred from the above reaction, is an unstable chemical. Heat or reduced pressure favors the backward reaction, forming ammonia and water. Ammonium hydroxide is a very weak base.

Uses. Huge quantities of ammonia are employed in the manufacture of nitric acid, ammonium hydroxide (household ammonia) and ammonium sulfate. The latter compound is a common constituent of fertilizer.

Test for Ammonia and the Ammonium Radical. Ammonia gas will turn litmus from red to blue provided water is present. A piece of red litmus paper moistened with water is used for the test. An ammonium salt when heated with a base such as NaOH liberates ammonia:

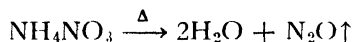


Oxides of Nitrogen

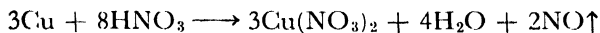
Nitrogen reacts with oxygen to form five different oxides. These five oxides are of interest to us principally because they illustrate the fact that an element may have more than one valence.

<i>Oxide</i>	<i>Name</i>	<i>Valence of Nitrogen</i>
N_2O	Nitrous oxide	1
NO	Nitric oxide	2
N_2O_3	Nitrogen trioxide	3
N_2O_4 or NO_2	Nitrogen peroxide	4
N_2O_5	Nitrogen pentoxide	5

Nitrous Oxide. Nitrous oxide (N_2O), commonly known as "laughing gas," is a colorless gas having a pleasant odor and sweet taste. It does not burn, but *supports combustion*. Nitrous oxide is a valuable anesthetic for short operations; in major surgery it is employed with other agents. The gas is prepared by heating ammonium nitrate:

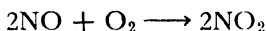


Nitric Oxide. Nitric oxide (NO) is produced when an electric spark passes through a mixture of nitrogen and oxygen. In the laboratory it is readily produced by the action of dilute nitric acid on metals:

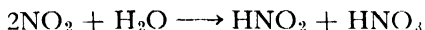


Nitric oxide is a colorless gas, slightly heavier than air, and insoluble in water. It does not burn or support combustion. On contact with air, it reacts with oxygen, forming nitrogen peroxide.

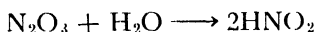
Nitrogen Peroxide. Nitrogen peroxide (NO_2) is formed when nitric oxide is exposed to the air:



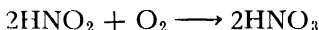
Nitrogen peroxide is a brown gas with a disagreeable odor. It is heavier than air and is soluble in water, with which it reacts to form nitrous acid (HNO_2) and nitric acid:



Nitrogen Trioxide. Nitrogen trioxide (N_2O_3) is an unstable red-dish-brown gas. It is the acid anhydride of nitrous acid:



Nitrous acid is an unstable compound, reacting with the oxygen of the air to form nitric acid:



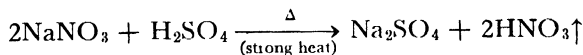
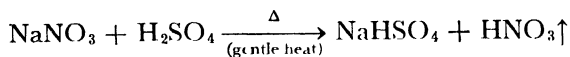
Nitrous acid is thus a reducing agent, and is employed in this capacity in the laboratory and industry. Salts of nitrous acid are called nitrites.

Nitrogen Pentoxide. Nitrogen pentoxide is an unstable white solid. It is the acid anhydride of nitric acid:



Nitric Acid (HNO_3)

Laboratory Preparation. In the laboratory nitric acid is prepared by heating sodium nitrate with sulfuric acid. Since nitric acid has a lower boiling point than sulfuric acid, it is removed as fast as it is formed, and recovered by condensing the vapors (Fig. 15):



Commercial Preparation. Commercially, the chemist has turned to the synthetic processes, i.e., the utilization of atmospheric nitrogen to produce nitric acid. The term *nitrogen fixation* is applied to any process in which free nitrogen is converted into useful compounds. At present more than one-half the world's needs for ammonia, nitric acid and nitrates are met by nitrogen fixation. The *Synthetic Ammonia Process* is a method of fixation which ranks next to the Haber Process in importance. All the nitric acid used commercially is now prepared in this way. The process is carried out by oxidizing ammonia (obtained from the Haber Process) to nitric oxide with the aid of a platinum catalyst.

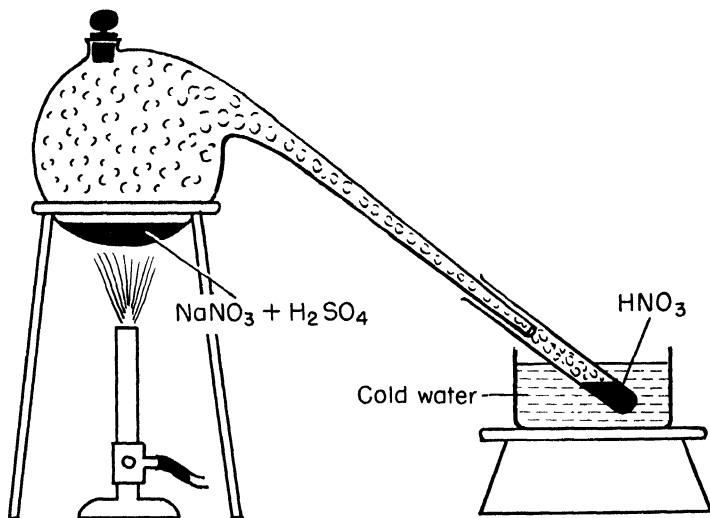
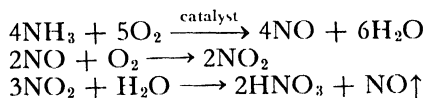


Fig. 15. Preparation of nitric acid.

The nitric oxide, in turn, is oxidized to nitrogen peroxide, which is then made to react with water to form nitric acid. The process may be summarized by the following equations:



Physical Properties. Pure nitric acid is a colorless liquid which boils at 86°C . with partial decomposition. An aqueous solution containing 68 per cent HNO_3 boils at 120.5°C . This solution constitutes the *concentrated nitric acid* of commerce.

Chemical Properties. Nitric acid is a strong acid. Because of its unstable character and large percentage of oxygen, concentrated nitric acid acts as a *powerful oxidizing agent*. This property is so pronounced that many substances react explosively with nitric acid. Nitric acid reacts with a few metals to produce hydrogen. With most metals, however, nitric acid usually forms nitric oxide.

Uses. The principal use of nitric acid is in the manufacture of nitroglycerin, nitrocellulose, dyes and nitrates. It also has many minor uses.

Nitrates. Nitrates are the salts of nitric acid (nitrites are the salts of nitrous acid). The most important nitrates are: sodium nitrate (*Chile saltpeter*, NaNO_3), used as a fertilizer and in the manufacture of ex-

plosives; and potassium nitrate (*saltpeter*, KNO_3), used as a preservative and in the manufacture of gunpowder. Most nitrates are white crystalline solids. All the normal nitrates are soluble in water and furnish metallic ions and nitrate ions.

Test For Nitrates. To identify a nitrate the following test is performed: A freshly prepared solution of ferrous sulfate (FeSO_4) is added to a solution of the substance being tested. Concentrated sulfuric acid is then allowed to run slowly down the side of the test tube and collect at the bottom. The formation of a *brown ring* at the junction of the two liquids indicates the presence of nitric acid or a nitrate. The result is explained thus: The sulfuric acid reacts with the nitrate to produce nitric acid which, in turn, reacts with the ferrous sulfate to form a brown colored compound.

SULFUR AND ITS COMPOUNDS

Sulfur is as old as history, and has played a vital part in man's conquest of matter. There is scarcely a laboratory or industry which does not employ sulfur or its compounds. Sulfur itself—from a chemical standpoint—is our most important raw material. The yearly production of sulfur in the United States alone is nearly 4,000,000 tons.

Frasch Process. Free sulfur occurs in huge deposits in the earth. The chief centers of production in the United States are in Texas and Louisiana; in Europe the chief centers are in Italy and Sicily. Although nature was kind enough to supply us with sulfur in the free state—thus obviating costly processes—we still had to solve the very difficult problem of mining it. We can easily understand the difficulty when we realize that sulfur in this country occurs under about 700 ft. of quicksand, thus making ordinary methods of mining impossible. Prior to 1900, our sulfur was imported because no one had solved the problem. Then in 1891 Frasch, an American engineer, supplied us with an ingenious answer. The Frasch Process has enabled us to raise our production from almost zero tonnage to nearly 4,000,000. The principle involved in this process is shown in Figure 16. Three pipes are sunk to the sulfur level. Water heated under pressure to about 170°C . is forced down the outermost pipe. The sulfur is thereby melted. Hot air is then forced down the innermost pipe, mixing the melted sulfur to make it foamy and light. The mixture is then piped into wooden bins where solid sulfur separates. Sulfur mined in this manner is 99.5 per cent pure!

Not all sulfur is in the free state. Sulfur occurs in the mineral world in many important sulfides and sulfates; in the organic world sulfur is a vital element in the fabric of many plant and animal proteins.

Physical Properties. Commercial sulfur is a golden-yellow solid with little taste or odor. It is insoluble in water, but soluble in carbon

disulfide and certain other organic solvents. Sulfur melts at 119°C ., and boils at 444.6°C . Sulfur exists in *five different allotropic forms*, three of which are solid, and two liquid.

SOLID SULFUR. Of the three solid forms, two are crystalline, and one amorphous (noncrystalline). These three allotropic forms are shown

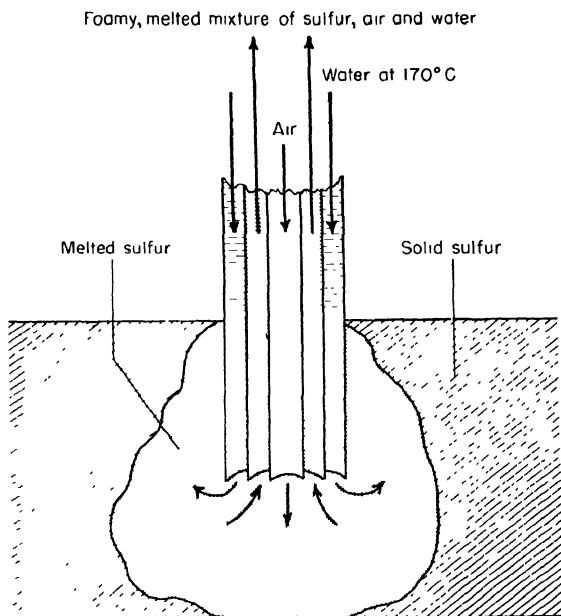


Fig. 16. The Frasch Process.

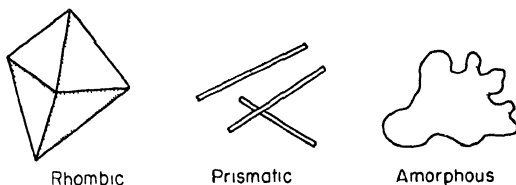


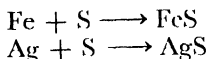
Fig. 17. Allotropic forms of sulfur.

in Figure 17. *Rhombic* sulfur is the most stable form of sulfur and is, therefore, the form which all sulfur assumes at room temperature. Rhombic sulfur is prepared by dissolving a little sulfur in carbon disulfide, and allowing this solution to stand in an evaporating dish; pure and perfect crystals remain. *Prismatic* (also called monoclinic) crystals can readily be obtained by melting some sulfur in a small crucible, allowing it to cool so that it partially solidifies, then pouring off the

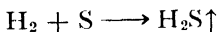
remaining liquid. The needle-shaped crystals adhering to the bottom and walls belong to the prismatic system. *Amorphous sulfur* is prepared by pouring boiling sulfur into cold water. This form of sulfur is a rubbery, amorphous mass, which returns to the rhombic form upon standing.

LIQUID SULFUR. Just above its melting point sulfur is a thin, light yellow liquid. This is one form of sulfur. As the temperature is raised, this liquid becomes dark, and at about 200° C. becomes viscous. On further heating, the liquid becomes thin again, and boils at 444.6° C. This dark liquid is the second form.

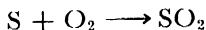
Chemical Properties. Sulfur has an atomic structure similar to oxygen and, therefore, has chemical properties much like that element. Both elements occur in the same family (Family B, Group VI). Oxygen forms oxides with metals; sulfur forms sulfides:



Like oxygen, sulfur vapor supports combustion. For example, hydrogen burns in a vapor of sulfur:



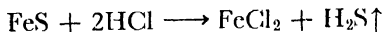
Sulfur reacts with nonmetals as well as with metals. Thus, sulfur reacts with oxygen (i.e., burns) to form sulfur dioxide gas. Sulfur burns with a pale blue flame:



Hydrogen Sulfide (H₂S)

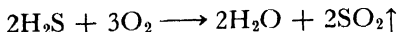
Hydrogen sulfide is a highly odoriferous gas formed by decaying organic matter which contains sulfur. The characteristic odor of the water from "sulfur" springs is due to this gas. Hydrogen sulfide is also a constituent of the gases issuing from volcanoes.

Preparation. Hydrogen sulfide is readily prepared in the laboratory by the action of dilute hydrochloric or sulfuric acid on a sulfide:



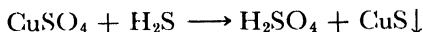
Physical Properties. Hydrogen sulfide has the offensive odor of rotten eggs. It is heavier than air and slightly soluble in water.

Chemical Properties. Hydrogen sulfide burns readily:

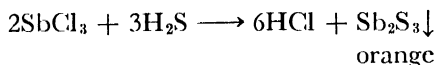
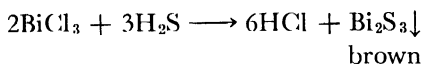
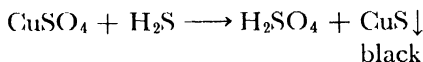


In water it dissolves sparingly to form hydrosulfuric acid (H₂S). The most characteristic property of hydrogen sulfide is its reaction with

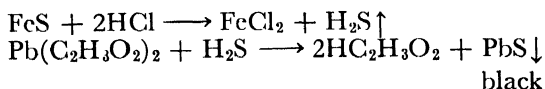
certain metallic ions to *form insoluble colored sulfides*. When this gas is bubbled through a solution of copper sulfate, for example, a black precipitate forms immediately. The reaction is one of double decomposition between hydrosulfuric acid (the gas in water forms the acid) and the metallic salt:



Use. Hydrogen sulfide finds its principal value in qualitative chemical analysis, where it is used to identify those metallic ions with which it forms characteristic sulfides. The following equations are illustrative:



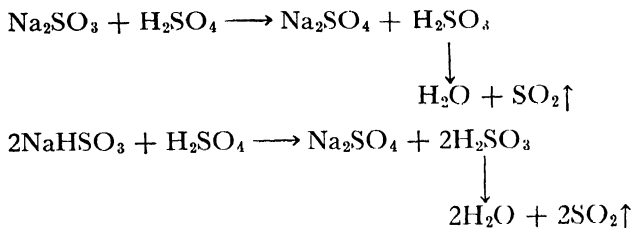
Test for a Sulfide. To identify a sulfide we carry out the following test: A little dilute hydrochloric acid is added to the compound under investigation, and then a strip of paper moistened with lead acetate solution is held over the mouth of the test tube. If the paper turns dark, the unknown is a sulfide. As discussed above, the acid reacts with the sulfide to form hydrogen sulfide, and the hydrogen sulfide then reacts with the lead acetate to form the black compound, lead sulfide. The test is illustrated by the following equations:



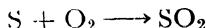
Sulfur Dioxide (SO₂)

Sulfur dioxide is found to a limited extent in volcanic gases. It is also evolved by burning coal, which usually contains small quantities of sulfur, whether free or in the combined form.

Preparation. In the laboratory sulfur dioxide is readily prepared by gently heating a *sulfite* or a *bisulfite with an acid*. The reaction produces sulfurous acid (H₂SO₃), which immediately decomposes into water and sulfur dioxide:

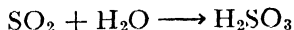


Commercially, sulfur dioxide is manufactured by burning sulfur in air:

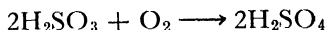


Properties. Sulfur dioxide is a colorless gas with a strong and pungent odor. It is more than twice as heavy as air, extremely soluble in water, and easily liquefied.

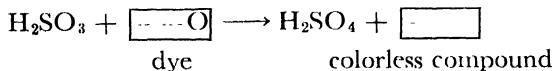
Chemically, sulfur dioxide is a stable compound. It does not burn or support combustion. Its most important and valuable property is that it combines with water to form sulfurous acid and is, therefore, the *acid anhydride* of that acid:



Sulfurous acid is an unstable substance, as shown by its odor of sulfur dioxide. Moreover, it slowly takes up oxygen from the air or certain oxygen compounds to form sulfuric acid:



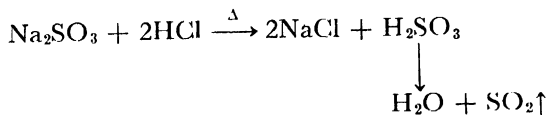
Sulfurous acid is thus a *reducing agent*, and is employed to bleach materials which are decolorized by reduction. This action may be represented as follows:



Uses. Sulfur dioxide is used to bleach straw, wood pulp, wool, silk, and dried and canned fruits. It is also employed as a disinfectant and refrigerant (as a substitute—with certain advantages—for ammonia). Its chief and most important use, however, is in the manufacture of sulfuric acid.

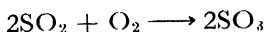
Test for Sulfur Dioxide and Sulfites. When sulfur dioxide is passed into a solution of *potassium permanganate*—which is purple in color—the solution is immediately *decolorized*. When sulfur dioxide is passed into water, an acid solution is formed (H_2SO_3). These two tests, along with the characteristic odor of sulfur dioxide, will establish its identity. To test for a *sulfite* (a salt of *sulfurous acid*), we add an acid

to the unknown. Acids readily liberate sulfur dioxide from sulfite salts, thus:

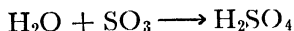


Sulfur Trioxide (SO₃)

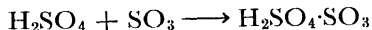
Sulfur trioxide is a white solid (melting and fuming at room temperature) made by reacting sulfur dioxide and oxygen in the presence of hot platinum (which acts as a catalyst). The equation is as follows:



Sulfur trioxide is the acid anhydride of sulfuric acid:



It also reacts with concentrated sulfuric acid to form *fuming sulfuric acid*:



Sulfur trioxide is employed almost exclusively in the manufacture of sulfuric acid by the *Contact Process*.

Sulfuric Acid (H₂SO₄)

Sulfuric acid is unquestionably the "king of compounds." Directly or indirectly, it is used in practically every industry. It is an economic fact that of a country's degree of civilization bears a direct proportion to the consumption of this vital chemical. Sulfuric acid is the most typical of the typical acids.

Preparation. Most of the sulfuric acid at the present time is made by the *contact process*. This is an important process not only for its industrial worth, but also because the student is supplied with an example of a good (easy to understand) industrial synthetic procedure. Every step in the sequence of events employs a familiar chemical reaction. Figure 18 illustrates the production of sulfuric acid as may be carried out in the laboratory. The industrial method is nothing more than a chemical amplification of this working model. The steps are as follows:

1. Sulfur dioxide is produced by burning sulfur.
2. A mixture of this sulfur dioxide and air (O₂) is cleaned and dried by passing through cotton and sulfuric acid, respectively (sulfuric acid is a dehydrating agent).

3. Sulfur trioxide is formed when the sulfur dioxide and air are passed over the heated catalyst (platinum).

4. The sulfur trioxide is then absorbed by concentrated sulfuric acid to form fuming acid ($\text{H}_2\text{SO}_4 \cdot \text{SO}_3$).

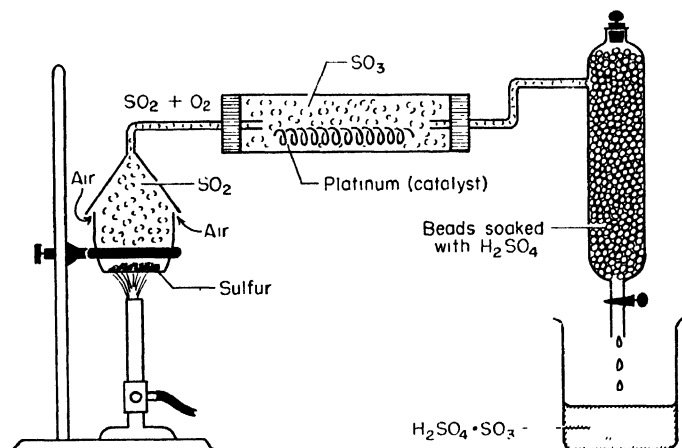
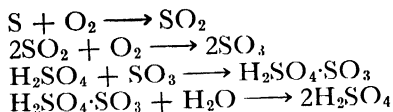


Fig. 18. The Contact Process.

5. The fuming sulfuric acid is then diluted with water to form concentrated sulfuric acid. Every molecule of $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ yields 2 molecules of concentrated sulfuric acid.

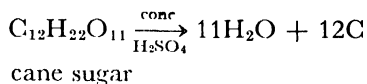
The above steps may be summarized as follows:



Properties. Concentrated sulfuric acid is a heavy, syrupy and corrosive liquid. It has a boiling point of 338°C ., and is thus the least volatile of all ordinary acids. Much heat is evolved when the acid and water are mixed. When preparing the dilute solution, the *acid is added to the water—never the reverse—to avoid dangerous spattering*. Even with this procedure the solution becomes very hot.

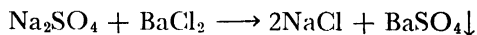
The chemical properties of sulfuric acid depend on whether it is dilute or concentrated. The dilute acid is a typical acid; it reacts with metals to liberate hydrogen, and neutralizes hydroxides, yielding salts—*sulfates*. Concentrated sulfuric acid is a powerful *oxidizing and dehydrating agent*. Its oxidizing properties are well illustrated by its action on metals, forming sulfur dioxide. The concentrated acid has such a powerful

affinity for water (dehydrating agent) that it will extract the hydrogen and oxygen from certain compounds in the proportion of 2 to 1 (as in water). Wood, paper and sugar, for example, are readily charred because of the removal of these two elements, leaving a residue of carbon. This dehydrating action may be represented thus:



Uses. As indicated above, sulfuric acid has a great many uses both in the laboratory and in industry. The dilute form is employed in numerous processes where the action of an "acid substance" is needed—e.g., storage batteries, electroplating, refining of metals and "pickling." The concentrated form is often used for its oxidizing and dehydrating properties. The salts of the acid—the sulfates—are of equal importance. Their various uses are too numerous to mention. Of significance to us, however, is the fact that sulfates are common in the pharmacy. *Epsom salts*, for example, is *magnesium sulfate*. Potent drugs such as morphine, codeine and many others are often used in the form of sulfate salts.

Test for Sulfates. Barium sulfate is a highly insoluble substance in both water and dilute acids. The formation of this substance is used as a test for the sulfate ion. The test is carried out by adding a solution of barium chloride to a solution of the unknown. If a white precipitate is formed—insoluble in dilute hydrochloric acid—the unknown is sulfuric acid or a sulfate salt. The reaction is as follows:



CARBON AND ITS OXIDES

Carbon is an element of tremendous import. Since it possesses the unique chemical property of combining with itself, there is no limit to the possible number and complexity of its compounds. For the moment, however, we are just interested in the element and its oxides. The study of its complex organic compounds will be pursued in the chapter on organic chemistry.

Carbon is extensively distributed in nature. *In the free state carbon occurs as coal, graphite and diamond*; in the combined state it is found in an astronomic number and variety of compounds of plants and animal origin, i.e., organic compounds. Of the free element, there are three definite allotropic forms recognized: *diamond, graphite and amorphous carbon*. Diamond and graphite are *crystalline* varieties. Amorphous carbon is the shapeless form which includes such substances as *coke, charcoal, boneblack and lampblack*. The importance and uses of these various forms of the free element are common knowledge.

Carbon Dioxide

Carbon dioxide gas is a vital constituent of the atmosphere, where it is present to the extent of about 0.04 per cent by volume. Important minerals such as marble, limestone and calcite contain carbon dioxide in the form of calcium carbonate. In addition to its ubiquity in nature, carbon dioxide is of interest to us because of its many and varied uses.

Preparation. Carbon dioxide is easily prepared in the laboratory by the action of an acid on a carbonate. Usually it is prepared by react-

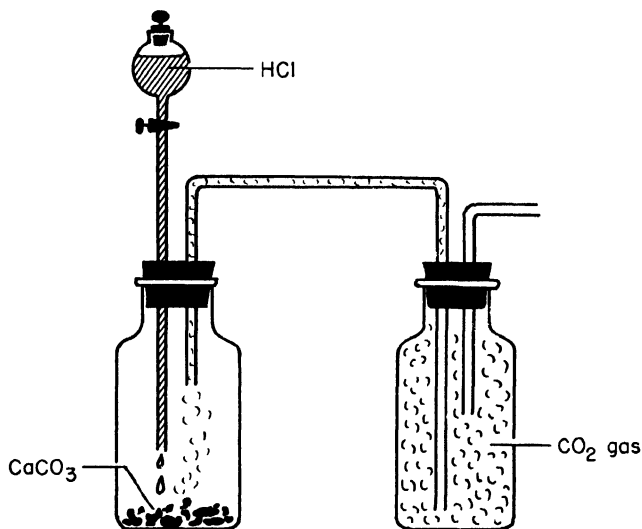
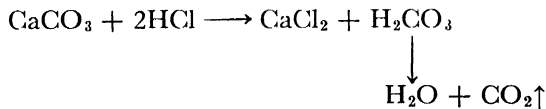


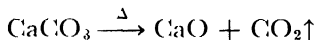
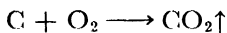
Fig. 19. Preparation of carbon dioxide.

ing calcium carbonate with hydrochloric acid. The gas is immediately evolved, and may be collected by displacement of water or by displacement of air as shown in Figure 19. The equation for the reaction is:



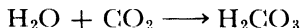
It is to be noted that carbonic acid (H_2CO_3) is first formed. This is an unstable compound, however, and instantly breaks up to form water and carbon dioxide.

Commercially, carbon dioxide is prepared by the burning of carbon (usually in the form of coke) or the heating of limestone. The reactions are as follows:

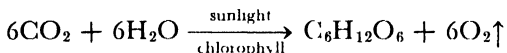


Physical Properties. Carbon dioxide is a colorless gas, with a slight taste and odor. It is about one and one-half times as heavy as air. Carbon dioxide is moderately soluble in water. Soda water and similar carbonated beverages contain relatively large quantities of the gas held in solution under pressure. The *effervescence* (gas escaping from a liquid) observed when a bottle of pop is opened is due to the release of pressure. Solid carbon dioxide ("snow") is formed when the liquid variety is allowed to escape; the rapid evaporation causes such a sharp drop in temperature that some of the liquid freezes. The useful refrigerant, "dry ice," is made by pressing this snow into a compact form.

Chemical Properties. Chemically, carbon dioxide is a stable and rather inactive gas. It does not burn or support combustion. Carbon dioxide reacts with water to form the weak and unstable carbonic acid and is, therefore, the acid anhydride of that acid:



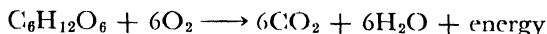
Photosynthesis. Carbon dioxide is a participant in probably the most important chemical reaction on earth—*photosynthesis*. This is the term applied to the reaction in which *carbon dioxide* and *water* form simple sugar (glucose) in green plants. Volumes have been written concerning the mechanism involved to accomplish this chemical feat. Although a great deal is known about the intermediate chemical steps, the complete picture is still somewhat nebulous. The biologist, however, is content with the following established facts: *Sugar (glucose) is manufactured in the leaves of plants with the aid of chlorophyll—the complex green pigment of all green plants—and sunlight.* Chlorophyll acts as a *catalyst*, and sunlight furnishes the necessary energy for the reaction. The following equation summarizes the process:



As can be seen from the equation, oxygen is also formed in photosynthesis. The sugar, or glucose, is converted by the plant into starch, and stored in this form, chiefly in the roots. When the plant needs energy starch is reconverted to sugar.

The cosmic implication—and fact—is that photosynthesis is the means by which the *sun's energy becomes the earth's energy*. Specifically, the energy of the sun is locked in the sugar molecule, for when

sugar is burned within the cells of plants and animals energy is released, thus:



It is also to be appreciated that the fuels of the earth—coal, oil, and so on—are formed from the decay of plants and animals and, therefore, are an indirect result of photosynthesis.

Carbon Cycle. The process of respiration and the process of photosynthesis are mutually sustaining chemical reactions; together they make life on earth possible. The relation between these two processes is

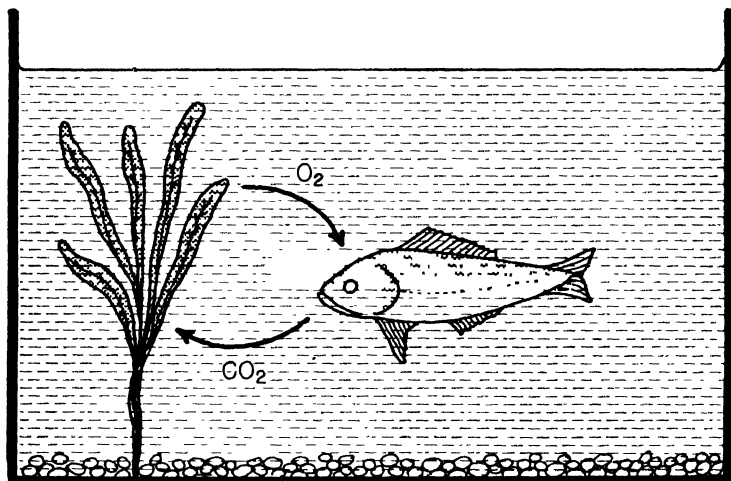


Fig. 20. The Carbon Cycle. The aquarium microcosmically demonstrates the relation between plants and animals. The fish supplies carbon dioxide to the plant, and the plant supplies the fish with oxygen and food.

commonly referred to as the *carbon cycle*. In this cycle, carbon dioxide is constantly being added to the atmosphere by the processes of respiration, burning and decay. At the same time it is being withdrawn by plants for photosynthesis. Plants utilize carbon dioxide (as explained above) to manufacture food. Oxygen, which is a by-product of this reaction, is given off to the atmosphere, thus allowing animals to carry on respiration. Carbon—which is lost during respiration—is returned to the animal via his food—directly (in plants) or indirectly (other animals). Thus, the carbon cycle involves respiration, photosynthesis and food (see Fig. 20).

Physiologic Importance. Carbohydrates—sugars and starches—and fats are burned within the cells of the body to furnish energy. Since these substances contain carbon, carbon dioxide is given off. Therefore,

on a basis of chemistry, respiration may be defined as *the taking in of oxygen and the giving off of carbon dioxide*. This and other physiologic facts of the gas will be treated later on in detail.

Fire Extinguishers. The common soda-acid fire extinguisher (Fig. 21) operates on the following principle: When the extinguisher is

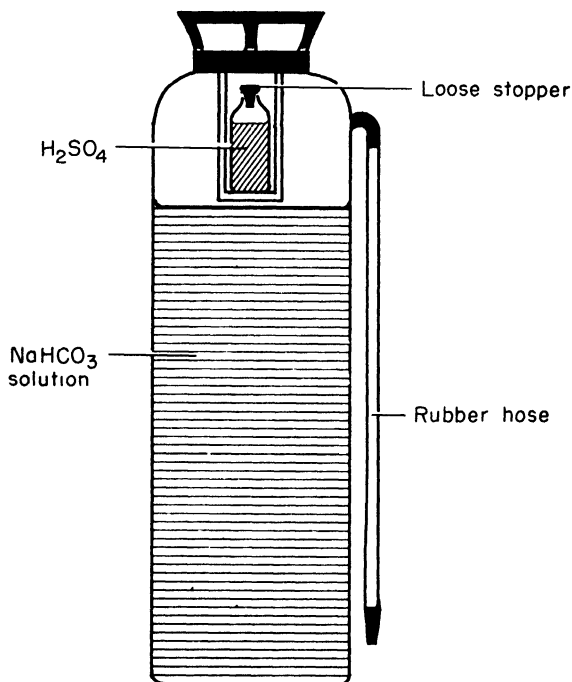


Fig. 21. The soda-acid fire extinguisher.

inverted, the sulfuric acid (contained in a bottle at the top with a loose stopper) reacts with the sodium bicarbonate solution to produce carbon dioxide:



The gas forces the liquid out of the nozzle under high pressure. This type of extinguisher is successful in putting out small fires.

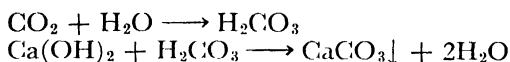
The soda-acid extinguisher should not be used against oil or electrical fires. For oil fires, the *Foamite* method is effective. This type of extinguisher operates in a similar fashion (carbon dioxide is formed), but has the advantage that a foam is produced due to the presence of licorice extract. The foam, unlike water, floats on the surface of the oil.

For electrical fires, *carbon tetrachloride* is recommended. This type of extinguisher ("pump") is operated by pumping the fluid out of its container.

The use of plain carbon dioxide gas is becoming popular against all types of fires. This type of extinguisher is operated by opening the valve of a cylinder containing carbon dioxide under pressure; the gas escapes through the funnel-shaped nozzle in dense clouds, and extinguishes the fire almost instantly.

Other Uses. Large quantities of carbon dioxide are employed in the soft drink industry. In the baking of bread, carbon dioxide is formed in the dough by the action of water on baking powder. Baking powder contains some acid substance, such as cream of tartar, and sodium bicarbonate (baking soda). When water is added, these two chemicals react in a manner indicated earlier; i.e., an acid plus a bicarbonate yield carbon dioxide. The gas causes the dough to rise, thus making the bread light and digestible. Dry ice, mentioned earlier, is a useful refrigerant for perishable foods during shipment.

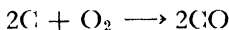
Test for Carbon Dioxide and Carbonates. The presence of carbon dioxide may be detected by passing the gas through a solution of *limewater* ($\text{Ca}(\text{OH})_2$ dissolved in water). If carbon dioxide is present, the solution turns *milky* due to the formation of calcium carbonate:



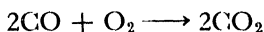
A carbonate or bicarbonate is tested for by adding an acid to the unknown, and passing the gas (if formed) through limewater.

Carbon Monoxide

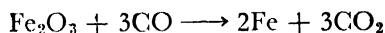
Carbon monoxide is formed whenever carbon or some compound containing carbon (e.g., a fuel) is made to burn with an insufficient supply of air. In this instance oxidation is not complete, and the monoxide forms instead of the dioxide:



Properties. *Carbon monoxide is a colorless, odorless and tasteless gas.* It is somewhat lighter than air, and only slightly soluble in water. The chemical properties of carbon monoxide are referable to the fact that it is able to take on an additional atom of oxygen. When this happens, it burns with a hot, blue flame, forming carbon dioxide:



Carbon monoxide is, therefore, a reducing agent, and employed with great success in the reduction of metallic oxides (ores) to liberate the free metal:



Toxicity. Of prime significance to us is the action of carbon monoxide on the body. This gas causes more deaths than all other poisons combined. Its omnipresence—in automobile exhaust, illuminating gas, and so on—and physical characteristics—tasteless, odorless, colorless—are insidious qualities. The toxicity of carbon monoxide is a result of its action on *hemoglobin* in the red corpuscles of the blood. Carbon monoxide reacts with hemoglobin to form *carboxyhemoglobin*, a compound of hemoglobin which is incapable of carrying oxygen. The signs and symptoms of poisoning, therefore, are those of *asphyxia*. If carbon monoxide possessed the same affinity for hemoglobin as displayed by oxygen, there would indeed be few cases of poisoning. Unfortunately, however, carbon monoxide has an affinity about 300 times that of oxygen. As a result, toxic reactions and death occur at low concentrations. A concentration of as little as 0.1 per cent in the atmosphere is dangerous, and may cause death.

Treatment of carbon monoxide poisoning is successful if administered early—even in severe cases. For the victims of mild intoxication, removal from the polluted air to the out-of-doors is usually sufficient. Severe intoxication demands oxygen and artificial respiration. Since carboxyhemoglobin is an unstable compound, it is easily decomposed in the presence of a heavy concentration of oxygen to hemoglobin and carbon monoxide. This latter substance is removed from the body via the lungs.

THE HALOGENS

The halogen family includes: *fluorine*, *chlorine*, *bromine* and *iodine*. These nonmetals deserve special mention for two reasons: First, they epitomize the term *chemical family*; i.e., their chemical properties are very similar; and second, these elements and many of their compounds possess valuable qualities. The halogens belong to Family B of Group VII in the Periodic Table. As can be inferred from this location, the halogens are typical nonmetals. The name “halogen” (salt-former) is used because all four elements form salts which resemble common table salt—sodium chloride. The very similar chemical properties of the halogen elements are explained by their atomic configuration: Each element is composed of atoms containing 7 electrons in their outer orbit. Hence, fluorine, chlorine, bromine and iodine have a valence of -1 (Fig. 22).

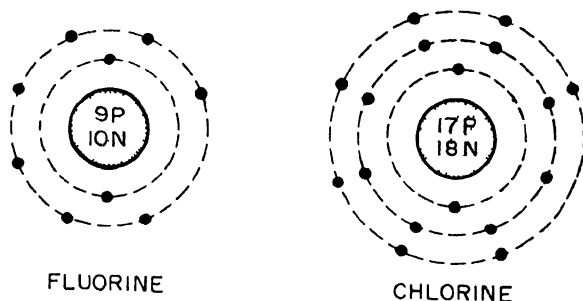


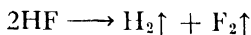
Fig. 22.

Fluorine

Fluorine is widely distributed in nature. Since it is the *most active* of the halogens, it occurs in the combined state—mostly as *calcium fluoride* (*fluorspar*) and *cryolite*. In the body, traces of fluorine are present in the teeth and bones, perhaps as calcium fluoride.

Properties. Fluorine is a pale yellow gas, a little heavier than air, and has an extremely pungent odor. Fluorine is a *powerful poison*. Chemically, fluorine possesses more action than all the other nonmetallic elements. Fluorine readily reacts with hydrogen to form the gas, *hydrogen fluoride*. When hydrogen fluoride is passed into water, the resulting solution is *acidic*. Therefore, this solution is correctly called *hydrofluoric acid*. Salts of this acid are called *fluorides*.

Preparation. Fluorine is prepared by passing an electric current through liquid hydrogen fluoride; fluorine gas collects at the anode. The equation for the reaction is as follows:



Uses. Fluorine and its compounds are not widely used. Hydrofluoric acid is employed to etch glass. It is the only acid known that readily attacks silicon dioxide (SiO_2), the chief constituent of glass. Since fluoride salts are highly toxic, they enjoy some use as insecticidal agents.

Of considerable importance, however, was the discovery that the fluoride ion plays a vital role in the chemistry of the teeth. Tooth decay in areas where the water contains fluoride is *significantly lower* than in other parts of the country. It is believed that drinking water should have a concentration of about *1 part fluoride to 1 million parts water*. Many towns and cities throughout the country are now adding fluoride to the water if the water in that area proves fluoride-deficient. It should be pointed out in a discussion of this subject, however, that too much of

the ion in the water may harm tooth enamel. It follows, therefore, that before adding fluorine to water, an analysis of the water should be carried out. Some differences of opinion have always attended the use of fluorine for this purpose. At the present time, a vote of approval from the people of the area is required for *fluoridation*.*

Chlorine

Since chlorine is far too active to exist in the free state, it occurs chiefly as sodium chloride and other chlorides in the oceans and solid salt beds. The chloride ion is an essential inorganic constituent of protoplasm.

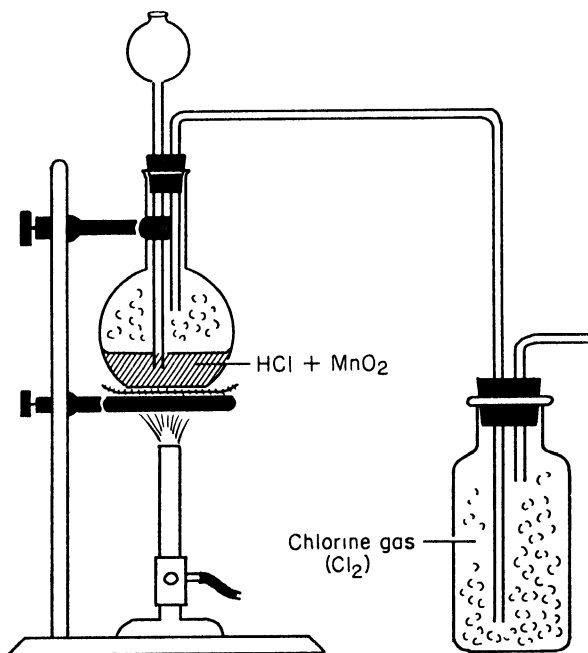
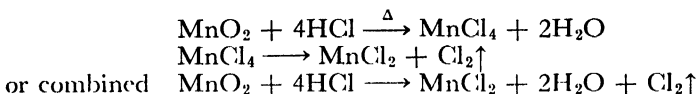


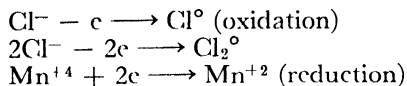
Fig. 23. Preparation of chlorine.

Preparation. In the laboratory chlorine gas is easily prepared by heating a mixture of *manganese dioxide and concentrated hydrochloric acid* (Fig. 23). The equations for the reaction are as follows:



* Evidence available at the present time overwhelmingly demonstrates that fluoridation decreases the incidence of dental caries.

This reaction is a good example of one of the two types of *oxidation-reduction* or *redox* reactions. Note that Cl has a valence of -1 in HCl; in Cl_2 the valence is zero. Also, Mn in the compound MnO_2 has a valence of a $+4$, and in the compound MnCl_2 , a valence of a $+2$. In other words, *chlorine has been oxidized*, and *manganese reduced*. In this type reaction, whenever one element loses electrons—is oxidized—another element accepts these electrons, and becomes reduced. This may be stated as follows:

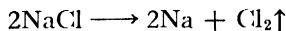


A little thought will substantiate these rules:

1. An *oxidizing agent* brings about the actual oxidation (loss of electrons) of some other substance.
2. A *reducing agent* brings about the actual reduction (gain of electrons) of some other substance.
3. An *oxidizing agent itself* undergoes *reduction*.
4. A *reducing agent itself* undergoes *oxidation*.

In the above reaction MnO_2 is the oxidizing agent; HCl is the reducing agent. A great many reactions are of the oxidation-reduction type. At the present, it appears that most of the chemical transformations in protoplasm are of this type.

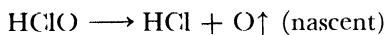
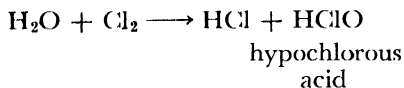
Commercially, chlorine is prepared by the *electrolysis of brine* (sodium chloride in water). The gas escapes over the anode. The reaction is as follows:



Properties. Chlorine is a greenish-yellow gas, with a powerful, irritating odor. It is about two and one-half times as heavy as air, and fairly soluble in water, forming a yellow solution. Chlorine is easily liquefied.

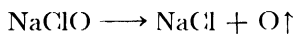
Chemically, chlorine is very active—second only to fluorine. It reacts directly with many elements and compounds, forming a huge variety of useful substances. With hydrogen, chlorine forms *hydrogen chloride*, which when dissolved in water forms *hydrochloric acid* (HCl). Salts of hydrochloric acid are called *chlorides*.

Bleaching and Disinfecting Actions of Chlorine. Chlorine water is a useful *bleach*, *antiseptic* and *disinfectant*. The dry gas does not possess these qualities. Calico, for example, is not bleached when placed in a bottle of dry chlorine. The bleaching and antiseptic actions are explained by the following reactions:



The nascent oxygen (O instead of O₂) combines with certain dyes to produce colorless derivatives. The antiseptic action is no doubt due in part to the direct action of this nascent oxygen on the protoplasm of microorganisms.

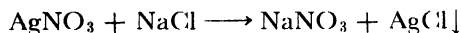
Although chlorine has wide use in the disinfection of drinking water, swimming pools, and similar uses, *sodium hypochlorite* (NaClO) is the most common form of this element in use as a household bleach and antiseptic. The action of sodium hypochlorite is analogous to the action of hypochlorous acid:



Dakin's solution and *Javelle water* are weak solutions of sodium hypochlorite. *Clorox* and similar bleaching agents are stronger solutions of sodium hypochlorite (about 5 per cent solutions). Bleaching powder, or chloride of lime (CaOCl₂), is also widely used as a bleach, disinfectant, germicide and deodorant.

Other Uses. Chlorine is a constituent of many important laboratory, industrial and pharmaceutical compounds. *Chloroform* (CHCl₃) and *carbon tetrachloride* (CCl₄) are familiar examples of such substances. Of historical importance is the fact that chlorine was the first gas used in warfare. Chlorine is also present in the molecules of three other war gases: *mustard gas*, *chloropicrin* and *phosgene*. *Nitrogen mustard* (a derivative of mustard gas) has proven to be an enemy of cancerous growths in man; it brings about dramatic relief in certain types of leukemia. Although not a cure, nitrogen mustard appears to be one of the chemotherapeutic agents of choice in this baffling condition.

Test for a Chloride. When a solution of silver nitrate is added to a solution of a chloride, a *dense white precipitate—silver chloride* (AgCl)—*forms immediately*. The test may be confirmed by the ability of ammonium hydroxide to dissolve the precipitate. The equation is as follows:



Bromine

Bromine occurs in nature combined with other elements in the form of bromides. Sodium bromide and magnesium bromide are found in vast beds throughout the world. Ocean water contains substantial

amounts of bromide salts, and serves as an excellent (cheap) source of this element.

Preparation. In the laboratory, bromine is readily prepared by oxidizing some bromide salt with a mixture of manganese dioxide and sulfuric acid (Fig. 24). In reactions involving three chemicals, as in this case, it is not always easy to predict the products. Once the products

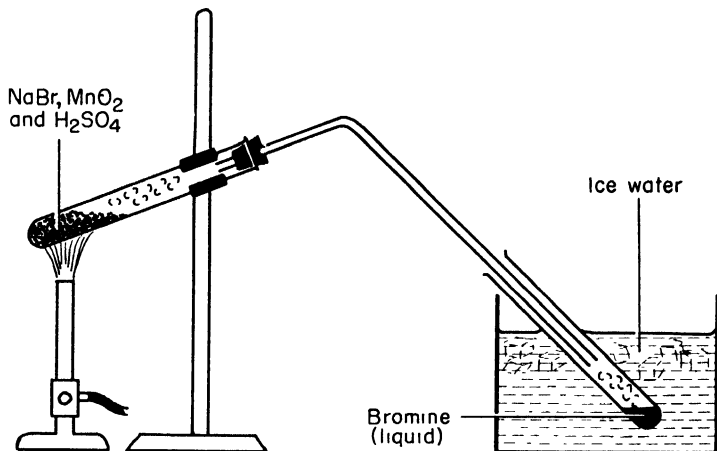
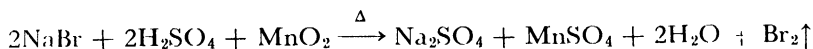
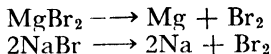


Fig. 24. Preparation of bromine.

are known, however—and this can be ascertained experimentally—balancing is simple. In our work, we shall not have occasion to deal with many reactions of this type:



Commercially, bromine is usually prepared by the electrolysis of a bromide. Ocean water is the source of choice. The only expense in this method is the electricity. The reaction may be represented thus:

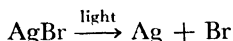


Also note that metals—in the above case magnesium and sodium—are produced along with the bromine.

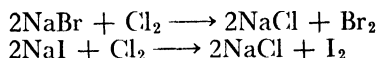
Properties. Bromine is a dark red liquid about 3 times as heavy as water. It has a disagreeable, pungent and irritating odor. The liquid is extremely volatile, and the vessel within which it is contained is filled with the red gas. Bromine is fairly soluble in water, forming a reddish solution. In certain organic solvents, e.g., carbon tetrachloride, it is readily soluble. Physiologically, the liquid and gas are irritating to the skin, and highly poisonous.

Bromine reacts with hydrogen to form *hydrogen bromide*. When this gas is passed into water, the resulting solution is called *hydrobromic acid*. Salts of this acid are called *bromides*.

Uses. Bromine is a constituent of many important substances. The element itself is seldom employed outside the laboratory. Several inorganic bromide salts and organic derivatives are used in medicine. *Sodium and potassium bromides* have been used for years as *depressant drugs* to induce sleep, and in certain forms of *epilepsy*. Large quantities of *silver bromide* are consumed in the manufacture of photographic film. This is the most important use of bromine. Essentially, the taking of a picture involves the decomposition of silver bromide (present in a gelatin base on the emulsion side of the film) by the light permitted to enter during exposure. This photochemical reaction is as follows:



Test for a Bromide. To test for the bromide ion, chlorine water is added to the dissolved unknown. If a brown color appears, the unknown may be a *bromide* or an *iodide*. The test is confirmed by adding starch: *Iodine and starch* produce a deep blue or purple color; bromine and starch *do not* produce a color. As may be inferred, chlorine—being more chemically active than either bromine or iodine—replaces these two elements from their compounds. The brown color formed after the addition of the chlorine water is due to free bromine or iodine. The reactions are as follows:



Iodine

Iodine occurs in nature as *iodides* in sea water, and as *iodates* in Chile saltpeter deposits. In the body iodine is a constituent of *thyroxin*, a hormone manufactured by the thyroid gland.

Preparation. Iodine is prepared by the same reaction as is used to prepare bromine. The equation for the reaction is as follows:



In this method the iodine evolves as a purple vapor which condenses as purplish-black crystals on the under side of the cool evaporating dish (Fig. 25).

Iodine is prepared commercially from seaweed (kelp), ocean water and Chile saltpeter by methods which free the element from its compounds (iodides and iodates).

Properties. Iodine is a crystalline, steel-gray solid, which quickly turns to purplish-black upon contact with air. The solid vaporizes easily to beautiful fumes. The vapor returns to the solid state when cooled. This process of passing from the solid state to vapor, and then back to the solid state is called *sublimation*. Substances, such as iodine, which undergo sublimation are purified by this method. Sublimation is a simple, easy and economical method of extraction and purification.

Iodine combines directly with many elements, forming *iodides*. Chemically, iodides may be considered as the *salts of hydriodic acid*. Of the halogens, iodine possesses the least activity.

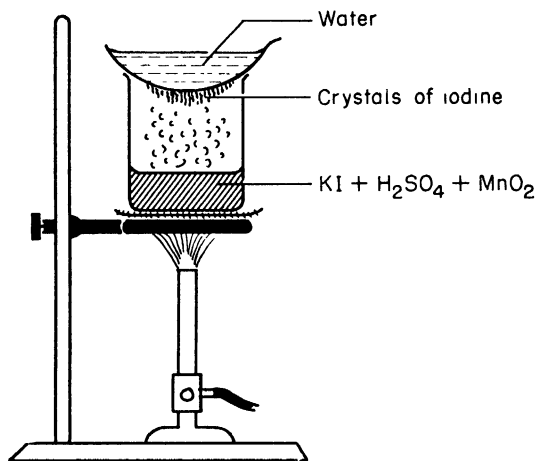


Fig. 25. Preparation of iodine.

Uses. The chief commercial outlet for free iodine is in the manufacture of *tincture of iodine*. Tincture of iodine is a 2 per cent solution of iodine in alcohol and water. The tincture is a valuable antiseptic and disinfectant. Sodium and potassium iodides are used in medicine, in conjunction with other drugs, in thyroid dysfunctions. The proven fact that a lack of iodine gives rise to goiter has prompted the sale of "iodized salt" (i.e., salt with a fraction of a per cent of sodium iodide). Other compounds of iodine—both organic and inorganic—enjoy a variety of uses in the laboratory, medicine and industry.

ARSENIC

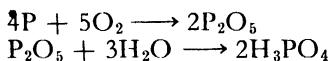
Arsenic is an *amphoteric* element; i.e., it possesses both metallic and nonmetallic properties. It is a gray solid which resembles a true metal in appearance. Chemically, however, it usually acts as a nonmetal. Arsenic and its compounds are poisonous substances. For this reason

they have been employed for years as insecticides and rodenticides. Copper arsenite (*Paris green*), lead arsenate and arsenic trioxide (*white arsenic*) are popular and familiar compounds of arsenic.

In medicine, arsenic has always played an important role. Of special significance is the organic arsenic compound *arsphenamine*, used in the treatment of syphilis. The introduction of *arsphenamine*—commonly referred to as “606”—by Ehrlich in 1909 marked a new era in man’s conquest of disease. For the first time the physician was given a true *specific*—i.e., an agent possessing the ability of destroying an invading pathogenic microorganism. The use of specific chemical agents in disease—aptly labeled *chemotherapy*—is without question the most outstanding development in medicine. The number of chemotherapeutic agents is ever on the increase. There can be little doubt that the sulfa drugs and the antibiotics (e.g., penicillin, Aureomycin, Terramycin, etc.) are only a preview of things to come.

PHOSPHORUS

Phosphorus is a solid which exists in two *allotropic* forms: *white phosphorus* and *red phosphorus*. These two forms display widely differing properties. White phosphorus ignites at room temperature (it must be kept under water), is soluble in ether and carbon disulfide, and is extremely poisonous. Red phosphorus will not burn until heated, is not soluble in ether and carbon disulfide, and is not poisonous. Red phosphorus is prepared by heating white phosphorus in the absence of oxygen. Both red and white phosphorus in the presence of oxygen are oxidized to *phosphorus pentoxide* (P_2O_5)—the acid anhydride of phosphoric acid (H_3PO_4):



Phosphorus is too active to be found in the free state. It occurs chiefly in the form of *phosphates*, i.e., salts of phosphoric acid. Phosphates are found in the soil and in certain phosphate rock deposits, such as in South Carolina and Florida. Phosphorus is an important constituent of the body. *About 80 per cent of the solid matter of bones and teeth is composed of calcium and magnesium phosphates* ($Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$). The blood, brain, nerve and muscle tissues contain organic and inorganic phosphates.

The principal use of elemental phosphorus is in the making of matches. Originally white phosphorus was used, but due to its high toxicity it has been replaced by red phosphorus. The sodium salts of phosphoric acid are used in medicine. Since phosphoric acid has three replaceable hydrogens, there are three “sodium phosphates”: *mono-*

sodium phosphate (NaH_2PO_4); disodium phosphate (Na_2HPO_4); and trisodium phosphate (Na_3PO_4).

SILICON

Next to oxygen, silicon is the most abundant (28 per cent) element of the earth's crust. Due to the activity of silicon, it is never found free, but in the combined condition—viz., as *silica* (SiO_2), *silicates* (SiO_4^{4-}) and *combined silicates*. *Quartz*, *zircon*, *asbestos*, *talc*, *mica*, *clay* and *feldspar* are silicate minerals of extreme importance.

Free silicon is employed almost exclusively in the steel industry. The addition of silicon to low-carbon steel increases its elastic limit and markedly increases its resistance to wear. Of the compounds of silicon, *silica* (sand) and *clay* are of chief concern. These two natural compounds are intimately related to the history of man. From sand man makes *glass*, and from clay, *cement*. It is indeed difficult to visualize our civilization without these two materials.

Although silicon is omnipresent and important, it has received little publicity in our chemistry texts. Recent developments (since World War II), however, have drastically changed this practice. A class of compounds called *silicones* offers promise of becoming one of our most valuable classes of compounds. Silicones are complex compounds whose molecules are constituted by silicon and oxygen atoms arranged—alternately—in chains. By varying the length of the chains, the chemist has been able to synthesize an array of diversified and useful products having the physical properties of oils, rubbers, resins, plastics, and so on. Of special significance is the fact that silicones are probably the most resistant compounds yet synthesized in the laboratory.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

A.

Column I

- ___ MnO_2
- ___ 21% of the atmosphere
- ___ the loss of oxygen
- ___ water
- ___ H_2O_2
- ___ distilled water
- ___ rust
- ___ saturated

Column II

- 1. miscible
- 2. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- 3. contains little solute
- 4. hydrogen monoxide
- 5. an allotropic form
- 6. osmosis
- 7. deliquescence

Column I

- _____ dilute
- _____ a hydrate
- _____ sodium hydroxide dissolves when exposed to air
- _____ efflorescence
- _____ an exchange of water through a membrane
- _____ alcohol and water
- _____ O_3

B.

- _____ 78% of atmosphere
- _____ $N_2 + H_2 \longrightarrow$
- _____ $KNO_3 + H_2SO_4 \xrightarrow{\Delta}$
- _____ ammonia water
- _____ $NH_4Cl + KOH \xrightarrow{\Delta}$
- _____ N_2O
- _____ legumes (clover, etc.)
- _____ $NH_3 \longrightarrow NO_2$
- _____ NO_2
- _____ N_2O_5

C.

- _____ a noncrystalline allotropic form
- _____ SO_2
- _____ rotten eggs
- _____ rhombic
- _____ $K_2SO_4 + HCl \longrightarrow$
- _____ Contact Process
- _____ $BaCl_2$
- _____ a reducing agent
- _____ $FeS + HCl \longrightarrow$
- _____ a dehydrating agent

Column II

- 8. acts as a catalyst
- 9. releases nascent oxygen
- 10. loss of water
- 11. free of dissolved solids
- 12. reduction
- 13. oxygen
- 14. a result of oxidation
- 15. solute falls out of solution

- 1. NH_3
- 2. source of nitrogen-fixing bacteria
- 3. N_2
- 4. anhydride of HNO_3
- 5. laughing gas
- 6. nitrifying bacteria
- 7. $NH_3 + H_2O \longrightarrow$
- 8. nitrogen peroxide
- 9. HNO_3
- 10. Haber Process

- 1. $2SO_2 + O_2 \longrightarrow 2SO_3$
- 2. SO_2
- 3. anhydride of H_2SO_4
- 4. H_2S
- 5. test for SO_4^{2-}
- 6. concentrated H_2SO_4
- 7. H_2SO_4
- 8. amorphous sulfur
- 9. most stable form of sulfur
- 10. test for sulfide

D.

*Column I**Column II*

- | | |
|--|---|
| ---- graphite | 1. CO |
| ---- $\text{MgCO}_3 + \text{H}_2\text{SO}_4 \longrightarrow$ | 2. insecticide |
| — oxygen evolved | 3. $\text{Ca}(\text{OH})_2$ |
| — combines with hemoglobin | 4. pure carbon |
| — Foamite | 5. $\text{NaI} + \text{Cl}_2 \longrightarrow$ |
| ---- a gaseous halogen | 6. added to tablet salt |
| $\text{NaBr} + \text{MnO}_2 + \text{H}_2\text{SO}_4$ | 7. CO_2 |
| — purple crystals | 8. allotropic forms |
| — bone | 9. $\text{Ca}_3(\text{PO}_4)_2$ |
| — As_2O_3 | 10. a red liquid |
| — NaI | 11. oxidation-reduction |
| — iodine formed | 12. fire extinguisher |
| — bromine | 13. iodine |
| — red and white phosphorus | 14. photosynthesis |
| ---- test for CO_2 | 15. fluorine |

1. Describe the preparation of oxygen.
2. Explain the medicinal use of H_2O_2 .
3. Describe the Contact Process.
4. How could you chemically distinguish between a solution of Na_2SO_4 and KCl ?
5. Describe the Nitrogen Cycle.
6. Describe the test for the NO_3^- ion.
7. Describe the Carbon Cycle.
8. Explain the toxicity of CO.
9. Describe the action of the soda-acid fire extinguisher.
10. Compare the halogens, chemically and physically.
11. What is tincture of iodine?
12. Describe the bleaching and antiseptic actions of chlorine.
13. What is fluoridation?
14. What are the principal compounds of arsenic and phosphorus? Write the formula for ammonium dihydrogen phosphate.
15. Briefly discuss silicon and its compounds.

CHAPTER 7

THE METALS

Of the 92 natural elements which constitute the earth, more than 70 are metals. Of this number, the great majority are so rare and of such limited commercial value that they are seldom mentioned, even among chemists. Only about 15 metals are commonly encountered in everyday life. Indeed, such an unbelievably complex substance as protoplasm contains no more than 10 metallic elements. In this chapter we shall study the important metals in some detail. The table below summarizes the principal facts and differences relating to metals and nonmetals.

<i>Metals</i>	<i>Nonmetals</i>
"Metallic" luster	Absent
Good conductors of heat and electricity	Poor conductors
Are malleable and ductile	Brittle
Crystalline in structure	Usually amorphous
Unite with nonmetals to form salts	Unite with metals to form salts
Form bases (basic anhydrides)	Form acids (acid anhydrides)
Combine with other elements by electrovalence—form positive ions in solution	Combine by electrovalence or covalence—form negative ions in solution
During electrolysis are liberated at the cathode	Are liberated at the anode

RELATIVE ACTIVITY OF METALS

When a strip of zinc is placed into a solution of copper sulfate, the strip becomes coated with copper. On the other hand, if a strip of zinc is placed into a solution of some aluminum salt, nothing happens. In the first case, zinc—*being more chemically active than copper*—replaces the copper from its compound; in the second case, there is no action because *zinc is less active chemically than aluminum*. When a metal replaces another metal from its salt it loses electrons (i.e., it is *oxidized*), while the metal which leaves the solution gains electrons (i.e., it is *reduced*). In other words, the chemical activity of a metal is determined by the ease with which it is oxidized. When the metals are arranged according to their activity, the series is known as the *replacement series* or *electrochemical series*. The electrochemical series is as follows:

1. Potassium (highest activity)
2. Sodium

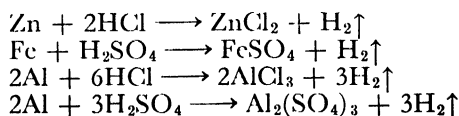
3. Calcium
4. Magnesium
5. Aluminum
6. Zinc
7. Iron
8. Nickel
9. Tin
10. Lead
11. HYDROGEN
12. Copper
13. Mercury
14. Silver
15. Platinum
16. Gold (lowest activity)

Each metal in this list will replace from its salt solution any metal below it, but will, in turn, be replaced by any metal above it. Hydrogen is included because it acts chemically like a metal. *All metals above hydrogen will liberate it from dilute acids, while the metals below hydrogen do not replace it from acids.*

HYDROGEN

Hydrogen enjoys the unique distinction of being the simplest and lightest element. Hydrogen is also unique in that it possesses the *chemical properties of a metal*, and the *physical properties of a nonmetal*. In the free state, hydrogen occurs in natural and volcanic gases; traces of the gas are found in the lower strata of the earth's atmosphere. Hydrogen occurs abundantly in the sun's atmosphere. In the combined state hydrogen is ubiquitous; it is present in water, and all animal and vegetable substances.

Preparation. Pure hydrogen is prepared commercially by the electrolysis of water: Hydrogen is liberated at the cathode, and oxygen at the anode (Fig. 26). In the laboratory, the gas is best prepared by reacting such metals as zinc and iron with certain dilute acids—usually sulfuric acid and hydrochloric acid. This reaction is an example of *simple replacement*, where the metal replaces the hydrogen of the acid and releases it as a gas (Fig. 27). The following equations are typical:



Physical Properties. Hydrogen is a colorless, odorless, tasteless gas, only slightly soluble in water. Its outstanding property, however, is

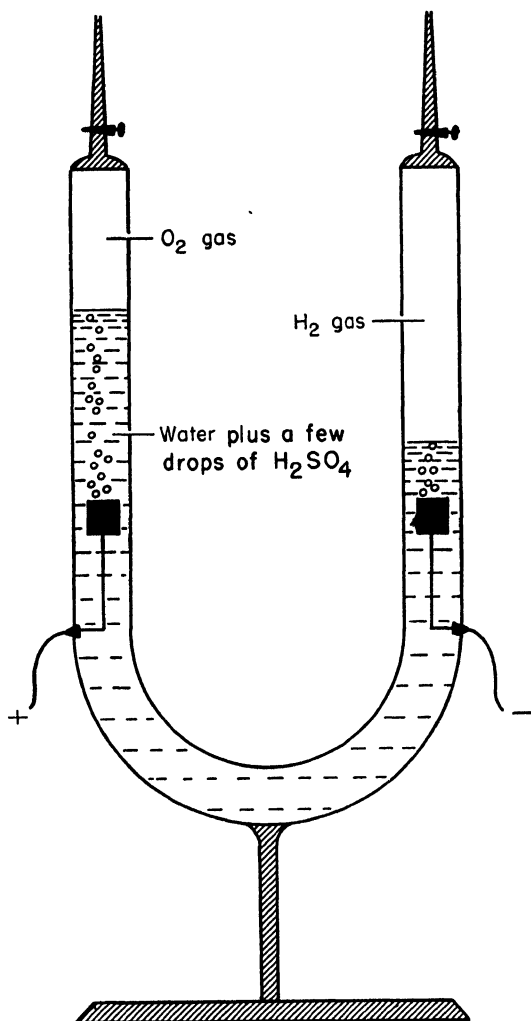
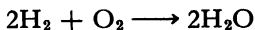


Fig. 26. Electrolysis of water.

that it is the lightest gas known. Certain metals, namely, palladium and platinum, have the power to absorb hydrogen in large volumes. This rather strange property is called *occlusion*.

Chemical Properties. Hydrogen gas burns with a very hot, pale blue flame, producing water. When mixed with oxygen or air it produces a violent explosion on the application of a flame or spark. The equation for the burning of hydrogen is as follows:



When substances which contain hydrogen—viz., *fuels* and *foods*—are burned, water is always formed. The water vapor in exhaled air is due

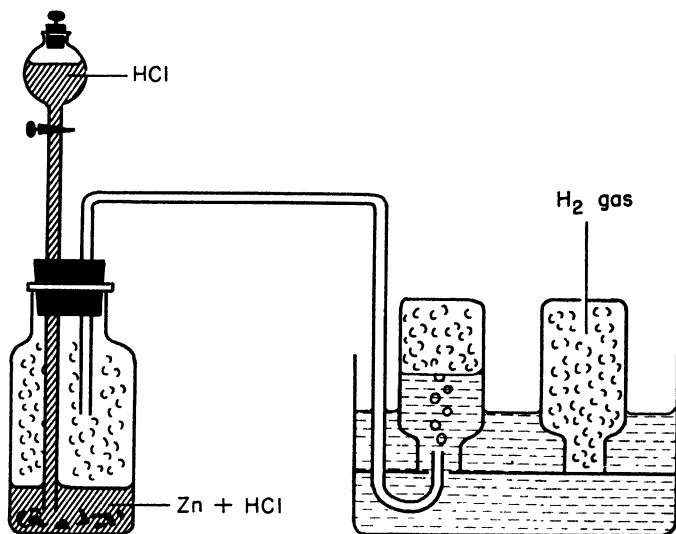
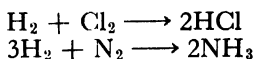
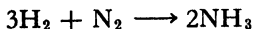


Fig. 27. Preparation of hydrogen.

to the oxidation ("burning") of fats and glucose within the cells of the body. At high temperatures hydrogen combines directly with other elements. The following equations are illustrative:

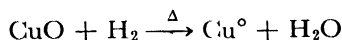


Uses of Hydrogen. The use of hydrogen in "lighter-than-air" craft has been almost completely superseded by helium. The tragic explosion of the *Hindenberg*, the world's largest dirigible, in May, 1937, served as a final indictment of hydrogen for this purpose. (Helium has about 90 per cent of the lifting power of hydrogen, although it is twice as heavy. Helium has the decided advantage of being noncombustible.) Huge quantities of hydrogen are used in the Haber Process to manufacture ammonia gas. As described before, ammonia is formed by the direct combination of hydrogen and nitrogen, thus:



Hydrogen is employed in welding, where temperatures between 2000° C. and 5000° C. are required. In the process known as *hydrogenation* (to be discussed later) liquid fats, such as cottonseed oil and coconut oil,

are converted into solids by being made to react with hydrogen. In the laboratory (and to some extent commercially) hydrogen is employed as a *reducing agent*, i.e., to remove oxygen from certain compounds. When, for example, hydrogen gas is passed over hot copper oxide, water is formed. The reaction is as follows:



SODIUM, POTASSIUM, AND THEIR COMPOUNDS

The so-called *alkali metals**—*lithium, sodium, potassium, rubidium, cesium and francium*—are the most active metallic elements. The activity and similarity of these elements arise from the fact that each of their atoms (Fig. 28) has a single electron in the outer ring. Reference

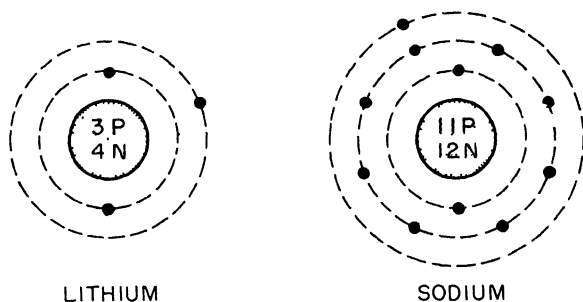


Fig. 28.

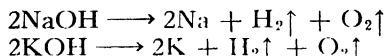
to the Periodic Table will show that the alkali metals constitute a *family of elements*—Family A, Group I. Of the alkali metals, sodium and potassium are by far the most important elements. The others (with the possible exception of lithium) are rare and of slight importance. We shall, then, concentrate on these two elements and their compounds.

Because of their extreme activity, sodium and potassium are never found free in nature. In the combined condition they are widely distributed. The more important compounds of sodium include: *sodium chloride* (common table salt), *sodium nitrate* (Chile saltpeter) and *sodium tetraborate* (borax). The principal natural compounds of potassium include: *potassium chloride* (potash) and *potassium aluminum silicate* (feldspar).

Preparation. The preparation of sodium and potassium is essentially the same process today as was used by the great English chemist, Davy. Both metals are prepared by the electrolysis of their fused

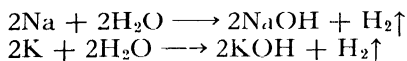
* So called because the hydroxides of these metals are strong bases in solution.

(melted) hydroxides; sodium and potassium are liberated at the cathode. The equations for the reactions are as follows:



Physical Properties. These two metals are very similar in appearance. Moreover, their texture is a surprise to one who sees them for the first time; *both are soft enough to be cut with a knife*. The freshly cut surface has a bright metallic luster, but soon darkens on exposure to air. Both are excellent conductors of heat and electricity.

Chemical Properties. Sodium and potassium react violently with other elements. Their reaction with water or water vapor is so explosive that both must be stored in kerosene. An interesting experiment in the laboratory is to place a *very tiny* piece of potassium or sodium on the surface of water contained in a wide-mouthed receptacle: A reaction ensues instantly, and so much heat is evolved that the metal melts into a globule which dances wildly across the surface of the water. If the piece is large enough, the heat is sufficient to ignite the hydrogen, which is one of the products formed in the reaction. A large piece will produce an explosion. The activity of potassium and sodium with water is a characteristic reaction—and an important reaction. In addition to hydrogen gas, the *hydroxide* of the metal is formed:



Uses. The *free* alkali metals are not important commercially; in the laboratory they are used only to a limited extent. Their compounds, however, are of extreme importance. The salts of sodium and potassium are by far the most common chemical substances employed either in the laboratory or commerce. Several of these salts deserve special mention.

Flame Test. When sodium or a sodium compound is directly heated in the Bunsen burner flame, an intense yellow color is imparted to the entire flame;* potassium and potassium compounds produce a violet color. Certain other metals and their compounds also impart characteristic colors to the flame. The colors produced are as follows:

Sodium.....	yellow
Potassium.....	violet
Lithium.....	crimson
Calcium.....	orange-red
Barium.....	green
Strontium.....	bright red

* When colored flames are examined through an optical instrument called a *spectroscope*, characteristic colored lines are seen. *Spectroscopy* is an important branch of analytical chemistry.

The test is carried out by dipping a clean platinum wire into the substance under investigation (either solid or water solution), and then holding it in the outer edge of the colorless part of the Bunsen flame. Although the test has certain inherent inaccuracies, it is simple to perform, and gives good results when the compound being tested is in the pure form.

Sodium Chloride (NaCl)

Sodium chloride, common table salt, is one of the most valuable compounds known to man. It is found in ocean water, salt beds in the earth and within the cells of living organisms. Students of physiology have a particular interest in this compound.

Extraction. Sodium chloride (usually referred to as "salt") is obtained from salt lakes and ocean water by the simple process of evaporation. The water is piped into shallow basins, and the heat of the sun is allowed to evaporate the water. Salt from salt beds is obtained by mining (similar to coal mining), or by driving pipes into the beds, and allowing water to dissolve the salt. The salt solution formed is then evaporated in the manner described above.

Properties. Sodium chloride is a white solid made up of cubical crystals. When heated the crystals crackle and explode. This action is called *decrepitation*. Decrementation is caused by the vaporization of the water which is *mechanically* trapped within the crystal. In other words, this water is not water of crystallization. Since table salt takes on moisture from the air (especially during humid weather), it would appear that sodium chloride is a deliquescent substance. Pure salt, however, is not deliquescent. This property of table salt results from the presence of deliquescent impurities, namely, magnesium chloride. As for the taste of sodium chloride, we say that it is simply "salty." Other *chemical salts* have a similar taste.

Uses. Sodium chloride has many uses other than being our favorite "mineral food." It is used in great quantities to preserve meat and fish. In the chemical industry sodium chloride is the starting chemical for practically all of the important compounds of sodium and chlorine.

Sodium Bicarbonate (NaHCO_3)

Sodium bicarbonate (*baking soda*) is a common compound, both in the laboratory and home. Of special interest to us is its method of manufacture—the *Solvay Process* (see Fig. 29). The Solvay Process is an example of chemical genius and ingenuity at the industrial level. In practice, the teachings of chemistry mean very little unless pure chemical compounds can be produced in sufficient quantities to supply

all needs—and *at low cost*. The Solvay Process is herewith described to illustrate the remarkable efficiency which prevails in the chemical industries. In the following steps, note the cheap and abundant raw materials, the use of the by-products to prepare the main product, and the relatively simple and direct chemical reactions.

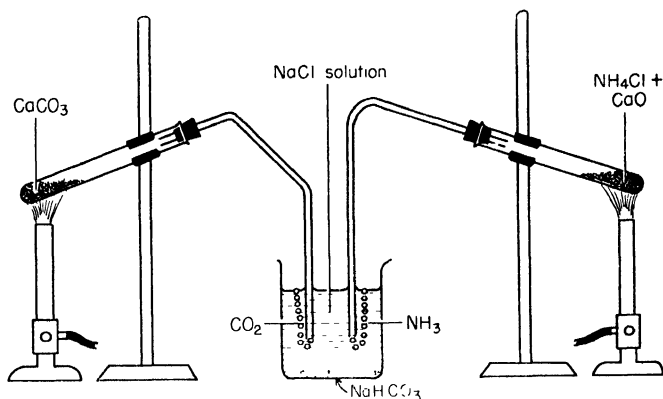
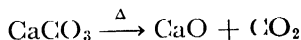


Fig. 29. Laboratory representation of the Solvay Process.

1. The heating of limestone to produce calcium oxide and carbon dioxide:

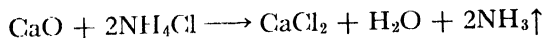


2. The carbon dioxide, under pressure, is passed into a saturated solution of ammonia and salt water. The following reactions occur:

- a. $\text{NH}_3 + \text{H}_2\text{O} \longrightarrow \text{NH}_4\text{OH}$
- b. $\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3$
- c. $\text{NH}_4\text{OH} + \text{H}_2\text{CO}_3 \longrightarrow \text{NH}_4\text{HCO}_3 + \text{H}_2\text{O}$
- d. $\text{NH}_4\text{HCO}_3 + \text{NaCl} \longrightarrow \text{NaHCO}_3\downarrow + \text{NH}_4\text{Cl}$

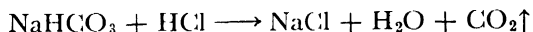
In reaction (d) sodium bicarbonate precipitates from the solution because it is not soluble in a solution of ammonium chloride (NH_4Cl). This is most fortunate, since sodium bicarbonate is water-soluble. The bicarbonate is now filtered from the solution.

3. Ammonia is recovered by heating CaO (a by-product of the first step) and NH_4Cl (a by-product of the second step), thus:



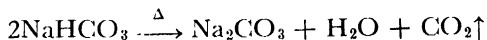
In the whole process, calcium chloride (CaCl_2) is the only substance which is not used over again. Nothing is lost, however, as calcium chloride has a market of its own.

Properties and Uses. Sodium bicarbonate is a white solid which dissolves in water; its solutions are mildly alkaline. Sodium bicarbonate is a good source of carbon dioxide, and is employed to generate this gas in the soda-acid fire extinguisher (described earlier) and in baking powders. In medicine, it is still the most popular agent to neutralize excess acid in the stomach (*hyperacidity*). The belching following a dose of sodium bicarbonate results from the reaction between the bicarbonate and the hydrochloric acid in the stomach:



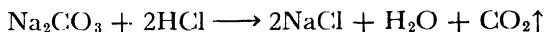
Sodium Carbonate (Na_2CO_3)

Sodium carbonate (*washing soda*) is prepared by heating sodium bicarbonate:



The above equation applies to all bicarbonates: *They are decomposed into a carbonate, water and carbon dioxide when subjected to heat.*

Properties and Uses. When a water solution of sodium carbonate is slowly evaporated, large transparent crystals are formed, having the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. When exposed to air this compound (the *hydrous* form) slowly loses its water of crystallization (*efflorescence*), and crumbles into a white powder (Na_2CO_3)—the *anhydrous* form. Solutions of sodium carbonate are basic in reaction, *owing to hydrolysis. For this reason sodium carbonate and sodium bicarbonate should not be confused*; the greater alkalinity of the former compound would cause severe irritation if taken internally. Like all carbonates, it reacts with acids to produce carbon dioxide:



Sodium carbonate enjoys many commercial uses. It is employed in the manufacture of soap, soap powders, water softeners and glass. In the laboratory it is used whenever a typical soluble carbonate is needed.

Sodium Hydroxide (NaOH)

Sodium hydroxide is made commercially by the electrolysis of a sodium chloride solution (*brine*). This process (called the *Nelson* or *Vorce Process*) is interesting in that there are two products formed other than sodium hydroxide. It is easy to understand this process if we apply what we already know. The chloride ion (Cl^-), being negative, will be attracted to the anode, and there become *chlorine gas*; the sodium ion (Na^+) will be attracted to the cathode, and become sodium metal. However, it was pointed out under our discussion of sodium

that the metal is extremely active, especially with water. As soon as the sodium ions become sodium atoms, therefore, the atoms react with the water of the solution to form *sodium hydroxide and hydrogen*. The Nelson Process thus enables us to manufacture chlorine, hydrogen and sodium hydroxide simultaneously. In the laboratory the following simple experiment is most instructive: A drop of phenolphthalein indicator solution is added to a beaker of salt solution. When electrodes are placed into this solution and a current applied, bubbles of gas are formed around each electrode. The gas coming off the anode has the odor of chlorine; the gas off the cathode has no odor, but is inflammable—hydrogen. Moreover, the area around the cathode turns red (phenolphthalein turns red in basic solution) showing that sodium hydroxide has been formed. The equations for the reactions are as follows:

1. $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$ (ionization)
2. $2\text{Cl}^- - 2e \longrightarrow \text{Cl}_2^\circ$ (at the anode)
3. $\text{Na}^+ + 1e \longrightarrow \text{Na}^\circ$ (at the cathode)
4. $2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2\uparrow$ (at the cathode)

Properties and Uses. Sodium hydroxide is a white deliquescent solid, freely soluble in water. It is a typical strong base due to the fact that it is highly ionized in solution, furnishing an abundance of hydroxyl ions. Sodium hydroxide neutralizes all acids, forming sodium salts. It neutralizes hydrochloric acid, for example, forming sodium chloride and water:



Sodium hydroxide is highly caustic to living tissues, dissolving both protein and fat substances. For this reason it is commonly known as *caustic soda*.

In the laboratory sodium hydroxide has many uses. It is, without question, the most frequently used base. Commercially, sodium hydroxide is employed in many ways. Huge quantities are consumed in the manufacture of soap from fats. Most everyone is familiar with the word *lye*. Lye is a commercial form of sodium hydroxide used to clean toilets and sink drains. Lye cleans by attacking and dissolving organic matter—especially fats, oils and grease.

Sodium Nitrate (NaNO_3)

Huge deposits of sodium nitrate, known as *Chile saltpeter*, are found in Chile and Peru. These deposits were formed by a “natural coincidence,” since *organic matter, sodium salts and dry air* must be present. For years the world was dependent upon these deposits for a source of cheap nitrate.

Properties and Uses. Sodium nitrate is a white crystalline solid, very soluble in water. Great quantities of sodium nitrate are used in the manufacture of fertilizer and nitric acid. The nitric acid, in turn, is employed to manufacture a greater number of organic and inorganic nitrate compounds. In our discussion of artificial nitrogen fixation as applied to ammonia and nitric acid, we learned that man no longer depends upon natural nitrogen compounds, namely, the Chile deposits. At present more than half the world's needs are supplied by artificial fixation, viz., the *Haber Process and the Synthetic Ammonia Process*.

Potassium Compounds

Compounds of potassium, although frequently encountered in the laboratory, pharmacy and commerce, are decidedly less common than those of sodium. Probably the chief reason for this is that potassium is more expensive than sodium. Chemically and physically, sodium and potassium salts are almost identical in their behavior. Physiologically, however, they are not similar; protoplasm readily sustains an insult when a K^+ ion is substituted for a Na^+ ion, and vice versa. The body, for example, would soon show signs of metabolic dysfunction if potassium chloride were to be substituted for sodium chloride. Some of the common and important compounds of potassium are herewith briefly described.

Potassium Chlorate ($KClO_3$). Potassium chlorate is a white crystalline solid, possessing strong powers of oxidation. As with all powerful oxidizing agents, great care should be exercised in its use. Potassium chlorate is a valuable oxidizing agent both in the laboratory (it is used, you will remember, to prepare oxygen) and in industry where it is employed to manufacture matches, fireworks and explosives.

Potassium Chloride (KCl). Potassium chloride occurs in the minerals *carnallite* ($KCl \cdot MgCl_2 \cdot 6H_2O$) and *sylvite* (KCl). These two minerals are obtained from mines at Strassfurt, Germany. Potassium chloride is probably, by virtue of its relative abundance, the most important compound of potassium. It is used as a fertilizer, and in the preparation of other potassium compounds. Potassium is an essential element to plants.

Potassium Hydroxide (KOH). Potassium hydroxide, commonly known as *caustic potash*, is physically indistinguishable from sodium hydroxide. Moreover, it is prepared by the same process—the *electrolysis of potassium chloride*. Potassium hydroxide is probably the second most common base in the laboratory; industrially, however, it has a rather limited usefulness. Of interest is the fact that *soft soaps* are made from the reaction between fats and potassium hydroxide; *hard soaps* are made from solid fats and sodium hydroxide.

Potassium Nitrate (KNO_3). Potassium nitrate, commonly known as *saltpeter* (*Chile saltpeter is sodium nitrate*), is of some importance. It is a white crystalline solid, freely soluble in water. Chemically, it is a rather potent oxidizing agent, and is sometimes employed as an oxidizing agent in the laboratory. Commercially, it is used as a fertilizer, meat preservative and in the manufacture of gunpowder. Gunpowder, which has probably directed the destiny of man more than any other substance, is a simple mixture of *potassium nitrate, sulfur and charcoal*. In medicine, potassium nitrate has been used as a diuretic (to increase production of urine) and as a hypotensive agent, i.e., to reduce blood pressure.

CALCIUM AND ITS COMPOUNDS

Calcium is the principal member of the *alkali-earth metals*. The alkali earth metals are a family of elements—Family A, Group II of the Periodic Table. The family includes the following elements: *calcium, beryllium, magnesium, strontium, barium and radium*. The physical and chemical properties of these elements and their compounds are very similar.

Next to aluminum and iron, calcium is the most abundant metal of the earth's crust. Since it is chemically reactive, it occurs in a number of compounds. The most abundant and important calcium salts in nature are *calcium carbonate, calcium sulfate, calcium fluoride and calcium phosphate*. In the body, calcium is by far the most important metallic element; the bulk of *bones and teeth* is constituted by calcium in the form of *calcium phosphate*.

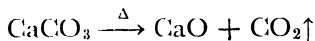
Properties and Preparation. Calcium is a light, silver-white metal which tarnishes rapidly in moist air. It reacts with oxygen to form calcium oxide, and with water to form calcium hydroxide and hydrogen. Calcium metal is prepared by the electrolysis of calcium chloride.

Uses. Calcium in the free state has few uses. Its compounds, however, are of vast importance in the laboratory, medicine and industry. The more important calcium compounds are herewith described.

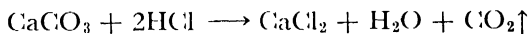
Calcium Carbonate (CaCO_3)

Calcium carbonate is the most abundant calcium compound in nature. Of considerable interest is the fact that calcium carbonate occurs as *marble, limestone, chalk and calcite*. The mineral calcite is the only crystalline variety of calcium carbonate—all the other forms are amorphous solids.

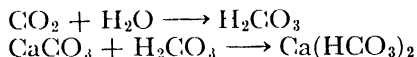
Properties. Calcium carbonate is a white amorphous solid, insoluble in water. It is decomposed by heat into calcium oxide and carbon dioxide;



Like other carbonates, it reacts with acids to form salts and carbon dioxide gas:



Limestone Caves. In regions where there are large deposits of limestone, the slow solvent action of soil water has formed tremendous caves of weird and awesome beauty. The solvent action of soil water on limestone is due to its acidity; the acidity, in turn, is due to the presence of carbon dioxide which rain water dissolves on its journey through the air. The above may be summarized by the following equations:



Calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) is a *soluble compound*, and is removed by the ground's water. A singular feature of limestone caves is the icicle-like projections from their roofs and floors. These are easily explained by the fact that calcium bicarbonate readily decomposes into calcium carbonate, carbon dioxide and water. Therefore, when water containing calcium bicarbonate drips from the roof of a cave, some of the water evaporates, leaving $\text{Ca}(\text{HCO}_3)_2$, which subsequently decomposes as follows:

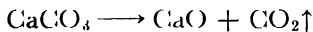


These downward projections are called *stalactites*. The upward projections, or *stalagmites*, are formed in the same way from the water which has dripped to the floor. In time, the stalagmites meet the stalactites to form columns. Eventually (thousands of years) this process will fill the cave up again. Famous limestone caves in the United States include: Mammoth Cave (Kentucky), the Luray Caverns (Virginia), Carlsbad Caverns (New Mexico) and Howe Caverns (New York State).

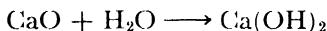
Uses. Calcium carbonate in its natural forms (marble and limestone) has served the building needs of man for thousands of years. Limestone is consumed in huge quantities to make glass, lime and cement. In the blast furnace, limestone is employed in the extraction of iron from its ore. Pure calcium carbonate (commonly referred to as *precipitated chalk*) is used to make tooth powder, toothpaste and polishes. Calcium carbonate has proved to be an excellent medicinal agent in hyperacidity. In the laboratory it is often used to prepare carbon dioxide.

Calcium Oxide (CaO)

Calcium oxide (*quicklime*) is prepared by heating crushed limestone in a special furnace or *kiln*:



Properties and Uses. Calcium oxide is a white solid which reacts with water, forming calcium hydroxide (*slaked lime*):

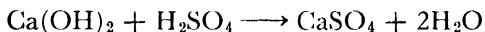


Calcium oxide is employed in the preparation of other calcium compounds. Its chief use is in the production of calcium hydroxide.

Calcium Hydroxide (Ca(OH)₂)

Calcium hydroxide (or *slaked lime*) is prepared, as stated above, by the reaction between calcium oxide and water.

Properties and Uses. Calcium hydroxide is a white powder, slightly soluble in water. In water solution it undergoes appreciable ionization, and is quite alkaline. Calcium hydroxide reacts with acids to form the corresponding salt. It reacts with sulfuric acid, for example to form calcium sulfate and water:

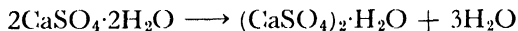


Calcium hydroxide enjoys wide use in commerce. It is employed in the manufacture of glass, sodium hydroxide, bleaching powder, mortar and plaster. In the laboratory it is employed as a base of moderate activity. Medicinally, *limewater*—a clear saturated solution of calcium hydroxide in water—has been used for years to control hyperacidity.

Calcium Sulfate (CaSO₄)

Calcium sulfate occurs in nature as *gypsum*, a white crystalline solid with the formula $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Properties and Uses. When gypsum is heated, it loses three quarters of its water of crystallization, and forms a white powder called *plaster of Paris*. This may be represented as follows:



When plaster of Paris ($(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$) is mixed with water, the above reaction is reversed, and a hard crystalline mass of artificial gypsum results. This constitutes the "setting" or hardening of plaster of Paris. During the setting process the mixture slightly expands, and for this reason affords a suitable molding medium in making accurate copies of

such articles as medals, teeth, and so on. Plaster of Paris is extensively employed in medicine for making casts. Natural gypsum is also used in the manufacture of fertilizers (as a source of calcium) and cement.

Other Calcium Salts

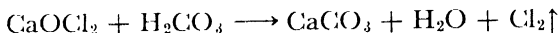
Calcium Chloride (CaCl_2). Calcium chloride is the chief by-product of the Solvay Process. The hydrous form ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is a white crystalline solid—and *extremely deliquescent*. On exposure to the air, the crystals become wet and finally dissolve. For this reason, calcium chloride is extensively used, both in the laboratory and commerce, as a drying agent. Calcium chloride has been used in medicine as a source of calcium in certain deficiency states.

Calcium Phosphate ($\text{Ca}_3(\text{PO}_4)_2$). Vast deposits of calcium phosphate are found in Tennessee, South Carolina and Florida. In the human body, calcium phosphate is the chief constituent of bone. The most important use of this compound is as a fertilizer (principally to supply phosphorus).

Chloride of Lime (CaOCl_2). When calcium hydroxide reacts with chlorine gas, a white unstable powder called *chloride of lime* (or *bleaching powder*) is formed, thus:

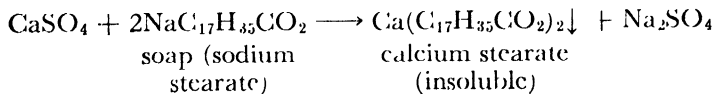


The use of chloride of lime as a bleach and disinfectant depends upon its ability to release *chlorine*. Moisture and air greatly facilitate and enhance its decomposition. This may be explained by the fact that water absorbs sufficient carbon dioxide from the air to form carbonic acid; the carbonic acid then reacts with the chloride of lime to release chlorine. The reaction is as follows:

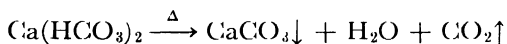


Hard Water

That the water in certain localities is “hard” is common knowledge. Chemically, hardness of water is explained by the fact that certain mineral salts—*soluble salts of calcium and/or magnesium*—react with soap to form insoluble products. Such water is obviously undesirable for washing. Moreover, it is expensive, since a good portion of the soap is converted to a worthless precipitate. The reaction between hard water and soap may be represented as follows:

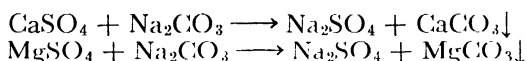


Temporary Hard Water. Temporary hard water is hard water which may be "softened" by boiling. Temporary hardness results from the presence of either *calcium or magnesium bicarbonate*. When such water is heated, the bicarbonates are decomposed into *insoluble carbonates*, thus:



Permanent Hard Water. Permanent hard water usually contains the chlorides and sulfates of calcium and magnesium. Boiling does not alter its hardness.

Water Softeners. Hard water presents a real problem in the household and industry. On a small scale, *washing soda* (Na_2CO_3) has been in use for years as a relatively cheap water softener. Washing soda softens water by reacting with the impurities to form *insoluble carbonates*, thus:



Other chemical substances which react in a similar manner are sold on the market. On a large scale, *permutit* is probably the most efficient water softener. Permutit is a complex chemical compound which contains replaceable sodium atoms. When water is allowed to pass through a tank of this substance, the calcium and magnesium ions in the water are *exchanged* for sodium ions; sodium salts in water do not react with soap. Another approach to the hard water problem was the advent of the so-called *detergents* (*Tide, Dreft, Vel, Fab, Cheer, etc.*). Detergent soaps are really not soaps; their molecular configuration is decidedly different. Being different, they do not mimic the action of soap toward hard water. Indeed, they clean as well in hard as soft water. Their general superiority to conventional soap is fully established.

IRON AND ITS COMPOUNDS

Iron is the second most abundant metal of the earth's crust (aluminum is first). It occurs chiefly in the form of oxides. *Hematite*, for example, an important iron ore, has the formula Fe_2O_3 . In the biologic world, iron—in the form of *hemoglobin*—is found in the blood of nearly all animals. Iron is of vast importance to man. In the form of steel, it has revolutionized our civilization. In addition, its chemical compounds have hundreds of diversified uses in the laboratory, commerce and medicine.

Extraction. Iron is obtained from its oxide ores by the chemical process of *reduction*, i.e., the removal of oxygen. The reduction or ex-

traction process is carried out in the *blast furnace* at tremendously high temperatures. The blast furnace is one of the most impressive sights on the industrial scene. The typical furnace is about 100 feet high and 25 feet in diameter. It is built of wrought iron and is lined with fire brick (Fig. 30). The furnace is charged with the following materials:

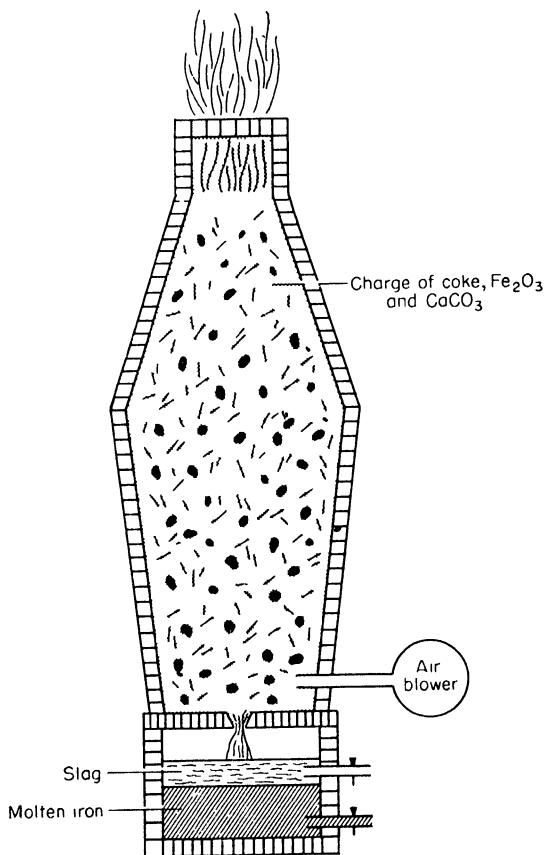


Fig. 30. The blast furnace.

(1) *iron ore*, usually hematite (Fe_2O_3); (2) *coke*, a porous form of carbon, to supply heat and act as a reducing agent; (3) *hot air*, to burn the coke; and (4) *flux*, usually limestone (CaCO_3), to combine with the impurities in the ore. When the furnace is started, a series of chemical reactions take place between these materials to produce molten iron. The first reaction is the combustion of the coke near the bottom of the furnace. The heat resulting from this reaction renders the upper

layers of coke red-hot. As carbon dioxide—formed in the combustion of the coke—passes up through the heated mass, it is reduced to carbon monoxide. Being a powerful reducing agent at high temperatures, the carbon monoxide removes oxygen from the iron ore, forming iron and carbon dioxide. At the same time some ore is directly reduced by the hot coke in the lower part of the furnace. The flux—calcium carbonate—is decomposed by the intense heat of the furnace, forming calcium oxide and carbon dioxide. The calcium oxide unites with the impurities of the ore—chiefly *sand and quartz* (SiO_2)—forming a glasslike *slag*, which has the formula CaSiO_3 (calcium silicate). At the bottom of the furnace, the molten slag floats on the surface of the molten iron. It is then removed through the “slag notch.” Molten iron is run out through the “iron notch.” The following reactions summarize the reactions within the furnace:

1. $\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$
2. $\text{CO}_2 + 2\text{C} \longrightarrow 2\text{CO}$
3. $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
4. $2\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 4\text{Fe} + 3\text{CO}_2$
5. $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
6. $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$

The waste gases resulting from the reactions in the furnace pass out through the pipe located at the top. Since they contain about 25 per cent carbon monoxide, they are used to heat the air which is blown into the furnace.

Types of Iron. **CAST IRON.** Cast iron, or *pig iron*, is the iron obtained from the blast furnace. It is the least pure of all forms of iron, containing about 5 per cent carbon and 2 per cent of sulfur, silicon, phosphorus and manganese. Cast iron is a hard, brittle solid, with a crystalline structure. It melts in the vicinity of 1200°C . Seventy-five per cent of all the cast iron from the blast furnace goes into the making of wrought iron and steel. The remainder is *cast* into various articles such as radiators, stove parts and water pipes, i.e., articles which are not intended to sustain stress.

WROUGHT IRON. Wrought iron is the *purest form of commercial iron*, containing less than 0.5 per cent foreign matter. It is made by oxidizing the impurities in cast iron. The process is carried out in a *reverberatory furnace*. Wrought iron—in contrast to cast iron—is tough, flexible, malleable and ductile. It cannot, however, be tempered. Wrought iron is the principal type of iron used in making pipes, boiler tubes, chains, anchors, bolts and electromagnet cores.

STEEL. Steel is, without question, the most important form of iron. It can be tempered, forged into any desired shape, cast into molds,

rolled into bars and sheets, and drawn into wire. By virtue of the variety of ways it may be worked, steel is our most useful metallic material of construction.

Chemically, steel is a form of iron intermediate in purity between cast iron and wrought iron. The various types of steel contain from 0.2 per cent to 2 per cent of carbon. It is a most interesting fact that the type of steel depends on the *concentration of the various impurities—especially carbon*. In contrast to cast and wrought iron, therefore, the making of steel demands strict analytic control. Essentially, the making of steel involves the removal of impurities from cast iron, and the subsequent addition of *measured amounts of carbon* and/or other metals. The *Bessemer Converter*—an early, but still important process—illustrates the method. About 15 tons of molten cast iron—direct from the blast furnace—are placed in an egg-shaped converter. A strong blast of heated air is then blown through the liquid to bring about the oxidation of carbon and other impurities. After about fifteen minutes, the oxidation is complete, as indicated by the size and color of the flame issuing from the mouth of the converter. At that time, weighed quantities of carbon and manganese are added to provide the correct amount of foreign matter.

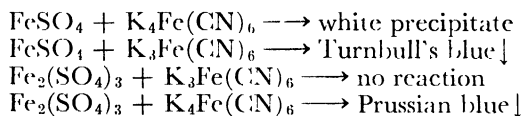
Bessemer steel is only one variety of steel. At the present time most of our steel is made by the *Open-Hearth Process*. Open-hearth steel is of a much higher grade than Bessemer. Other important processes for making steel include the *Crucible Process* and the *Electric Furnace Process*. Special steels are produced when a certain property is desired, such as unusual hardness, toughness and chemical resistance. Special steels—i.e., steel alloys—are produced by adding small amounts of other metals to ordinary steel. Chrome steel, for example, is the steel of choice where resistance to corrosion is desired. Chrome steel contains 3 per cent chromium.

Compounds of Iron

When the atoms of iron combine with other elements, they are capable of losing 2 or 3 electrons, forming the ions Fe^{++} or Fe^{+++} . In other words, an atom of iron has 3 electrons in its outer orbit. Whether it loses 2 or 3 electrons depends upon the nature of the reaction, and the element with which it is combining. Therefore, we possess two types of iron compounds: those in which iron has a *valence of 2*, and those in which iron has a *valence of 3*. Those in which iron has a valence of 2 are called *ferrous* compounds; those in which iron has a valence of 3 are called *ferric* compounds. In general, ferrous salts are green, while ferric compounds are yellow, brown or red. It is most important to understand that ferrous compounds are not as stable as ferric com-

pounds. This is to be expected, since a ferrous ion is capable of losing an additional electron. Ferrous compounds, then, especially when exposed to air for long periods of time, gradually change to ferric compounds. In the laboratory, therefore, ferrous compounds should always be freshly prepared in order to prevent "ferric contamination."

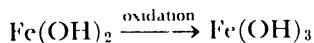
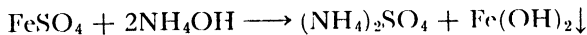
How do we know whether a given iron compound is in the ferrous or ferric condition? A very simple, specific, and highly sensitive test may be employed to differentiate the two types of compounds. When a dilute solution of *potassium ferricyanide* ($K_3Fe(CN)_6$) is added to a ferrous salt solution, a beautiful blue precipitate, called *Turnbull's blue*, forms immediately. Ferric salts, ferric sulfate ($Fe_2(SO_4)_3$), for example, react immediately with *potassium ferrocyanide* ($K_4Fe(CN)_6$) to form an intense dark blue precipitate called *Prussian blue*. The reactions for the above tests are as follows:



There are quite a few important compounds of iron—both ferrous and ferric—in the laboratory, industry and pharmacy. The following compounds are common in any chemical laboratory, and serve to illustrate the chemistry of iron.

Iron Oxides. From what was stated above, we can readily understand that iron forms two oxides with oxygen: *ferrous oxide* (FeO) and *ferric oxide* (Fe_2O_3). Ferrous oxide is an unstable black powder which readily takes on more oxygen from the air to form ferric oxide. Ferric oxide occurs abundantly in nature as the all important ore, *hematite*. Ferric oxide is a reddish compound. It is the chief compound formed as a result of the rusting of iron. Pure ferric oxide is employed as a paint pigment (*Venetian red*), and as a polishing powder (*jeweler's rouge*).

Iron Hydroxides. When a ferrous salt is treated with ammonium hydroxide, a fluffy white precipitate is formed. On standing a few minutes, the white color changes to a grayish-green color, and finally to a reddish-brown color. The white precipitate is *ferrous hydroxide* ($Fe(OH)_2$); the reddish-brown compound is *ferric hydroxide*. This experiment illustrates not only the mode of preparation, but the unstable chemical nature of ferrous compounds. The reactions are as follows:

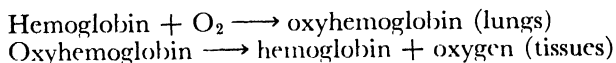


Iron Chlorides. When an excess of iron is reacted with hydrochloric acid, *ferrous chloride* ($FeCl_2$) is formed. Ferrous chloride, being

extremely unstable, changes to *ferric chloride* (FeCl_3). Ferric chloride is a reddish-brown compound, quite soluble in water. *Tincture of ferric chloride* (ferric chloride dissolved in alcohol) has been used for years as a *hemostatic agent*, i.e., to arrest bleeding. In the laboratory ferric chloride serves the chemist as a generally useful iron compound.

Iron Sulfates. Ferrous sulfate (FeSO_4) is probably the most common compound of iron. The hydrous, or crystalline, form ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is known as *copperas* or *green vitriol*. When ferrous sulfate is heated it loses its water of crystallization and, as a result, changes to an impalpable white powder. Provided ferrous sulfate is properly stored—out of contact with air and light—it is relatively stable. Ferrous sulfate finds use in making ink, tanning, and as a dye mordant. It is to be recalled that in the laboratory freshly prepared ferrous sulfate is employed to identify the nitrate radical. In medicine, ferrous sulfate is the *compound of choice* to supply iron to the body. Upon oxidation, ferrous sulfate is converted into ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$). Ferric sulfate is used to prepare a class of compounds called *alums*.

Hemoglobin. Without question, hemoglobin is the most singular compound of iron in the biologic world. For the present, let us appreciate that hemoglobin is a highly complex substance whose molecules contain an atom of iron in combination with a protein called *globin*. Hemoglobin is the compound which imparts the characteristic red color to blood. Another fact to be recalled is that hemoglobin is contained in the erythrocytes or red blood corpuscles; none is found in the plasma. In our future discussions of blood chemistry, we shall have occasion to talk at some length on the chemistry of hemoglobin. For now, let us simply state the all-important function of hemoglobin: *to carry oxygen to the cells*. As the blood passes through the lungs, the hemoglobin molecules of the red cells combine—by virtue of their affinity for oxygen—with oxygen to form *oxyhemoglobin*. Since oxyhemoglobin is an unstable compound, oxygen is released in the tissues. The relation of oxygen and hemoglobin may be summarized in a simple way as follows:



ALUMINUM AND ITS COMPOUNDS

Aluminum is the most abundant metal of the earth's crust. It is present to the extent of about 7 per cent. Since aluminum possesses a high degree of chemical activity, it is not found in the free state. Perhaps this explains why most people are surprised to learn that aluminum is our most common metal. In the combined state, it is present in the form

of complex silicates such as *clay*, *feldspar* and *mica*. Aluminum is also found in *bauxite* ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and *cryolite* (Na_3AlF_6).

Preparation. The tremendous value of aluminum stems from the ingenious work of Charles M. Hall. Prior to the so-called *Hall Process* for extracting aluminum from its ore, aluminum metal was on an economic par with gold. It was not until 1886 that the earth's reservoir of this valuable metal yielded to the efforts of man. In that year Hall, while still a student at Oberlin College, Ohio, devised an electrolytic method of extraction. The Hall Electrolytic Process, essentially the same as the original, employs *pure bauxite* and *melted cryolite* (which acts as a solvent). The aluminum oxide dissociates (ionizes) in solution to form aluminum ions (Al^{+++}) and oxygen ions (O^{--}). When a direct

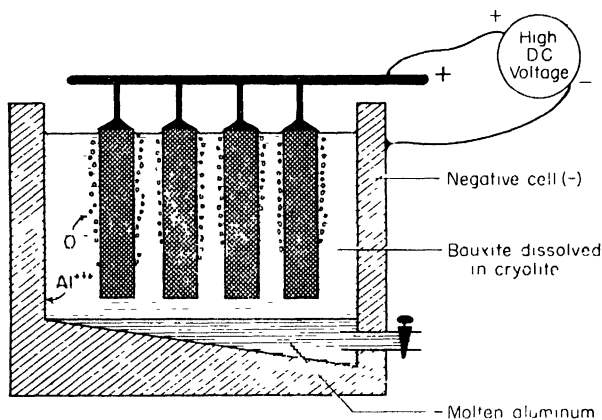
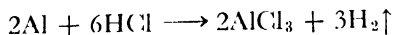


Fig. 31. The Hall Process for the extraction of aluminum.

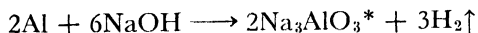
current of electricity is passed through the solution, the *aluminum ions are attracted to the cathode*, and the *oxygen ions to the anode*. Because of the high temperatures of the electrolytic cell (Fig. 31), molten aluminum forms at the bottom.

Properties. Aluminum is silvery-white in color, and is the lightest of the common metals. It possesses great tensile strength. Aluminum is malleable, ductile, and an excellent conductor of heat and electricity.

Chemically, aluminum is rather active. It readily reacts with oxygen to form aluminum oxide. Aluminum reacts with acids—especially hydrochloric acid—to form salts and hydrogen:



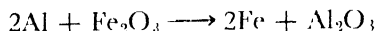
Aluminum, *unlike most metals*, is dissolved by strong bases. In this reaction, hydrogen and a class of salts called *aluminates* are produced. The reaction between sodium hydroxide and aluminum is as follows:



By virtue of this characteristic action, alkaline solutions should *not* be employed to clean aluminum utensils.

Uses. The Hall Process, as indicated above, drastically reduced the price of aluminum. This made it possible for industry to develop fully and put to use the wonderful and outstanding properties of this metal. Indeed, aluminum is a *sine qua non* to aviation and the culinary arts. At the present time, automotive and aircraft construction provide the largest single market for aluminum. When used for construction purposes, aluminum alloys—e.g., *duralumin* (Al, Cu, Mg), *aluminum bronze* (Al, Cu) and *magnalium* (Mg, Al)—are preferred to the plain metal. Huge quantities of aluminum are employed in the manufacture of kitchen utensils, where its lightness and freedom from tarnish are unsurpassed. Large quantities of aluminum are also used in the making of electric transmission lines and aluminum foil.

Since aluminum has an affinity for oxygen, it is used as a reducing agent. When mixed (in the form of a powder) with certain metallic oxides—viz., Fe_2O_3 , Cr_2O_3 and MnO_2 —and ignited by a magnesium fuse, the aluminum removes oxygen from the oxide. Such an enormous amount of heat is evolved that the metal is produced in the molten state. *Thermite* (the name applied to a mixture of aluminum and ferric oxide (Fe_2O_3)) is used for emergency welding. In this procedure, the thermite powder is placed in a heat resistant, funnel-shaped receptacle which is held over the parts to be welded. When ignited by a piece of magnesium ribbon (magnesium burns with the evolution of tremendous heat) the mixture reacts, and molten iron flows out from the bottom. The chemical reaction of thermite is as follows:



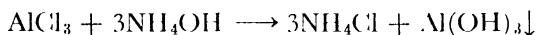
Chromium, manganese and other metals are extracted from their oxide ores by this so-called *thermite reaction*.

Aluminum Compounds

Aluminum Oxide (Al_2O_3). Aluminum oxide exists in several physical forms in nature. These forms include *bauxite*, *corundum*, *emery*, *rubies* and *sapphires*. All of these forms are of extreme importance. Bauxite is the chief ore of aluminum; corundum and emery are extremely hard, and are used as abrasives. Rubies and sapphires are precious stones of characteristic beauty. The color of these gems is due to minute quantities of impurities.

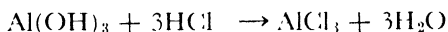
* Also written as NaAlO_2 .

Aluminum Hydroxide ($\text{Al}(\text{OH})_3$). When a base, for example, ammonium hydroxide, is added to a solution of an aluminum salt, a white, *gelatinous precipitate* of aluminum hydroxide is formed:



Aluminum hydroxide has several important uses and applications. In *dyeing*, aluminum hydroxide is employed as a *mordant*. A mordant is a substance which helps a dye stick to the cloth. A mordant acts by absorbing the dye and forming an insoluble product called a "lake." Aluminum hydroxide, by virtue of its physical character, is used to remove turbidity in water. This is done by adding aluminum sulfate and lime to the water. The gelatinous aluminum hydroxide (*coagulum*) which forms slowly settles to the bottom, carrying with it suspended particles.

In the management of peptic ulcer, aluminum hydroxide is the agent of choice to reduce the attending hyperacidity. The following neutralization reaction occurs in the stomach, where hydrochloric acid is present:*



Note that 1 molecule of aluminum hydroxide neutralizes 3 molecules of hydrochloric acid. Since aluminum hydroxide is *insoluble*, it is not *alkaline* or *basic*; this is an advantage, because alkaline solutions are irritating to the stomach's mucosa. In addition, aluminum hydroxide possesses demulcent action—i.e., it is soothing to mucous membranes.

Alums. An alum is an interesting compound from a chemical standpoint; it is a sulfate salt containing *two metals*. One metal is always *univalent*, and the other, *trivalent*. The most common compound of this type is potassium alum (*common alum*) whose formula is $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Note that the law of valence—as applied to a compound—prevails; i.e., the charge of the potassium atom (K^+) added to the charge of the aluminum atom (Al^{+++}) equals or balances the negative charge of a minus 4 contained on the sulfate ($2 \times \text{SO}_4^-$). In addition, note that the alum molecule contains a large amount of water. Alum salts, therefore, are crystalline substances. Alum is used to prepare aluminum hydroxide and certain baking powders. In medicine, potassium alum is used as an *astringent*. An astringent is a substance which "tightens" and "hardens" tissue. The "styptic pencil," commonly employed to check the flow of blood from a small cut, contains alum. The flow is arrested by virtue of astringent action.

* Aluminum hydroxide is unique in that it reacts with strong bases, such as NaOH , to form salts called *aluminates*. This property of an insoluble base to react with both acids and bases is called *amphoterism*. Certain other metallic hydroxides (viz., $\text{Pb}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$) are also amphoteric.

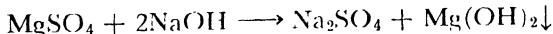
Aluminum Silicates. Complex compounds of aluminum with *silicon*, *oxygen* and other elements are referred to as *silicates*. Pure aluminum silicate, for example, has the theoretical formula $\text{Al}_2(\text{SiO}_3)_3$. Most of the earth's aluminum is present in silicates. *Clay*, an impure aluminum silicate, is found in varying amounts in all soils save pure sand. Huge quantities of clay are employed in the manufacture of *ceramics* (porcelain, china, earthenware) and *cement*.

Pottery is of special concern to the archaeologist; it was used by man long before the dawn of written history. Indeed, the making of pottery was one of man's first talents. While pottery marks—in a sense—the dawn of man, cement epitomizes (like steel) his present status. It would indeed be difficult to visualize our present society without cement structures. Perhaps even more philosophical is the idea that man has taken clay—earth, if you please—and from it molded his civilization.

OTHER IMPORTANT METALS

Magnesium. Magnesium is a light, silvery-white metal. It is very active chemically, and burns with a brilliant white light, forming magnesium oxide (MgO). Magnesium readily reacts with acids, forming hydrogen and salts. Magnesium metal is used chiefly in the production of light alloys. *Duralumin*, for example, an extremely tough and light alloy, is composed of aluminum, copper and magnesium. Another important alloy called *magnalium* (an alloy of aluminum and magnesium) is extensively employed in aircraft construction. Magnesium is also used in making fireworks and flashlight powders. Several compounds of magnesium have important uses and applications. The following compounds are of interest to us because of their extensive use in medicine.

MAGNESIUM HYDROXIDE ($\text{Mg}(\text{OH})_2$). When a base is added to a magnesium salt, a light, white precipitate of magnesium hydroxide forms immediately. The reaction is as follows:



Magnesium hydroxide is used extensively as an *antacid* to neutralize excess hydrochloric acid in the stomach (hyperacidity). The reaction is one of simple neutralization. Larger doses of magnesium hydroxide produce catharsis. In the pharmacy, magnesium hydroxide is sold in tablet form and liquid form. The liquid form of magnesium hydroxide is a white viscous suspension of the compound in water. The preparation is known commonly as *milk of magnesia*. In pharmacy, it is referred to as *magnesia magma*.

MAGNESIUM SULFATE (MgSO_4). Crystalline magnesium sulfate has the formula $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The anhydrous form, of course, has the formula MgSO_4 . Most people know magnesium sulfate by its popular

name, *Epsom salt*. Epsom salt is without doubt the most popular saline laxative. It is also a potent anticonvulsant when administered by injection into the body. Larger doses produce anesthesia. Since magnesium sulfate is not absorbed from the intestine, there is no anticonvulsant and anesthetic action following oral administration. Orally, then, magnesium sulfate produces only cathartic action.

MAGNESIUM OXIDE (MgO). Magnesium oxide is a white, light and fluffy powder, insoluble in water. It is formed when magnesium ribbon is burned. Magnesium oxide enjoys some use as a laxative and antacid. Its antacid action is as follows:



MAGNESIUM CARBONATE (MgCO₃). Magnesium carbonate is a white, light and fluffy powder, insoluble in water. Like magnesium oxide, it enjoys some use as an antacid. It reacts with the acid in the stomach as follows:



MAGNESIUM TRISILICATE. Magnesium trisilicate is a compound of rather indefinite molecular constitution. The formula $2\text{MgO} \cdot 3\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (x means an unknown quantity of water per molecule) has been assigned to this substance. Magnesium trisilicate is an excellent antacid. Being very insoluble, it affords sustained antacid action. In addition, magnesium trisilicate is bland, and somewhat of a demulcent. Several antacid preparations in the pharmacy contain this compound alone, or in combination with other neutralizing agents.

Mercury. Mercury possesses the unique distinction of being the only metal that is liquid at room temperature. Mercury is a very heavy silvery-white metal. Chemically, mercury is interesting because it forms two series of compounds: *mercurous*, in which the mercury atom displays a valence of a *plus 1* (Hg^+); and *mercuric*, in which the mercury atom has a valence a *plus 2* (Hg^{++}). In this connection—and with reference to the valences of iron, i.e., Fe^{++} and Fe^{+++} —note that when a metal (like mercury and iron) possesses two valences, the suffix *-ous* is attached to the state of the lower valence (*mercurous*, *ferrous*), and the suffix *-ic* to the higher valence (*mercuric*, *ferric*). Like iron, the “double” valence of mercury in its compounds should be thoroughly understood and appreciated. This is dramatically illustrated by the two chlorides of mercury: *mercurous chloride* (HgCl) and *mercuric chloride* (HgCl_2). *Mercurous* chloride may be taken internally; *mercuric* chloride is *extremely poisonous*.

Mercury metal is particularly well adapted for use in thermometers,

barometers, and many electrical devices. Mercury alloys, called *amalgams*, are also of importance. Perhaps the most important amalgam is *silver amalgam*, employed in dentistry for filling tooth cavities. In ancient times, metallic mercury was used to treat disease. There are many compounds of mercury employed commercially and in medicine. Those compounds of medicinal value are of special interest to us. The following compounds of mercury—often referred to in the healing arts as *mercurials*—are in common use today.

MERCUROUS CHLORIDE (HgCl_2). Mercurous chloride is a heavy white powder, insoluble in water. It is prepared by reacting any soluble mercurous salt with hydrochloric acid. Mercurous chloride has enjoyed wide use as a rather potent laxative. In pharmacy and medicine it is commonly known as *calomel*.

MERCURIC CHLORIDE (HgCl_2). Mercuric chloride is usually referred to in pharmacy and medicine as *bichloride of mercury* or *corrosive sublimate*. It is a heavy, odorless, crystalline or white, powdery substance, soluble in water. In contrast to *mercurous chloride*, mercuric chloride is a potent poison. Because of its wide use in medicine and industry, mercuric chloride is responsible for many deaths—both accidental and suicidal. Solutions of mercuric chloride are useful for the disinfection of the skin, instruments, excreta and discharges. Solutions of from 1:100 to 1:10,000 are generally employed. A solution of mercuric chloride (1:1,000) in 25 per cent alcohol is a very efficient germicide.

MERCURIC OXIDE (HgO). Mercuric oxide is a yellow-orange, heavy impalpable powder. It is insoluble in water. This compound of mercury is employed almost exclusively in medical practice as *yellow mercuric oxide ointment*, which contains 1 per cent HgO . This preparation is used mainly for application to the eye as a mild antiseptic in conjunctivitis, blepharitis and stytes.

MERCURY AMINO CHLORIDE (HgNH_2Cl). Mercury amino chloride is commonly known in pharmacy as *ammoniated mercury*. It is a white, amorphous powder, insoluble in water. Ammoniated mercury is prepared by reacting mercurous chloride with ammonium hydroxide. *Ammoniated mercury ointment* is successfully employed in the treatment of numerous skin lesions.

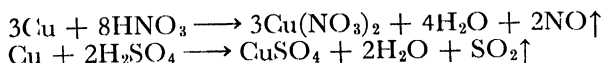
ORGANIC MERCURIAL COMPOUNDS. At this point it would be premature to enter into a discussion of metallic derivatives of organic molecules. We shall study this interesting subject under organic chemistry. However, it can be stated that certain metallic organic compounds are of prime importance in certain areas of medicine. This is particularly true of mercury. Several organic mercurials are employed today. *Mercurochrome*, *Merthiolate* and *Metaphen* are popular antiseptics con-

taining mercury in organic combination. The antiseptic potency of the inorganic salts of mercury, viz., bichloride of mercury, suggested the synthesis of less toxic organic compounds. They are less toxic because they do not undergo ionization—for it is the mercury ion which is toxic.

Several organic mercurials have been synthesized for use as *diuretics*, i.e., agents which increase the formation of urine. The salts of mercury have been known for many centuries to elicit diuretic response. However, as explained above, inorganic salts—due to extensive ionization—are toxic. The modern era of the mercurial diuretic began with the use of organic compounds. The first organic mercurial, *Mersalyl*, was introduced in 1924. Soon other mercurials followed with even lower toxicity *Mercuraphylline*, *Mercurhydrin* and *Thiomerin* are three popular such agents. Mercurial diuretics appear to be the most potent and dependable of all diuretics. In edema of cardiac origin, they are the drugs of choice.

Copper. Due to the fact that copper occurs rather abundantly in the free state, it was the first metal which primitive man learned to use as a material for tools and weapons; *this was the first step forward from the Stone Age*. The passing of time has not diminished the importance of this reddish metal—indeed, centuries have *enhanced* the role of copper. Our present economic life would be paralyzed without copper, for this metal is the most logical medium for the transmission of electric currents. More than half the world's supply of this vital metal is produced in the United States. There are rich deposits of free copper in northern Michigan. In the combined state, the principal ore, *chalcopyrite*, is found in Montana and Utah.

Copper is a heavy metal with a characteristic reddish color. Next to gold and silver, it is the most malleable and ductile of the common metals. As a conductor of electricity, it is surpassed only by silver. In air copper oxidizes slowly, forming a protective coating which prevents further corrosion. This green protective coating, called *basic copper carbonate* ($\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$), results from the action of the moisture, oxygen and carbon dioxide present in the air. In the electrochemical series, copper is below hydrogen; therefore it *cannot* displace the hydrogen of acids. Dilute acids have little effect on copper; concentrated acids, however, of the oxidizing type, such as sulfuric and nitric, readily attack copper. The reaction results in the evolution of gases other than hydrogen:



Note that in each reaction copper has gone from a valence of zero (Cu^0) to a valence of plus 2 (Cu^{++}); in other words, the copper has

been *oxidized*. Therefore, concentrated sulfuric and nitric acids are oxidizing agents.

Copper, like mercury, has two valences— Cu^+ and Cu^{++} . In other words, there are two series of salts: *cuprous* (Cu^+) and *cupric* (Cu^{++}). It is therefore important in dealing with copper compounds to state the degree of valence. Copper oxide, for example, is not a specific name, for there are two oxides of copper: cuprous oxide (Cu_2O) and cupric oxide (CuO).

Almost 2 million tons of copper are produced annually. Of this tremendous amount, about one third is employed in the manufacture of all types of electrical apparatus. Copper is also widely used in the making of copper pipe, alloys (brass, bronze) and in copper-plating. Copper-plating is an interesting laboratory experiment. In order to plate

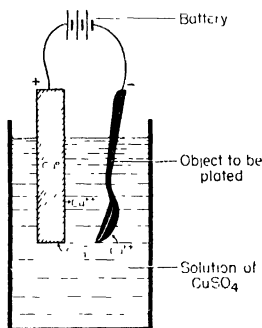


Fig. 32. A demonstration of electroplating.

copper upon some metallic object, we employ the following materials: a copper metal strip, a copper salt, and a battery to supply direct current. The copper salt—usually copper sulfate—is dissolved in water, and the copper strip wired to the anode terminal; the object to be plated is wired to the cathode (Fig. 32). When the current is turned on, the copper ions in the solution (Cu^{++}) are attracted to the negative object; at the object each ion takes on 2 electrons and becomes a copper atom (Cu^0). In this manner, the object becomes coated with copper. As copper ions leave the solution, copper atoms of the anode enter the solution to replace the lost ions. In time, the copper strip will be consumed. This process is called *electroplating*. Metals other than copper may be plated. Silver, for example, may be plated on some object by using the same apparatus as outlined above, and employing silver for the anode and silver nitrate for the electrolyte.

COPPER SULFATE ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Copper sulfate is the most important salt of copper. The hydrous form, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is composed of beautiful deep blue crystals. Upon heating the crystals 5 molecules of

water are driven off, leaving a white anhydrous powder, CuSO_4 . When water is added to this white powder, a blue color develops; i.e., the hydrous, or blue, variety is re-formed. Copper sulfate—or, more correctly, cupric sulfate—is employed in electric batteries, as a mordant in dyeing, and in copper plating. In medicine, copper sulfate is used as an astringent and emetic; it is also used as an antidote in phosphorus poisoning. Benedict's solution, used for testing the presence of sugar in urine, contains copper sulfate. This important test will be thoroughly presented when we discuss sugars.

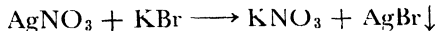
Silver. Silver is *the most common of the precious metals*. It occurs in nature both in the free and combined state. Silver is a soft, white metal having a high luster. Next to gold, it is the most ductile and malleable metal. Silver possesses the distinction of *surpassing* all metals as a conductor of electricity.

Chemically, silver metal is inert to oxygen. Toward sulfur, i.e., sulfur compounds, however, it reacts to form a black compound, *silver sulfide* (Ag_2S). The tarnishing of silver is due to the formation of deposits of this substance. Since sulfur compounds are present in the air and in certain foods (such as eggs and mustard), silver utensils require frequent polishing—a fact every housewife knows. Silver salts are prepared by reacting the metal with the appropriate concentrated acids. Dilute acids do not attack silver. Silver nitrate, for example, is prepared by reacting silver with concentrated nitric acid. Since silver is *below* hydrogen in the electrochemical series, no hydrogen gas is released.

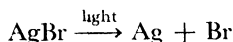
Because silver occurs in the free state, man at an early date was fascinated by its beauty and utility. Silver is used in coins and jewelry, and as a coating on silver-plated ware. So-called “solid silver” contains a certain percentage of copper to increase its hardness. Silver coins, for example, contain 90 per cent silver and 10 per cent copper. Such silver is said to be *900 fine* (900 parts of silver in 1000). Sterling silver is *925 fine*. Silver compounds are also important. The following compounds are of special importance.

SILVER NITRATE (AgNO_3). Silver nitrate (*lunar caustic*) is the most important compound of silver. It not only possesses valuable qualities, but also is used to prepare other silver compounds. Silver nitrate has been used in medicine for years as a caustic (to cauterize wounds), and as an antiseptic. Silver nitrate in a solution of 1:1000 inhibits microorganisms. For the prevention of *gonorrheal conjunctivitis* in the newborn, a drop of 1 per cent solution is instilled into each eye as soon as practicable after delivery.

SILVER BROMIDE (AgBr). When a silver nitrate solution is added to a solution of a bromide, a copious white precipitate of silver bromide is formed, thus:



Enormous quantities of silver bromide are used each year in photography. Today the photographic arts and sciences have grown to giant proportions, consuming about *200 tons of silver annually*. As pointed out before, the taking of a picture depends upon the photosensitive nature of silver bromide. In the presence of light, silver bromide decomposes as follows:



Note that in this reaction silver is reduced, i.e., $\text{Ag}^+ \longrightarrow \text{Ag}^0$.

SILVER PROTEIN. Silver protein is a dark brown or almost black shining crystalline (*scales*) or granular substance. It has been used in medicine for many years as an antiseptic and demulcent. Silver protein is prepared by reacting silver nitrate with a protein substance; the silver atoms "add on" to the large protein molecules. A popular form of silver protein on the market is sold as *Argyrol*, a dark aqueous solution of silver protein. Silver protein preparations—in contrast to the inorganic salts, viz., silver nitrate—are not irritating to the skin or mucous membranes.

Lead. Lead is the heaviest of the common metals. It is unusually soft and malleable. When lead is freshly cut it has a bright luster, but soon dulls due to the formation of a protective coating. Nitric and acetic acids readily attack lead, but hydrochloric and sulfuric acids have little action.

Lead is used extensively in the manufacture of water pipes, sheeting and certain alloys. Its chief uses, however, are in making lead plates for storage batteries, and *white lead for paints*. White lead is the most important compound of lead. It has the following (rather complex) formula: $\text{Pb}(\text{OH})_2 \cdot 2\text{PbCO}_3$. White lead is a heavy white powder which serves as our most popular paint *base*. A "complete paint" consists of a *base*, usually white lead; a *vehicle*, usually linseed oil; a *thinner*, usually turpentine; a "*dryer*," i.e., a chemical which catalytically hastens drying (e.g., lead oxide); and a *pigment* to give color.

LEAD POISONING. More has been written about the toxicology of lead than any other substance. Lead poisoning (*plumbism*) is as old as the history of man. In spite of the tremendous growth of the chemical industry, *lead is still the leading industrial poison*. Lead poisoning is almost always chronic, and occurs among workers in a host of industries where lead metal is employed. The signs and symptoms are insidious because of their gradual onset and their similarity to other abnormalities. Modern methods of industrial hygiene have done a great deal in re-

ducing the incidence of this form of poisoning. Treatment for *plumbism* is largely symptomatic.

Bismuth. Bismuth is a grayish-white metal which occurs both in the native and combined state. Bismuth metal is used principally in the preparation of alloys with low melting points, such as *Wood's metal*. This alloy is used in automatic sprinklers, electric fuses and other safety devices. Several salts of bismuth are employed in medicine. The following compounds are important.

BISMUTH SUBCARBONATE. Bismuth subcarbonate is a white powder, insoluble in water. This compound is used extensively in treating conditions characterized by irritation along the alimentary tract. Being insoluble and demulcent, it forms a coating over an irritated or ulcerated surface, and thus protects against mechanical and chemical injury. Bismuth subcarbonate is also employed, for the same reasons, on the skin. Bismuth subnitrate is sometimes used for the same purposes. The subcarbonate, however, is the preferred compound.

BISMUTH POTASSIUM TARTRATE. At one time bismuth salts were used routinely—usually along with the salts of mercury and arsenic—as *antisyphilitics*. The advent of penicillin, however, has all but replaced “heavy metal” therapy. In the event a soluble bismuth salt is desired, bismuth potassium tartrate is usually preferred. This salt is administered by intramuscular injection.

BISMUTH SUBSALICYLATE. Bismuth subsalicylate is a white amorphous powder, insoluble in water. As an antisyphilitic, it is sometimes injected intramuscularly as a suspension in oil. Being insoluble, the subsalicylate provides sustained action, in contrast to the above compound, which gives a prompt bismuth effect. Orally, bismuth subsalicylate, like the subcarbonate, acts as a protective and an astringent.

BISMUTH SUBGALLATE. Bismuth subgallate is an amorphous, bright yellow powder, insoluble in water. Its action is similar to that of the subcarbonate. It is used rather commonly as a *dusting powder* to protect the skin and promote healing.

Zinc. Zinc is a bluish-white metal which reacts with the air, forming a protective coating. The metal occurs in the combined state, chiefly as the sulfide (ZnS). Zinc readily reacts with most dilute acids, liberating hydrogen gas and forming zinc salts. Zinc metal is used for roofing, lining tanks, and coating iron to prevent rusting (*galvanizing*). The metal is also widely used to make alloys such as *brass*, *bronze* and *German silver*. Several zinc salts are employed in industry and medicine. The following compounds are of medicinal and pharmaceutical importance.

ZINC SULFATE (ZnSO_4). Zinc sulfate is probably the most popular and important compound of zinc. Zinc sulfate is a colorless, transparent

crystalline substance or a granular powder. It is commonly employed in medicine as an astringent, styptic and emetic. Zinc sulfate finds much use in eye washes—especially in conjunctivitis.

ZINC OXIDE (ZnO). Zinc oxide is a fine, white, amorphous powder, insoluble in water. It enjoys wide popularity—either alone or in combination with other agents—as a mild antiseptic, astringent and protective agent. Zinc oxide is the active constituent of two very popular external remedies: *zinc oxide ointment* and *calamine lotion*.

OTHER ZINC SALTS. Other zinc salts of some use include: *zinc chloride* (ZnCl_2), an antiseptic and astringent; *zinc peroxide* (ZnO_2), an antiseptic; and *zinc undecylenate* ($\text{Zn}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$), a fungistatic agent.

Tin. Tin is a silvery-white metal which is practically inert to air and ordinary corrosive agents. For this reason tin finds its widest use as a protective material for other metals. Tinware, for example, is made by dipping sheet iron into a bath of molten tin. The common “tin can” is made in this manner. Tin is a constituent of many important alloys. *Bronze, pewter, solder, Babbitt metal* and *type metal* are familiar alloys of tin. Tin salts are of limited value and of little concern to us.

Manganese. Manganese is a hard, steel-like metal. Its principal use is in the making of *iron alloys* and *manganese steel*. Manganese steel is one of the hardest and toughest steels. Of the manganese compounds, *manganese dioxide* (MnO_2) and *potassium permanganate* (KMnO_4) are the most important. Both of these agents are extensively employed in the laboratory as oxidizing agents. In addition, potassium permanganate is employed in medicine as an antiseptic and fungistatic agent.

Nickel. Nickel is a hard, silvery-white metal not oxidized by dry air. It is commonly used for protecting other metals. A coat of nickel is put on another metal by the process of *electroplating*. Nickel is also extensively employed in the making of valuable alloys. *German silver, nickel coin, invar, nickel steel*, and *nichrome* are popular alloys of nickel. The salts of nickel are of limited value.

Chromium. Like manganese, chromium is a hard metal resembling steel. Chromium is employed in electroplating and in making certain special steel alloys such as stainless steel and chrome steel. Certain compounds of chromium are important laboratory chemicals. Of these compounds, *potassium chromate* (K_2CrO_4), a yellow crystalline substance, and *potassium dichromate* ($\text{K}_2\text{Cr}_2\text{O}_7$), an orange crystalline substance, are the most popular. Both are excellent oxidizing agents.

Gold. From time immemorial gold has appealed to man's economic and esthetic senses. Gold occurs almost exclusively in the free state in dust, nuggets and gold-bearing quartz. Gold is soft, heavy and bright yellow in color; it is the most *malleable* and *ductile* of all the

metals. Chemically, it is inert to all common chemicals. *Aqua regia* (a mixture of nitric and hydrochloric acids), however, readily dissolves gold, forming gold chloride (AuCl_3). The use of gold for jewelry and coinage is common knowledge. Since gold is so soft, it is necessary to alloy it with copper to increase its hardness.

Platinum. Platinum is a white lustrous metal; it is harder, heavier and more expensive than gold. Platinum has an extremely *high* melting point, and is *resistant* to all common chemical reagents. Because of these qualities, it is employed to make crucibles, wires and similar apparatus for the chemical laboratory. In a highly subdivided state, platinum is an important industrial catalyst. About 90 per cent of the world's supply of this interesting element comes from the Ural Mountains of Russia.

Radioactive Metals. The concept of radioactivity usually requires considerable exposition to impart a clear idea. For this reason, radioactivity will be thoroughly treated in a subsequent chapter. For the sake of continuity, however, let us make a few broad statements concerning radioactive metals. The story begins with the discovery of *radium* by Professor and Madame Curie. Radium is different from all the other elements heretofore known in one outstanding characteristic: The metal undergoes constant disintegration as a result of the giving-off of three invisible forms of radiation: *alpha rays*, *beta rays* and *gamma rays*. Although invisible, these rays have potent chemical and physiologic effects. Under carefully controlled concentrations, radium rays are useful in the treatment of cancer and tumors. At the present time, several other important radioactive metals have been produced by atomic machines such as the cyclotron. Radioactive materials are of vital importance to our present society. Later on we shall fully discuss their theoretical and practical applications.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- — — electrochemical series
- — — alkali metals
- — — metals + acids $\longrightarrow$
- — — a strong hydroxide
- — — softens water
- — — explosives
- — — protects steel

Column II

1. chromium
2. photography
3. hematite
4. double salts of aluminum
5. relative activity of the metals
6. bismuth subcarbonate
7. diuretics

Column I

- an expensive metal
- — AgBr
- — — ZnO
- soothes irritated surfaces
- — — a poisonous antiseptic-disinfectant
- — — white lead
- — — the most valuable electrical conductor
- — — alums
- — — Al
- — — Fe₂O₃
- — — $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$
- — — organic salts of mercury
- — — CaO

Column II

- 8. Na and K
- 9. blast furnace
- 10. hydrogen
- 11. basic anhydride of Ca(OH)_2
- 12. KOH
- 13. most common metal
- 14. paint base
- 15. KNO₃
- 16. HgCl₂
- 17. a mild antiseptic
- 18. copper
- 19. platinum
- 20. Na₂CO₃

1. What is lye?
2. What metal imparts a violet color to the Bunsen flame?
3. Explain how limewater neutralizes acids.
4. Name a metal whose salts possess astringent qualities.
5. When silver nitrate is dissolved in tap water, a slight precipitate usually forms. Explain.
6. Name two inorganic salts of mercury employed in medicine.
7. Write the formulas for ferrous and ferric carbonates.
8. What is the most common and valuable compound of copper?
9. Name 3 compounds of magnesium and their uses.
10. What are the two types of hard water? Why is it difficult to form a lather with hard water?
11. Name two important uses for each of the following metals (or their compounds): gold, platinum, tin, manganese, nickel, chromium, bismuth, zinc, lead and iron.
12. Write the equation for the reaction between magnesium and phosphoric acid.
13. Write the equation for the reaction between zinc and cupric nitrate.
14. Explain why milk of magnesia becomes clear when nitric acid is added.
15. When sodium carbonate is added to hard water a precipitate forms. Explain.

CHAPTER 8

CHEMICAL ARITHMETIC

Any area of science *requires* and *demand*s a certain degree of mathematical treatment; *this is especially true of chemistry*. Unfortunately, it seems to be well established that most people are reluctant to employ mathematics in any form. As far as the advanced disciplines of mathematics (e.g., calculus) are concerned, perhaps this reaction is justifiable. It is not justifiable, however, when one ignores the most beautiful, applicable and simple branch of mathematics, *arithmetic*. A working knowledge of arithmetic is entirely satisfactory in disclosing the *elementary basic facts* of any study. All facts and problems presented in this chapter are resolved and solved via arithmetic.

THE METRIC SYSTEM

The metric system is the most logical system of measurement yet devised and, for this reason, is the one employed in all sciences. This system is based upon the *meter* (39.37 inches) as the unit of length; the *gram* (15.43 grains) as the unit of weight; and the *liter* (1.06 quarts) as the unit of volume. Measurements greater than or less than these units are designated decimally. The Greek prefix *deca-*, or *deka-*, before a unit means 10; *hecto-*, 100; *kilo-*, 1000; *mega-*, 1,000,000; thus, a hectometer is 100 meters. Similarly, the Latin prefix *deci-* before a unit means 0.1; *centi-*, 0.01; *milli-*, 0.001; and *micro-*, 0.000001. The metric system is presented in the table below:

Length

Millimeter (mm.)	0 001 meter (m.)
Centimeter (cm.)	0 01 meter
Decimeter (dm.)	0 1 meter
Meter (m.)	1 0 meter
Dekameter (dkm.)	10 meters
Hectometer (hm.)	100 meters
Kilometer (km.)	1000 meters

Weight

Milligram (mg.)	0.001 gram (gm.)
Centigram (cg.)	0.01 gram
Decigram (dg.)	0.1 gram
Gram (gm.)	1.0 gram
Dekagram (dkg.)	10 grams
Hectogram (hg.)	100 grams
Kilogram (kg.)	1000 grams

Volume

Milliliter (ml.)	0.001 liter (l.)
Centiliter (cl.)	0.01 liter
Deciliter (dl.)	0.1 liter
Liter (l.)	1.0 liter
Dekaliter (dkl.)	10 liters
Hectoliter (hl.)	100 liters
Kiloliter (kl.)	1000 liters

In chemistry, the *millimeter*, *centimeter*, *gram*, *liter*, *milliliter* and *cubic centimeter* are the most commonly used expressions. The *cubic centimeter* (cc.) is numerically equal to a *milliliter* (ml.). Actually, there is a very slight difference, but for all practical purposes they are used interchangeably. Obviously, it is of value to appreciate the relationship between the metric and English systems. The following table presents the important comparisons of length, weight and volume.

Approximate Equivalents

1 inch	25.4 millimeters
39.37 inches	1 meter
15 grains	1 gram
1 avoird. ounce	28 grams
1 pound	454 grams
1 fluid ounce	30 cubic centimeters or 30 milliliters
1 quart	950 cubic centimeters or 950 milliliters

HEAT

Heat is a form of energy, and is probably best understood by its influence on matter. The *Kinetic Theory* of heat states that a hot body differs from a cold body in one fundamental respect—the *speed of molecular motion*. In a hot body, the molecules are moving at a tremendous rate. At a theoretical point called *absolute zero* (-273° C.) all motion ceases: *This is the lowest possible temperature*. In other words, the molecular motion of a substance is proportional to the intensity of heat. From a practical point of view, however, we are interested in measuring the *intensity* (*temperature*) and *quantity* of heat. The concept of intensity and quantity of heat usually provokes a little

confusion. These terms may be readily differentiated if we compare the quantity and intensity of heat in the flame of a match with the quantity and intensity of heat of a large body of warm water, e.g., a lake. Obviously, there is a greater amount (*quantity*) of heat in the lake than in the match flame. The intensity, though, is reversed; one will place his finger in the lake, but not in the flame.

Temperature. Temperature, or the intensity of heat, is recorded by an instrument with which we are all familiar—the *thermometer*. In this country, we are accustomed to expressing temperature measurements on the common *Fahrenheit* scale. On this scale, water freezes at 32 degrees (32°), and boils at 212°. In scientific work, the *Centigrade* scale is preferred to the Fahrenheit. On this scale, the freezing point of water is 0°, and the boiling point 100°. A comparison of the two scales will disclose that 1 scale division Centigrade equals $\frac{9}{5}$ scale divisions Fahrenheit. A temperature on one scale may be readily converted to the corresponding temperature on the other scale by the following formulas:

$$\begin{aligned} F. &= \frac{9}{5}C. + 32 \\ C. &= \frac{5}{9}(F. - 32) \end{aligned}$$

Example: Convert 212° F. to degrees Centigrade.

$$\begin{aligned} C. &= \frac{5}{9}(212 - 32) \\ C. &= \frac{5}{9}(180) \\ C. &= 100^{\circ}C \end{aligned}$$

Quantity of Heat. Quantity of heat is measured in *calories*. A so-called *small calorie* (*cal.*) is the quantity of heat required to raise the temperature of 1 gm. of water 1° C.; a large Calorie (*Cal.*) is the quantity of heat required to raise the temperature of 1 kg. of water 1° C. A large calorie, therefore, contains 1000 small calories. In scientific work, heat energy is usually expressed in small calories. In the English system, heat is measured in *British Thermal Units* (B.T.U.). One B.T.U. of heat is the quantity of heat required to raise the temperature of 1 lb. of water 1° F. The B.T.U. is a convenient unit to express the heat value of fuels, such as coal, oil and gas.

An exact comparison between temperature (i.e., intensity) and quantity of heat is now possible by a consideration of the following problem. Compare the caloric value of 1 gm. of water at 100° C. (boiling water) with 100 gm. of water at 10° C. From our definition of calorie, we know that 1 gm. of water at 100° C. represents 100 *cal.*; and 100 gm. at 10° C. represents 1000 *cal.* We conclude, therefore, that while the temperature of the 1 gm. of water is 10 times the temperature of the 100 gm. of water, it contains only 1/10 the quantity of heat.

It is often desirable to measure the calories of heat liberated during a chemical reaction. In the field of nutrition, the caloric value of various foods constitutes essential information. To measure calories, an instrument called a *calorimeter* is employed. Figure 33 presents in a diagrammatic fashion the essential elements of a calorimeter. An *accurately* weighed sample of the substance under investigation (e.g., bread, alcohol, carbon) is placed into the internal chamber, or "bomb." The contents are then ignited by means of an electrically controlled fuse. Oxygen gas is passed into the bomb prior to ignition in order to insure complete combustion. The heat liberated is thereon absorbed by an accurately measured quantity of water surrounding the bomb. Any rise in temperature is registered by the thermometer. A motor-driven water

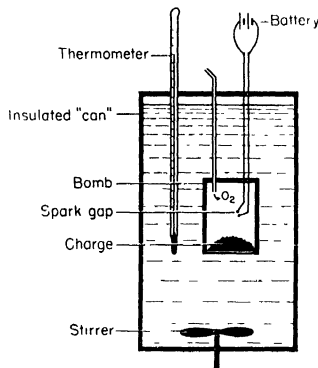


Fig. 33. Calorimeter.

stirrer assures an even distribution of heat. The number of calories liberated is readily calculated by multiplying the *number of grams of water times the number of degrees rise in temperature (Centigrade)*. Since a weighed sample is burned, the number of calories may be expressed in terms of calories per unit weight—usually *calories per gram*.

Example: Ten grams of a certain substance under investigation were placed into the bomb of a calorimeter. After complete combustion, there was a 4° C. rise in temperature. Assuming that the calorimeter contained 1000 gm. of water, what was the caloric value of the substance? Express answer as calories per gm.

1. cal. liberated = degrees C. rise $\times$ number of gm. water
2. cal. liberated = 4×1000
3. cal. liberated = 4000
4. cal. per gm. = $\frac{\text{cal. liberated}}{\text{weight of sample}} = \frac{4000}{10}$
5. cal. per gm. = 400

Latent Heat. Latent, or "hidden," heat is an interesting physical phenomenon of wide theoretical and practical importance. If a thermometer is placed in boiling water, it registers 100°C. ; if it is held in the steam issuing from the water, it still registers 100°C. This would indicate that steam and water contain the same quantity of heat. That this is not true is easily demonstrated. When equal quantities of steam and boiling water are added to cold water, for example, the steam causes a greater rise in temperature (of cold water) than the boiling water does. Also, we can all testify to the fact that steam produces a much more severe burn than boiling water. We may conclude, therefore, that a certain quantity of "hidden" heat must be added to boiling water to change it to steam. Since this added heat causes *no change in temperature*, it is an example of *latent heat*, specifically called *heat of vaporization*. All liquids in passing from the liquid to the gaseous state have heats of vaporization. The heat of vaporization is expressed as calories per gm.—for water, it is 540 calories per gm.; i.e., *540 calories of heat are required to convert 1 gram of water (at 100°C.) to steam*. Conversely, when 1 gram of steam condenses, *540 calories are liberated*.

There is one other form of latent heat, called *heat of fusion*. The explanation is analogous to the above. Ice and ice water (i.e., water in which ice is floating) both have the same temperature (0°C.). It is easily demonstrated and verified by experience, however, that ice is "colder" than ice water. What happens is this: Additional heat (*latent heat*) must be *removed* from water at 0°C. to convert it to ice. When ice melts, this latent heat—*heat of fusion*—is absorbed. For ice, *the heat of fusion is 80 calories per gm.* Every solid substance has a heat of fusion.

The true explanation of the phenomenon of latent heat is probably best given by assuming that in passing from one state to another, there is a change of molecular motion. This change involves a definite amount of heat energy. In passing from ice to water, for example, the molecular motion would increase. Since motion involves energy, heat must be added. The reverse accounts for the liberation of heat.

DENSITY AND SPECIFIC GRAVITY

Density and specific gravity are physical attributes of considerable practical importance. Every gas, liquid and solid has a definite density and specific gravity. These two terms together with their applications and calculations are described below.

Density. Density is defined as *weight per unit volume*. Mathematically, it is stated thus:

$$\text{Density (D)} = \frac{\text{Weight (W) in gm.}}{\text{Volume (V) in cc.}}$$

In chemistry, density is determined as *grams per cubic centimeter* (gm. per cc.).

Example: Ten cubic centimeters of a certain liquid weigh 20 grams. Calculate its density.

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

$$D = \frac{20}{10}$$

$$D = 2 \text{ gm. per cc.}$$

Specific Gravity. Specific gravity is a more frequently employed term than density. It is defined as the *ratio of the weight of a given liquid or solid to the weight of an equal volume of water*.^{*} Mathematically it is expressed as follows:

$$\text{Specific gravity} = \frac{\text{Weight of substance}}{\text{Weight of an equal volume of water}}$$

Since the above expression is a ratio, specific gravity is simply a number without units. A specific gravity of more than 1 means that a substance is *heavier* than water; a specific gravity of less than 1 means that a substance is *lighter* than water. The calculation is made easy by the fact that water has a density of 1 gram per cc.[†] In other words, we find the weight of an equal volume of water by simply changing the volume (in cc.) to grams.

Example: A sample of glycerin measures 40 cc. and weighs 50 gm. What is the specific gravity of glycerin?

$$\text{Specific gravity} = \frac{\text{Weight of substance}}{\text{Weight of an equal volume of water}}$$

$$\text{Specific gravity} = \frac{50}{40}$$

$$\text{Specific gravity} = 1.25$$

To facilitate the determination of specific gravity of liquids, an instrument called a *hydrometer* is employed. By floating this device in a liquid, the specific gravity can be read directly at the point where a line on the scale meets the surface (see Fig. 34). The hydrometer operates on the principle that an object will float "high" in a liquid of high

^{*} For gases, a so-called *vapor density* is calculated. The vapor density of a gas is the *ratio of the weight of the gas to the weight of an equal volume of hydrogen*.

[†] Strictly speaking, water has a density of 1 gram per cc. only at 4° C. For practical purposes, however, this density is assumed for any temperature under 100° C.

specific gravity, and “low” in a liquid of low specific gravity. A specially scaled hydrometer, called a *urinometer*, is used to read the specific gravity of urine. With this instrument it is possible to obtain an accurate reading to the third decimal. When using any type of hydrometer, the temperature of the liquid should be adjusted to the temperature

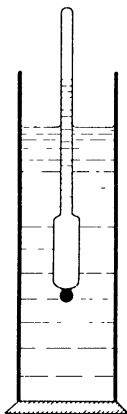


Fig. 34. Hydrometer.

indicated by the manufacturer. This is the temperature at which the instrument was calibrated.

THE GAS LAWS

The volume that a gas occupies depends upon the *temperature and pressure*. Unless these two factors are known it is impossible to state the volume of any gas. Since the gaseous state is commonly encountered in chemistry, we must understand and have a working knowledge of the *gas laws*. In physiology, for example, the gaseous constituents of the air and blood are an integral part of the body's chemistry. It would not be possible to comprehend their action without a knowledge of their relation to temperature and pressure. Fortunately, the gas laws which apply to pressure and temperature are easy to understand; indeed, they may be derived intuitively.

Boyle's Law. In the seventeenth century the English scientist, Boyle, presented one of the most fundamental laws in chemistry. It is simple, and may be stated as follows: *If the temperature remains constant, the volume of a gas varies inversely as the pressure on it.* If, for example, a given gas has a volume of 100 cc. under a certain pressure, and the pressure is *doubled* (at a constant temperature), the new volume of the gas will be reduced to 50 cc.; if, on the other hand,

the pressure is *halved*, the gas will *expand* to a volume of 200 cc. The law may be stated mathematically as a simple *inverse* proportion:

$$\frac{\text{New volume}}{\text{Old volume}} = \frac{\text{Old pressure}}{\text{New pressure}} \quad \text{or} \quad \frac{V_1}{V} = \frac{P}{P_1}$$

In scientific work, volume is usually expressed in cc. or liters, and pressure in millimeters (mm.) of mercury—i.e., the height of the mercury column in the barometer (760 mm. = atmospheric pressure at sea level).*

Example: *The volume of a gas measures 600 cc. at 740 mm. pressure. Calculate the volume at 780 mm.*

Since the pressure *increases*, the volume must *decrease*. The solution is as follows:

$$\begin{aligned} \frac{V_1}{V} &= \frac{P}{P_1} \\ V_1 &= \frac{VP}{P_1} \\ V_1 &= \frac{600 \times 740}{780} \\ V_1 &= 569 \text{ cc.} \end{aligned}$$

Charles' Law. The exact relation between the volume of a gas and its temperature was first stated by the French chemist, Charles. Like Boyle's Law, it proved to be one of the building stones of modern chemistry. Charles discovered that when a gas, under constant pressure, is heated 1° C., it expands $\frac{1}{273}$ of its volume; and, when cooled 1° C., contracts $\frac{1}{273}$ of its volume. Theoretically, then, at -273° C. it would have a volume of *zero*. It was Charles who designated the temperature of -273° C. as *absolute zero*. Charles' Law is stated as follows: *If the pressure remains constant, the volume of a gas varies directly as the absolute temperature*. Mathematically, the law is stated as a direct proportion:

$$\frac{\text{New volume}}{\text{Old volume}} = \frac{\text{New temperature (Absolute)}}{\text{Old temperature (Absolute)}}$$

$$\text{or} \quad \frac{V_1}{V} = \frac{A_1}{A}$$

In order to use the above proportion, all Centigrade temperature readings must be converted to Absolute readings. This is done by merely adding degrees Centigrade and 273 algebraically. A -10° C., for example, is 263° Absolute; and 10° C. is 283° A.

* A pressure of 760 mm. and a temperature of 0° C. are referred to as *standard conditions*.

Example: *The volume of a gas measures 500 cc. at 50° C. What will be its volume at 0° C.?*

Since the temperature decreases, the volume will decrease. The solution is as follows:

$$\begin{aligned}\frac{V_1}{V} &= \frac{A_1}{A} \\ V_1 &= \frac{A_1 V}{A} \\ V_1 &= \frac{(0 + 273)(500)}{(50 + 273)} \\ V_1 &= 423 \text{ cc.}\end{aligned}$$

Simultaneous Solution. The formulas for Boyle's Law and Charles' Law may be combined into one formula. This formula enables us to find the new volume of a gas when there is both a temperature change and pressure change, and thus obviates two calculations. The combined formula is as follows:

$$\begin{aligned}\frac{PV}{A} &= \frac{P_1 V_1}{A_1} \\ \text{or} \quad V_1 &= \frac{PVA_1}{P_1 A}\end{aligned}$$

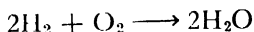
V_1 = new volume
 P_1 = new pressure
 A_1 = new Absolute temperature
 V = old volume
 P = old pressure
 A = old Absolute temperature

Example: *A gas has a volume of 100 cc. at 70° C. and 760 mm. pressure. What will be its volume at 20° C. and 700 mm. pressure?*

$$\begin{aligned}V_1 &= \frac{PVA_1}{P_1 A} \\ V_1 &= \frac{(760)(100)(20 + 273)}{(700)(70 + 273)} \\ V_1 &= \frac{(760)(100)(293)}{(700)(343)} \\ V_1 &= 93 \text{ cc.}\end{aligned}$$

Gay-Lussac's Law. Probably the very first correct chemical equations were those expressing the reactions between gases. This was due to the work of the French chemist, Gay-Lussac. Gay-Lussac's Law may be stated thus: *When gases react, the volumes of these gases, and the volumes of the products, if gases, are in a ratio to each other that may*

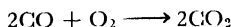
be expressed by small whole numbers. The law may be illustrated by the following equation:



From our earlier work, the above equation is read: 2 molecules of hydrogen plus 1 molecule of oxygen yield 2 molecules of water. Gay-Lussac's Law says the same thing, but in addition allows us to substitute the term "volume" for molecule. The equation, then, is also read: 2 volumes of hydrogen plus 1 volume of oxygen yield 2 volumes of water vapor. This is of vast practical importance, for it allows us to deal quantitatively with gaseous reactions.

Example: One hundred liters of carbon monoxide were burned in a gas stove. How many liters of oxygen were removed from the air?

It is first necessary to write an equation for the chemical reaction between the two gases. Carbon monoxide combines with oxygen to yield carbon dioxide. The reaction is as follows:



The above equation reads: 2 volumes of carbon monoxide plus 1 volume of oxygen yield 2 volumes of carbon dioxide. The specific problem, however, relates to the relation between carbon monoxide and oxygen. It will be noted that the ratio of carbon monoxide to oxygen is 2:1. Therefore, we conclude that 50 liters of oxygen are required to burn 100 liters of carbon monoxide. A ratio may be set up as follows:

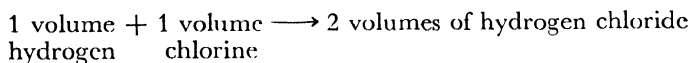
$$\begin{aligned} \frac{\text{vols. of monoxide}}{\text{liters of monoxide}} &= \frac{\text{vols. of oxygen}}{\text{liters of oxygen}} \\ \frac{2}{100} &= \frac{1}{x} \\ 2x &= 100 \\ x &= 50 \text{ liters} \end{aligned}$$

All problems relating to gaseous reactions, therefore, are solved by the following steps:

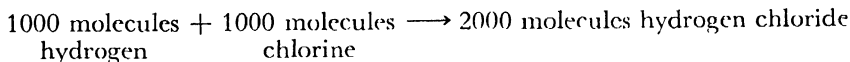
1. Write the balanced equation for the reaction.
2. Set up a ratio between the 2 gases concerned.
3. Substitute in the ratio and solve.

Avogadro's Law. One cannot fully appreciate the above gas law without an understanding of Avogadro's Law. Avogadro, an Italian scientist, made the brilliant deduction that *equal volumes of all gases, when measured under the same conditions of temperature and pressure, contain the same number of molecules.* The impact of Avogadro's Law upon the development of chemistry is well illustrated by the reasoning which led to the conclusion that *1 molecule of hydrogen contains 2 atoms, and therefore is written as H₂.* The reasoning goes like this: We

know by experiment that 1 volume of hydrogen reacts with 1 volume of chlorine to produce 2 volumes of hydrogen chloride. Let us assume that 1 liter of hydrogen and 1 liter of chlorine are reacted to produce 2 liters of hydrogen chloride. Further, let us assume that 1 liter of hydrogen contains 1000 molecules. It follows from Avogadro's Law that 1 liter of chlorine contains 1000 molecules, and that 2 liters of hydrogen chloride contain 2000 molecules. *Since each of the 2000 molecules of hydrogen chloride contains 1 atom of hydrogen, there must be 2000 atoms of hydrogen. Therefore, each molecule of hydrogen gas (we started with a 1000 molecules) must contain 2 atoms of hydrogen in order to produce 2000 atoms.* The above may be illustrated as follows:



and so,



Therefore, 1 mol of hydrogen contains 2 atoms (H_2)

By similar reasoning, it may be concluded that most of the common gaseous elements (e.g., oxygen, chlorine, nitrogen) are constituted by *diatomic* molecules.

Henry's Law. Henry's Law states that the *solubility of a gas in a liquid is directly proportional to the pressure over the liquid*. The effervescence seen when the top is removed from a bottle of pop results from the release of pressure in the bottle. Individuals who perform their work in an atmosphere of elevated pressure (e.g., *divers and caisson workers*) may develop a disease called the "bends." This condition is explained by Henry's Law: At the elevated pressures, the blood dissolves increased quantities of air. As soon as the individual returns to normal atmospheric pressure, however, this air is *released* from the blood. For this reason, great care must be exercised in adapting the body to the change of pressures; i.e., workers must *gradually* enter and leave the area of increased pressure. A sudden change from a high pressure area to atmospheric pressure allows the air to escape so rapidly that there is an actual effervescence in the blood. This causes severe pain, paralysis, and sometimes death.

MOLECULAR WEIGHT

The molecular weight (m.w.) of an element or compound is the *sum of the weights of all atoms in the molecule*. The calculation is carried out by adding the *atomic weights* of all the elements present—each atomic weight being *multiplied by its subscript in the formula*.

Example: *What is the molecular weight of sulfuric acid (H_2SO_4)?*

Element	Atomic weight	Subscript	
H	1	2	2
S	32	1	32
O	16	4	64
			—
			98

$$\text{m.w. of } \text{H}_2\text{SO}_4 = 98$$

Experimental Determination of Molecular Weight. There is a direct mathematical relationship between the molecular weight and the freezing and boiling points of a solution. It is an interesting fact that *1 mole* of a nonelectrolyte depresses the freezing point of 1000 gm. of water 1.86°C . (i.e., freezes at -1.86°C .), and raises the boiling point 0.52°C . (i.e., boils at 100.52°C .)* This laboratory fact enables the chemist to ascertain the molecular weight of a new compound. For example, if it is found that 50 gm. of a certain chemical elevate the boiling point of 1000 gm. of water 1.04°C . (i.e., boils at 101.04°C .), we may conclude that the molecular weight of this compound is 25.

The behavior of electrolytes depends on the number of ions furnished by each molecule. Thus, 1 mole of NaCl causes a 3.72°C . depression in the freezing point, and a 1.04°C . rise in the boiling point—i.e., twice the effect of a nonelectrolyte. This is due to the fact that each molecule of NaCl furnishes 2 ions. It seems, therefore, that the ion of an electrolyte and the molecule of a nonelectrolyte are equivalent in their colligative properties, i.e., their effects on the freezing and boiling points.

PERCENTAGE COMPOSITION

By knowing a substance's formula and molecular weight, it is a simple procedure to ascertain the *percentage composition* of any of its constituent elements. The calculation is performed by use of the following formula:

$$\text{Percentage composition (p.c.)} = \frac{\text{Atomic weight} \times \text{subscript}}{\text{Molecular weight}} \times 100$$

Example: *Calculate the percentage composition of hydrogen in water (H_2O).*

$$\text{m.w. of } \text{H}_2\text{O} = 18$$

$$\text{at.w. of H} = 1$$

$$\text{p.c.} = \frac{1 \times 2}{18} \times 100$$

$$\text{p.c.} = 11.1\% \text{ hydrogen}$$

Percentage composition permits us to deal quantitatively with any chemical substance. Obviously, this expression enjoys wide application and use. The following examples illustrate an area of their value.

* One mole (also referred to as the *gram molecular weight*) means the molecular weight expressed in grams.

Example: If 30 gm. of salt (sodium chloride) are ingested, how much sodium is available to the body's tissues?

$$\begin{aligned}\text{m.w. NaCl} &= 58.5 \\ \text{at.w Na} &= 23 \\ \text{p.c. of Na} &= \frac{23}{58.5} \times 100 \\ \text{p.c. of Na} &= 39\%\end{aligned}$$

The amount of sodium metal in 30 gm. of salt is now found by taking 39 per cent of 30 gm.—12 gm.

Example: Weight for weight, which compound contains the more iodine, sodium iodide (NaI) or potassium iodide (KI)?

$$\begin{aligned}\text{m.w. NaI} &= 150 \\ \text{at.w. I} &= 127 \\ \text{p.c I} &= \frac{127}{150} \times 100 \\ \text{p.c. I} &= 85\% \\ \hline \text{m.w. KI} &= 166 \\ \text{at.w. I} &= 127 \\ \text{p.c. I} &= \frac{127}{166} \times 100 \\ \text{p.c. I} &= 77\%\end{aligned}$$

Therefore, NaI furnishes more iodine than KI.

Determination of a Compound's Formula. The concept of percentage composition permits the chemist to ascertain the formula of an unknown compound. When dealing with an unknown, the chemist first determines the elements present (*qualitative analysis*) and then, by using *quantitative analysis*, determines the *per cent composition of each element*. From this, the formula is determined by *dividing the percentage of each element by its atomic weight*. The resulting quotients indicate the ratio of the atoms present in each molecule of the compound.

Example: What is the formula of a pure compound which was found to contain 2 per cent hydrogen, 33 per cent sulfur and 65 per cent oxygen? Such a problem is easily solved by means of the following table:

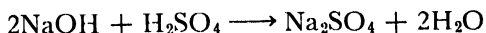
Element	% Composition	Atomic Weight	Quotient*
Hydrogen	2	1	2
Sulfur	33	32	1
Oxygen	65	16	4

Answer: H₂SO₄

* Nearest whole number.

QUANTITATIVE REACTIONS

Let us consider the following chemical reaction:



This reaction states that *2 molecules* of sodium hydroxide react with *1 molecule* of sulfuric acid to produce *1 molecule* of sodium sulfate and *2 molecules* of water. Since the weight of a molecule of a compound—i.e., the molecular weight—is constant, it stands to reason that these two chemical compounds *always react in definite amounts by weight*. This quantitative relationship applies to all chemical reactions. It is not difficult to perceive or understand, therefore, the tremendous importance of this fundamental fact. The following examples readily illustrate the methods employed to solve problems involving chemical reactions.

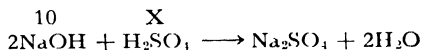
Weight-Weight. In the so-called *weight-weight* problem, the weight of a reactant or product in a chemical reaction is calculated from a given weight of any other reactant or product in the reaction. In the reaction cited above between sodium hydroxide and sulfuric acid, if we know the weight of any one member of this reaction, we can calculate the three other weights. For example, from a given weight of sodium hydroxide, we can calculate the weight of sulfuric acid needed to *just* neutralize the sodium hydroxide, and the weights of the products, i.e., sodium sulfate and water. The method of calculation of *weight-weight* problems is simply illustrated below.

Example: *What quantity of sulfuric acid is needed to neutralize 10 gm. of sodium hydroxide?*

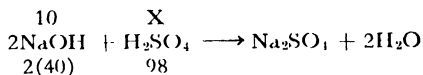
First we must write a balanced equation for the reaction, thus:



After the equation has been correctly balanced, the given quantity of the chemical is written above its formula in the equation; an X is placed over the formula of the chemical whose weight is desired. For the above equation we have the following:



Next, the molecular weights of the two compounds involved are determined and written under their respective formulas. In the event a coefficient is present, *the molecular weight is multiplied by this coefficient*. This is the reason why the equation must be correctly balanced. From the above we have the following.



Now we have a simple proportion involving our unknown X:

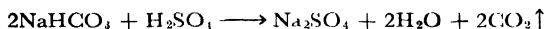
$$\begin{array}{l} \frac{10}{80} = \frac{\text{X}}{98} \\ 80\text{X} = 980 \\ \text{X} = 12.25 \text{ gm. of H}_2\text{SO}_4 \end{array}$$

In the same way, we can ascertain the quantities of sodium sulfate and water. It should be thoroughly understood that we are not confined to using the metric system. For example, the above problem could have read 10 oz. or 10 lbs. Since we are dealing with a proportion, however, the answer will be in the same units.

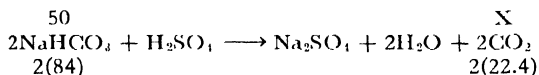
Weight-Volume or Volume-Weight. There are many reactions in which gases are either the reactants or products. As we know, when dealing with gases, volume is more significant than weight. The question arises, therefore: Can we solve reactions which involve both weight and volume? The answer is yes. By a slight alteration of the technique employed to solve weight-weight problems, we can solve weight-volume or volume-weight problems.

Example: *How many liters of carbon dioxide are liberated when 50 gm. of sodium bicarbonate are reacted with sulfuric acid?*

First, the balanced equation is written for the reaction:



The given weight of the chemical is now written above its formula, and its molecular weight below. Over the gas we place an X. Under the gas, however, we place 22.4, which is to be multiplied by the coefficient in the event one is present. From the above, we have the following:



$$\frac{50}{168} = \frac{\text{X}}{44.8}$$

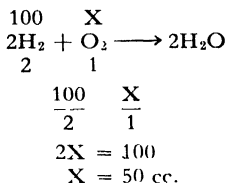
$$168\text{X} = 2240$$

$$\text{X} = 13.3 \text{ liters of CO}_2$$

The above calculation demands some explanation. The figure 22.4 is known as the *gram molecular volume* (g.m.v.). It has been demonstrated experimentally that *a molecular weight expressed in grams* (i.e., a mole) *of any gas occupies 22.4 liters at standard conditions, i.e., at 0° C. and 760 mm. pressure.* Thus, at standard conditions, 44 gm. of CO₂ and 64 gm. of SO₂ occupy the same volume—22.4 liters. For this reason, we are justified in writing a proportion such as given above. *In this type of problem, the weight must be stated in grams, and volume in liters.* Also, all volumes are at standard conditions. In the above example, the answer 13.3 liters of CO₂ means 13.3 liters of CO₂ at 0° C. and 760 mm. pressure. In practice, this volume must be corrected—using the gas laws—to the temperature and pressure under which the reaction was carried out.

Volume-Volume. Some reactions involve only gases. Gas reactions are solved simply by writing the volumes—in any unit—above the reactants or products, and the coefficients below. In the event no coefficient is present, the number 1 is written.

Example: *How many cc. of oxygen are required to react with 100 cc. of hydrogen to form water?*



This type of reaction was fully explained under Gay-Lussac's Law. Gay-Lussac's Law explains why we are at liberty to write the above proportion. Even without this law, however, the above solution makes practical sense.

ARITHMETIC OF SOLUTIONS

In every area of chemistry and applied chemistry, solutions are extensively employed. It is therefore essential that we understand the principal ways in which the strength of solutions are stated. Of course, this entails the application of simple arithmetic. The following types of solutions—and the necessary arithmetic—are widely used in chemistry, pharmacy, medicine and nursing—to mention a few.

Percentage Solutions. Percentage is the most common and popular method of stating a solution's strength or concentration. In this method, the total volume is usually taken as 100 per cent; the solute—solid or liquid—is taken as a percentage of the total volume. When a solid solute is dissolved in a liquid, the percentage concentration (of the solute) is calculated by *dividing the weight of the solute in gm. by the total volume in cc., and then multiplying the resulting quotient by 100*. This method of stating percentage is referred to as *weight to volume* (w./v.). When a solution is prepared from two or more miscible liquids, however, there are two ways of expressing the percentage of a constituent—*weight to volume* or *volume to volume* (v./v.). Volume to volume is calculated by dividing volume by total volume, and multiplying the quotient by 100. To be explicit, therefore, the percentage strength of such a solution should be qualified as being w./v. or v./v.

Example 1: *Two grams of salt were dissolved in water contained in a graduated cylinder. The volume of resulting solution measured 10 cc. What was the percentage concentration of this solution?*

$$\begin{array}{l} \frac{\text{gm. of salt}}{\text{vol. of solution}} \times 100 = \% \text{ salt} \\ \frac{2}{10} \times 100 = 20\% \end{array}$$

As calculated above, such a solution has a concentration of 20 per cent salt.

Example 2: *A pharmacist wishes to prepare 2 oz. of a 2 per cent solution of iodine in alcohol. How much iodine is needed?*

Two ounces are equal to 60 cc. The solution, therefore, has a volume of 60 cc. The amount of iodine is calculated by substituting the known values in the following formula, and letting x equal the unknown quantity:

$$\begin{aligned}\frac{\text{gm. of iodine}}{\text{vol. of solution}} \times 100 &= \% \text{ iodine} \\ \frac{x}{60} \times 100 &= 2 \\ \frac{100x}{60} &= 2 \\ 100x &= 120 \\ x &= 1.2 \text{ gm. of iodine needed}\end{aligned}$$

One and two-tenths gram of iodine would then be placed into a graduated cylinder, and a small amount of alcohol added to dissolve the iodine. After complete solution, sufficient alcohol is added to bring the volume of the solution up to the 60 cc. mark.

Example 3: *A solution was prepared from 700 cc. of alcohol, 100 cc. of glycerin and 200 cc. of water. What was the percentage of alcohol in such a solution—by volume?*

$$\begin{aligned}\frac{\text{vol. of alcohol}}{\text{vol. of solution}} \times 100 &= \% \text{ alcohol} \\ \frac{700}{1000} \times 100 &= 70\% \text{ alcohol by volume}\end{aligned}$$

Molar Solutions. Molar solutions are commonly prepared in the chemical laboratory. They are not as popular, however, in applied chemistry. *A 1 molar solution is a solution which contains 1 gram molecular weight of a chemical per liter of solution.* A gram molecular weight of a compound—commonly referred to as a *mole* (M)—is merely the molecular weight of the compound expressed in grams.* Probably the principal value of employing molar solutions in chemistry arises from the fact that the term is a simple and accurate way of expressing concentration—that is, to the chemist.

Example: *Prepare 500 cc. of a 2 molar (2M) solution of sulfuric acid.*

$$\begin{aligned}\text{formula} &= \text{H}_2\text{SO}_4 \\ \text{m.w.} &= 98 \\ 1 \text{ mole} &= 98 \text{ gm.} \\ \text{moles needed} &= 1 \text{ or } 98 \text{ gm. (2M for 1 liter, hence 1M for 500 cc. or } \frac{1}{2} \text{ liter)}\end{aligned}$$

A 500 cc. 2M solution of H_2SO_4 , then, is prepared by taking 98 gm. of H_2SO_4 and sufficient water to make 500 cc. of solution.

Normal Solutions. Normal solutions enjoy wide use in chemistry and applied areas. Normal solutions are especially valuable because of a unique quantitative relationship. In order to appreciate this rela-

* When preparing molar solutions of salts which have a hydrous and anhydrous form, it is necessary to know which form is being used. One mole of CuSO_4 , for example = 160 gm.; 1 mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 250 gm.

tionship, it is essential that we fully grasp the meaning of the following definition: *A 1 normal (1N) solution is a solution of a compound which furnishes 1 gm. of hydrogen ions (H^+) or its equivalent per liter of solution.* First of all, what is meant by the expression, "equivalent"? *An equivalent of 1 gm. of hydrogen means 1 gram atomic weight of any element which has a valence of a plus 1.* Thus, 36.5 gm. of HCl—1 gram molecular weight or mole—and 58.5 gm. of NaCl—1 gram molecular weight or mole—are "equivalent quantities": The 36.5 gm. of HCl furnish 1 gm. of hydrogen ions; the 58.5 gm. of NaCl furnish 23 gm. of sodium ions (the gram atomic weight of sodium). When dissolved in sufficient water to make 1 liter of solution, each forms a 1 normal solution.

To prepare a 1 normal solution of sulfuric acid (H_2SO_4), or any other acid which contains more than 1 atom of hydrogen per molecule, we take the appropriate fraction of the gram molecular weight. Thus, for dibasic acids we take *one half*, and for tribasic acids, *one third*. A 1 normal solution of sulfuric acid, therefore, contains 49 gm. ($\frac{1}{2}$ of 98 gm.) per liter. To prepare a 1 normal solution of $MgCl_2$, or any other salt or base containing a metal whose valence is greater than 1, we take the appropriate fraction of the gram molecular weight—e.g., $\frac{1}{2}$, $\frac{1}{3}$ or $\frac{1}{4}$. A 1 normal solution of $MgCl_2$, therefore, contains 47.7 gm. ($\frac{1}{2}$ of 95.3) per liter. In the case of salts which contain more than 1 atom of an element whose valence is greater than 1, a fraction must be employed whose denominator is the valence of the metal times its subscript. For example, the equivalent weight of aluminum sulfate is calculated by taking $\frac{1}{2 \times 3}$ or $\frac{1}{6}$ of 1 mole of $Al_2(SO_4)_3$.

Of course, normal solutions may be prepared of any desired strength—0.5 normal (0.5N), 3 normal (3N), and so on. The following examples thoroughly demonstrate how normal solutions are prepared. The careful reader has probably taken note of the fact that *a 1 normal solution and a 1 molar solution are the same for all monobasic acids and for all salts and bases with one atom of a monovalent metal.*

Example 1: Prepare 2 liters of a 1 normal solution of hydrochloric acid (HCl).

gm. of HCl required for 1 liter of 1N = 36.5 gm.

gm. of HCl required for 2 liters of 1N = 2×36.5 or 73 gm.

The solution is prepared by placing 73 gm. in a graduated cylinder, and adding sufficient water to make 2000 cc. or 2 liters of solution.

Example 2: Prepare 500 cc. of 1 normal sulfuric acid (H_2SO_4).

gm. of H_2SO_4 required for 1 liter of 1N = 49 gm. ($\frac{1}{2}$ of 1 mole of H_2SO_4)

gm. of H_2SO_4 required for 500 cc. of 1N = $\frac{49}{2}$ or 24.5 gm.

The solution is prepared by placing 24.5 gm. of H_2SO_4 in a graduated cylinder, and adding sufficient water to make 500 cc. of solution.

Example 3: *Prepare 1 liter of a 2 normal solution of AlCl_3 .*

gm. of AlCl_3 required for 1 liter of 1N = 44.5 gm. ($\frac{1}{3}$ of 1 mole of AlCl_3).

gm. of AlCl_3 required 1 liter of 2N = 2×44.5 gm. or 89 gm.

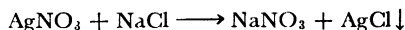
The solution is prepared by taking 89 gm. of AlCl_3 , and adding sufficient water to make 1 liter of solution.

Titration. It was stated above that normality is a valuable way of expressing concentration. This is so because solutions of the same normality react with one another in equal volumes. For example, 10 cc. of 1N sodium hydroxide will *exactly* neutralize 10 cc. of 1N hydrochloric acid. Also, 10 cc. of 0.5N sodium hydroxide will *exactly* neutralize 5 cc. of 1N hydrochloric acid. It follows, therefore, that if we know the volume and normality of one solution, we can easily calculate the volume required of some other solution of known normality. Of far greater import, however, is the fact that it is possible to determine the normality of a solution. This relationship between normal solutions is expressed by the following simple formula:

$$\begin{array}{ccc} N \times \text{cc.} & = & N \times \text{cc.} \\ (\text{solution A}) & & (\text{solution B}) \end{array}$$

Example: *What is the normality of a solution of silver nitrate which requires 30 cc. of 2N sodium chloride to react with 60 cc. of solution?*

Although not required for solution, the equation for the reaction is:



In other words, 30 cc. of 2N sodium chloride *exactly* react with 60 cc. of xN silver nitrate to form sodium nitrate and insoluble silver chloride. The normality of the AgNO_3 solution is calculated as follows:

$$\begin{array}{rcl} \text{AgNO}_3 & \text{NaCl} & \\ N \times \text{cc.} & = & N \times \text{cc.} \\ N \times 60 & = & 2 \times 30 \\ N60 & = & 60 \\ N & = & 1 \end{array}$$

The silver nitrate solution, therefore, has a 1N concentration.

How are problems such as the one cited above carried out? Specifically, how is it possible to determine the point at which one solution *exactly* reacts with another solution? More specifically, how do we know that 30 cc. of 2N sodium chloride exactly react with 60 cc. of silver nitrate solution? The answer to these questions is supplied by the word *titration*. *Titration is defined as the process of determining the normality of an unknown solution by using a solution of known normality.* The process is carried out by the apparatus shown in Figure 35.

The silver nitrate-sodium chloride reaction is carried out as follows: Burette A is filled with silver nitrate solution, and burette B with the sodium chloride solution. The stopcock of burette A is then opened and exactly 60 cc. of solution are delivered to the beaker. The beaker is then placed under burette B and *titrated* with the sodium chloride solution; i.e., the solution is allowed to enter the solution in the beaker *drop by drop*. As the sodium chloride solution enters the silver nitrate solution, a white precipitate of AgCl forms immediately. When carefully conducted, a point—the so-called *end point*—will be reached at which no further precipitate will form. At the end point, *just enough* of the solution in the burette has been added. The volume of sodium chloride solution added can then be read directly from the burette.

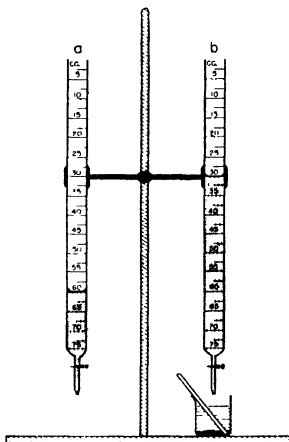


Fig. 35. Titration of AgNO_3 solution (A) with 2N NaCl (B). (See text for details.)

For reactions which do not form precipitates, the end point is ascertained by a so-called *indicator* (discussed previously). An indicator—usually a dye—will change color at the *end point* of the reaction. When titrating a base with an acid, for example, a drop of phenolphthalein solution is added to the base; this imparts a red color. At the point of neutrality—the end point—the red color disappears, and titration is stopped. Other indicators, such as litmus and methyl orange, may be similarly employed.

Titration has wide application in *quantitative analysis*—the branch of chemistry which is concerned with ascertaining the concentration of an element or compound. The following example illustrates its value in industry. Vinegar as sold on the market is required to have a concentration of 4 to 5 per cent acetic acid. Obviously, therefore, all batches of vinegar sold by a manufacturer must be subjected to a quantitative

analysis before being bottled. This is carried out by titrating a sample of the vinegar with a base such as sodium hydroxide. The normality of the vinegar is then calculated as above. From the normality we can calculate the amount of acetic acid and the percentage concentration. Suppose, for example, that a manufacturer has a batch of vinegar with a normality of 0.5. Knowing this, he can find the percentage of acetic acid, thus: 1 liter of 0.5N acetic acid contains 0.5 mole of acetic acid ($\text{H}\cdot\text{C}_2\text{H}_3\text{O}_2$) or 30 gm. The per cent acetic acid is then calculated by dividing 30 gm. by 1000 cc., thus:

$$\frac{30}{1000} \times 100 = 3\%$$

The analysis indicates that further fermentation is necessary. Subsequent titrations will then be required in order to stop fermentation between 4 to 5 per cent concentration.

CALCULATION OF pH

The meaning and value of pH were discussed very early in this text (p. 44). It will be recalled that pH is a short and accurate way of stating the reaction of a solution, i.e., whether it is *neutral*, *acidic* or *basic*. As we know, a pH of 7 means that a solution has a concentration of 0.0000001 gm. H⁺ ion per liter of solution. We stated that the 7 is derived from the number of places to the *right* of the decimal. Other pH values (0 to 14) are stated in the same way. Thus, a solution of pH 5 means a H⁺ ion concentration of 0.00001 gm. per liter.

Let us now see if we can treat pH a little more scientifically—and easily. A number such as 0.0000001 may be written more conveniently as 10^{-7} . The minus exponent—in this case 7—states the number of decimal places to the *right of the decimal*. If we form the reciprocal of 0.0000001 (i.e., $\frac{1}{0.0000001}$) and divide, we come out with the answer 10,000,000. Now, a large number such as this is more conveniently expressed as 10^7 . The positive exponent—in this case 7—states the number of *zeros* to the left of the decimal. What we have done thus far may be set down as follows:

$$\frac{1}{0.0000001} = 10,000,000 \quad \text{or} \quad \frac{1}{10^{-7}} = 10^7$$

Interestingly enough—especially for those of us who have forgotten—all that is necessary in solving an expression like $\frac{1}{10^{-7}}$ is to change the sign of the exponent, i.e., from a -7 to $+7$, or 7.

An exponent of 10 is formally referred to as a *common logarithm*. Thus, the logarithm of 10^7 is 7. Technically, therefore, pH is defined as the *logarithm of the reciprocal of the H^+ ion concentration—mathematically*:

$$pH = \log \left(\frac{1}{[H^+]} \right)^*$$

* $[H^+] = H^+$ ion concentration, expressed as gm. per liter.

Using this formula, let us calculate the pH of a solution having a H^+ ion concentration of 0.00001 gm. per liter, thus:

$$\begin{aligned} pH &= \log \left(\frac{1}{.00001} \right) \\ pH &= \log \left(\frac{1}{10^{-5}} \right) \\ pH &= \log \left(\frac{1}{10^{-5}} \right) = 10^5 \\ pH &= \log (10^5) \\ pH &= 5 \end{aligned}$$

Why is it necessary to employ this formula when we can derive the same answer by counting the number of places to the right of the decimal of the concentration? The answer is simple: Counting the number of places is applicable only to concentrations such as 0.01, 0.001, 0.0001, 0.00001, and so on. It is, for example, impossible to calculate the pH of a H^+ ion concentration of 0.0002 without using the formula. For those who understand the use of logarithms—or for those who are interested—the above problem is solved as follows:

$$\begin{aligned} (a) \quad pH &= \log \left(\frac{1}{[H^+]} \right) \\ (b) \quad pH &= \log \left(\frac{1}{0.0002} \right) \\ (c) \quad pH &= \log \left(\frac{1}{2 \times 10^{-4}} \right) \\ (d) \quad pH &= \log \left(\frac{10^4}{2} \right) \\ (e) \quad pH &= \log (10^4) - \log 2 \\ (f) \quad pH &= 4 - \log 2 \\ (g) \quad pH &= 4 - .3^* \\ (h) \quad pH &= 3.7 \end{aligned}$$

* The value 0.3 was taken from a table of logarithms.

QUESTIONS

1. Physiology texts state that the large intestine is about 1.5 meters in length. Convert to feet.
2. The esophagus is 10 inches long. Convert this to centimeters.
3. There are about 5,000,000 red cells per cubic millimeter of blood. Often students state that the figure is 5,000,000 per cc. How large an error is this?
4. How many cc. are there in 1 pint?
5. How many millimeters are there in 1 inch? How many centimeters?
6. Convert the normal body temperature— 98.6° F.—to Centigrade.
7. Convert 30° C. to degrees F.
8. Two grams of bread were completely burned in a calorimeter. Sufficient heat was produced to raise the temperature of water surrounding the bomb 8° C. If there were 1000 gm. of water present, what was the caloric content of the bread? Express as large Calories per gram.
9. Glycerin has a specific gravity of 1.25. How much do 2 oz. of glycerin weigh?
10. Two oz. of a certain liquid weigh 120 gm. What is the density of the liquid?
11. The numbers on the scale of a urinometer read lower at the top than at the bottom. Explain.
12. The specific gravity of urine varies slightly. Mention a factor which could cause the specific gravity to decrease.
13. Explain why the temperature usually rises prior to a snow storm.
14. Explain why ice is "colder" than water at the same temperature.
15. Explain why a burn from steam is more severe than a hot water burn.
16. The volume of a gas measures 500 cc. at standard pressure. If the temperature remains constant, what will its volume be at 790 mm.?
17. If 600 cc. of air at 20° C. are taken into the lungs, what will be the new volume, assuming that the air is heated by the body to 30° C.?
18. Employing a "simultaneous solution," find the new volume of a gas (at 25° C. and 700 mm.) which measures 200 cc. at 70° C. and 760 mm.
19. Compute the molecular weight of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.
20. When a person buys a pound of washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), for how many oz. of water is he paying?
21. How many gm. of HCl will 5 gm. of milk of magnesia neutralize in the stomach?
22. What volume of *air* must one breathe to "burn" 1 oz. of sugar ($\text{C}_6\text{H}_{12}\text{O}_6$) to CO_2 and H_2O ?
23. How much AgNO_3 is needed to prepare 2 oz. of a 1 per cent solution?
24. 1 liter of 5 per cent glucose solution was given by intravenous injection. How much glucose did the patient receive?
25. What volume (in cc.) of 70 per cent alcohol can be prepared from 1 liter of absolute (100 per cent) alcohol?
26. How much H_2SO_4 is needed to make 500 cc. of a 1 molar solution?
27. How much HNO_3 is needed to make 1 liter of a 2 normal solution?
28. A 10 cc. sample of lemon juice was titrated with 0.1 normal NaOH. If 5 cc. of base were required to just neutralize the citric acid in the juice, what was the normality of the juice relative to citric acid?
29. One liter of a solution has a H^+ ion concentration of 10^{-4} . What is its pH?
30. Convert pH 6 to grams of H^+ ion per liter.

CHAPTER 9

COLLOIDS

The subject of colloids demands a special chapter and special consideration. Heretofore, we were dealing primarily with the chemical properties of the elements and their compounds; in contrast, colloidal properties are essentially physical in nature. *A colloid may be defined as a solid, liquid or gas dispersed (subdivided) to such a degree that the size of the dispersed particles becomes an important factor in determining its properties.* It is hoped that a careful study of this chapter will bring full understanding and appreciation of this definition. The vast importance of colloidal chemistry—especially to the biologic sciences—will be amply disclosed throughout the chapter.

THE COLLOIDAL STATE

When sand is shaken with water and the mixture is allowed to stand, the sand soon settles to the bottom. Such a mixture is a true *suspension*. If, on the other hand, we add sugar to water, the molecules become separated from the crystals and are distributed uniformly throughout the solvent. As we know, such a mixture is a true *solution*. Now let us grind some clay into small particles, and stir these thoroughly into a beaker of water. When such a mixture is allowed to stand, the greater amount of the clay—owing to its weight and insolubility—settles to the bottom. If we filter this mixture through filter paper, the clay which settled out will remain on the paper. The liquid which passes through, however, is not clear—but *turbid*. This turbidity is due to the particles of clay which have passed through the pores of the filter paper. Of fundamental importance is the fact that these clay particles do not settle out, but remain suspended in the liquid. These particles of clay are said to be in the *colloidal* state.

The size of an individual colloidal particle is so small that it is usually measured in *millimicrons*. One millimicron, $1\text{ m}\mu$, is equal to one-millionth of a millimeter. A colloidal particle is usually somewhere between $1\text{ m}\mu$ (0.000001 mm.) and $100\text{ m}\mu$ (0.0001 mm.); i.e., it is smaller than a suspension particle, but larger than a solution particle.*

* The smallest particle which can be seen with the aid of the most powerful optical microscope is about $100\text{ m}\mu$.

COLLOIDAL SYSTEMS

The above example of colloidal clay in water represents a so-called *colloidal system*. A colloidal system may be defined as a two-phase heterogeneous mixture—i.e., one state of matter dispersed in another state of matter—in which the dispersed particles do not settle out. The phase which is suspended is called the *dispersed phase* or *internal phase*; the phase which holds or contains the dispersed phase is called the *dispersion medium* or *external phase*. In the example cited, clay represents the dispersed phase, and water the dispersion medium. The dispersed phase may be a solid, liquid or gas. Likewise, the dispersion medium may be a solid, liquid or gas. Theoretically, therefore, there are nine possible colloidal systems. Actually, however, there are only eight systems, since gases are miscible in all proportions; i.e., gases form true solutions. These eight colloidal systems are presented in the table below:

Classification of Colloidal Systems

<i>Dispersed Phase</i>	<i>Dispersion Medium</i>	<i>Name</i>
Solid	Solid	Solid sol
Solid	Liquid	Sol
Solid	Gas	Solid aerosol
Liquid	Solid	Solid emulsion
Liquid	Liquid	Emulsion
Liquid	Gas	Liquid aerosol
Gas	Solid	Solid foam
Gas	Liquid	Foam
Gas	Gas	

COLLOIDAL PROPERTIES

Before we study the individual colloidal systems, let us first direct our attention to the unique properties common to all colloids.

Tyndall Effect. Probably the most striking property of colloidal systems is the so-called *Tyndall effect*. This phenomenon is observed when a beam of light is passed through any colloid: *The path of light may be clearly seen*. The effect is similar to that observed when a beam of sunlight passes through a darkened room. A true solution, on the other hand, does not show the path of light because the molecules of solute are too small to *reflect light*. The following experiment vividly

demonstrates the Tyndall effect. Cigarette smoke is blown into a large jar. The room is then darkened, and a small pencil of light is directed through the smoke; *the smoke particles clearly outline the path of light*. The Tyndall effect is therefore a valuable aid in determining if a certain mixture is a true solution or a colloid (see Fig. 36).

Brownian Movement. An instrument called the *ultramicroscope* greatly magnifies the Tyndall effect. The essential parts of an ultramicroscope are a small cubical cell of quartz to hold the liquid, a powerful source of light to send a pencil of rays through the liquid, and a microscope mounted at right angles to the beam of light and against a dark background. Colloidal particles are seen as bright specks of light

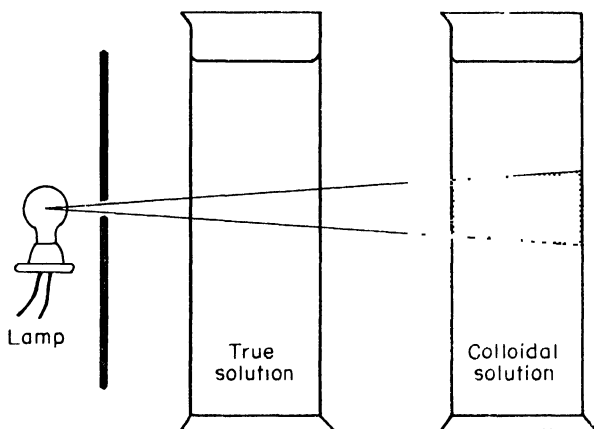


Fig. 36. Demonstration of the Tyndall effect.

in *rapid* zigzag motion. This zigzag motion or *brownian movement* (first observed by the English botanist, Brown) remained unexplained for fifty years. It is now known to be a necessary consequence of the high speed molecules of the solution colliding with the colloidal particles. Figure 37 depicts the path of a colloidal particle as observed under the ultramicroscope.

Electrical Charge of Colloidal Particles. Colloidal systems are fairly good conductors of electricity. Unlike solutions of electrolytes, however, which furnish both positive and negative ions, colloidal systems are either *all* positive or *all* negative. It appears that a colloidal particle gets its charge by the adsorption of some simple ion already present in the solution. If the dispersion medium happens to be water, the charges are probably furnished by the H^+ ions or OH^- ions. The electrical character of a colloidal system may be demonstrated by the

particles of the other; the two then form a neutral clump which grows larger and larger with subsequent precipitation.

Adsorption. First, it is appropriate to point out the distinction between *adsorption* and *absorption*. By adsorption we mean the adherence of molecules or ions of any kind to the surface of a solid or liquid, while by absorption we mean the penetration of the molecules or

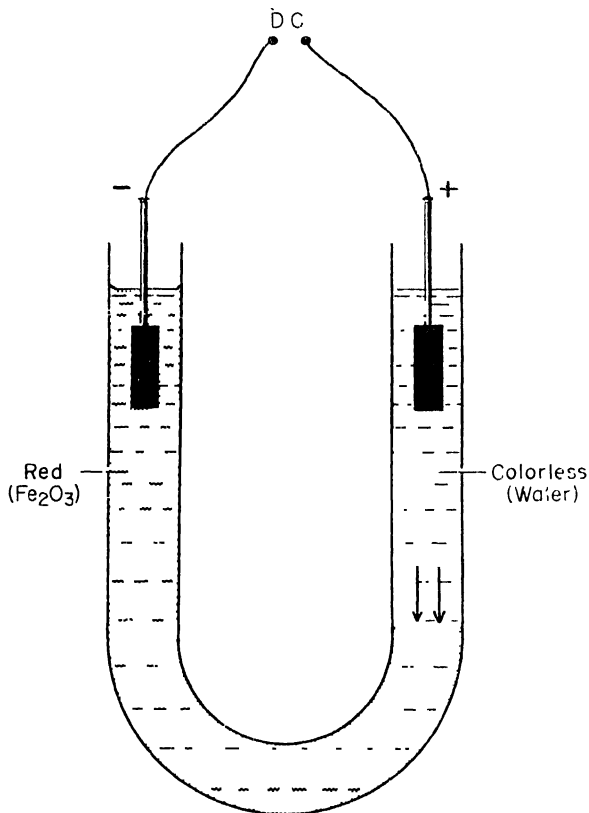


Fig. 38. Demonstration of the effect of a direct current on a positive colloid (cataphoresis).

ions into the interior of the solid or liquid. Actually, both processes often take place simultaneously.

Colloids adsorb substances to a high degree. This is due to the immense surface area of colloidal particles. For example, a cube having a length of 1 centimeter on each side has a total surface area of 6 square centimeters. If this cube is divided into cubes which measure 0.0001 mm. on each edge—i.e., subdivided into the colloidal state—the total

surface would be 600,000 square centimeters. It is quite evident that these "colloidal cubes" are able to adsorb more molecules of another substance than the larger cube can.

The property of adsorption is often taken advantage of in the laboratory and industry. Charcoal and boneblack (a form of charcoal from bones)—due to their vast surface area per gram—are excellent adsorbing agents. Charcoal is usually employed to remove odorous gases; boneblack is used to remove undesirable coloring matter.

Color. Many colloidal systems are highly colored. Colloidal color is explained by the fact that the minute particles *absorb certain wavelengths of light and reflect others*. The specific color, however, depends primarily upon the size of the particle rather than its character. For this reason the color gives little clue as to what substance is present. Thus, colloidal gold may be red, blue, green or violet, according to the size and uniformity of the particles.

It takes only a very small amount of colloidal substance to impart an intense color. Just a few milligrams of gold, for example, will color a liter of water. Red glass is manufactured by adding just a trace of selenium to ordinary glass. The blue of the sky and of the ocean is explained on a basis of colloidal dust in the air and water. It is thought that the blue of the eyes is due not to pigment, but to the presence of colloidal particles in the iris which scatter blue light and transmit red. The brilliant colors of some of the feathers of many birds are due to the presence of colloidal air bubbles.

Dialysis. When a colloidal solution is filtered, no solid is retained on the paper; i.e., the particles pass unimpeded through the pores of the paper—just like a solution. We find, however, that if the filter paper is replaced by a parchment or cellophane membrane, the colloidal particles are prevented from passing through. Solution particles (molecules and ions), on the other hand, pass through with ease. From a standpoint of particle size, therefore, there are two types of liquid mixtures: *mixtures whose particles do not pass through parchment or animal membranes*, and *mixtures whose particles do pass through*. The latter type of mixture, as we know, constitutes a true solution. The term *crystalloid* is applied to all substances which form true solutions. The terms *colloid* and *crystalloid* are therefore chemical antonyms.

Often times it is desirable—and essential—to separate substances in solution from substances in the colloidal state, i.e., to separate crystalloids from colloids. This can be easily accomplished by placing the liquid mixture in a parchment bag, and suspending the bag in water. After a certain period of time the crystalloid particles diffuse through the membrane; the colloidal particles do not. This process of separating the crystalloid state from the colloid state is called *dialysis*.

Dispersion. Dispersion consists in subdividing larger aggregates into particles of colloidal size. We start with an insoluble substance and by some means reduce it to particles of colloidal size, and then mix these particles with the desired dispersion medium. Grinding and agitation are common ways of reducing particle size; grinding is applied to solids, and agitation to liquids. At the commercial level, a so-called *colloid mill* is used to render a substance to the colloidal state. The mill consists of two rapidly revolving surfaces, about 0.002 inch apart, between which particles in suspension are drawn. The colloid mill is used to prepare colloidal substances such as paints, inks, ointments and emulsions.

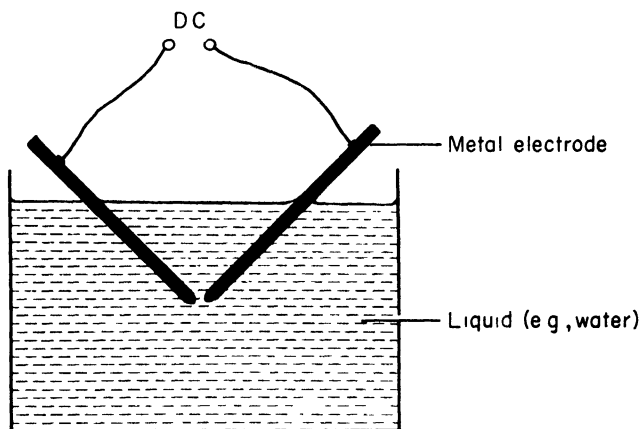


Fig. 40. The preparation of a colloid by passing an arc between two electrodes held under a liquid.

In many cases dispersion is carried out by treating a finely divided precipitate with some chemical. The chemical by some means—not chemical—reduces the precipitate to colloidal magnitude. Dilute sodium hydroxide, for example, causes clay particles to become colloidal. This action is called *peptization*, and the chemical employed is said to *peptize* the precipitate.

Colloidal systems of metals (e.g., gold, platinum, silver) dispersed in a liquid may be prepared by a unique method of dispersion: An arc is passed between two wires of the metal held under the liquid (Fig. 40). The arc causes colloidal particles of the metal to be separated from the wire, and spread throughout the solution.

Condensation. Condensation consists in the building up of colloidal particles from smaller particles—i.e., from molecules or ions. This is usually done by forming a colloidal precipitate via chemical action

between two solutions. When an acid is added to a dilute solution of sodium thiosulfate, for example, colloidal sulfur is formed, and a colloidal system of sulfur dispersed in water results. Many colloidal systems may be prepared in this manner. Since the formation of a colloid is probably the first step in precipitation, chemical condensation must be carefully controlled and stopped before the particles reach the upper limits of colloidal dimensions.

Condensation can also be accomplished by the addition of a liquid to a solution of a substance which is extremely insoluble in the liquid added. For example, if water is added drop by drop to a solution of benzoïn in alcohol, benzoïn is released from solution. When carefully carried out, i.e., if just the right amount of water is added, a colloidal system of benzoïn dispersed in an alcohol-water medium results.

SOLS

Sols are colloidal systems of solids dispersed in solids, liquids or gases. There are three types of sols according to our classification: *sols, solid sols and solid aerosols.* These three types are described below.

Sols. A sol is a colloidal system of a solid dispersed in a liquid. Some are natural, and some may be prepared artificially. Sols are classified as *emulsoids* or *suspensoids*.

EMULSOIDS. Nearly all naturally occurring colloidal systems are emulsoids. Emulsoid sols are formed from *lyophilic* substances. The term lyophilic is applied to a substance which upon dispersion shows an attraction or affinity for the dispersion medium, swelling as it passes into the colloidal condition. For this reason, emulsoids are much more viscous than the dispersion medium alone, and when concentrated often form *gels*, i.e., a jelly-like colloid. The higher viscosity is associated with the swelling of the particles as they become more and more "solvated," increasing the volume of the dispersed phase. Emulsoids are generally quite stable; they are especially resistant to electrolyte precipitation.

Emulsoids are usually prepared with ease, due to the lyophilic nature of the dispersed phase. Gelatin, glue, starch, proteins and gums are examples of lyophilic substances. A sol of starch or gelatin, for example, is prepared by merely adding warm water. Actually, this is a process of peptization, where the water brings about the dispersion of the particles.

The fact that protoplasm is best described as a jelly-like substance is indeed of singular importance. There is reason to believe that most of the organic substances within plant and animal tissues are of a colloidal character, and display the properties described in this chapter. Therefore, when dealing with biologic chemistry, we must appreciate the fact that we are not dealing with pure solutions; indeed, we must realize that nature is colloidal.

SUSPENSIDS. A suspensoid sol is one in which the suspended particles do not tend to combine with the dispersion medium. Suspensoids are prepared from *lyophobic* substances, i.e., substances which do not have an attraction or affinity for the dispersion medium. In contrast to emulsoids, suspensoids are not viscous, and they are not as stable, being susceptible to electrolyte precipitation.

Suspensoids rarely occur in nature. They may be prepared by dispersion or condensation methods. The dispersed phase is almost always an inorganic substance. Clay, sulfur and gold sols are examples of suspensoids.

The formation of deltas at the mouths of rivers is explained by colloidal chemistry. As the river flows toward the sea, clay becomes dispersed in the water—i.e., a suspensoid is formed. When the sea water comes into contact with the clay particles, the positively charged sodium and magnesium ions contained in the sea water neutralize the negatively charged clay particles. As a result, the particles coagulate into larger masses and settle at the mouth of the river. This deposition of clay at the bottom forms the delta.

Solid Aerosols. *A solid aerosol is a colloidal system of a solid dispersed in a gas.* Solid aerosols are commonly referred to as *smokes*. Smoke is produced from the incomplete combustion of carbonaceous materials such as coal, oil and tobacco; it also results from the condensation of vapors to the solid state. Certain dry gases combine chemically to form a smoke. For example, if a drop of hydrochloric acid is brought close to a drop of ammonium hydroxide, a dense white smoke of ammonium chloride is formed.

Enormous amounts of money are lost at the industrial level from the loss of valuable materials which escape via the smoke stack. Precious metals, zinc and potassium compounds are but a few examples. Ordinary carbon smoke causes great loss to the individual—but a profit to the laundry. An ingenious application of colloidal chemistry by Cottrell has presented industry with a solution to its smoke problems. The so-called *Cottrell Process* has proven to be a panacea for the health of those living in industrial areas, as well as the pocketbooks of industry. In this process, smoke is passed between two plates (usually installed at the bottom of the stack) maintained at a high voltage. The charged particles of the smoke are drawn to the plate of opposite charge and neutralized. In this manner a dust forms on the plates which quickly settles (see Fig. 41).

Solid Sols. *A solid sol is a colloidal system of a solid dispersed in another solid.* The best examples of solid sols are colored glass and precious stones such as ruby, sapphire and amethyst. Red glass is made by adding a little selenium to ordinary glass; ruby glass contains gold

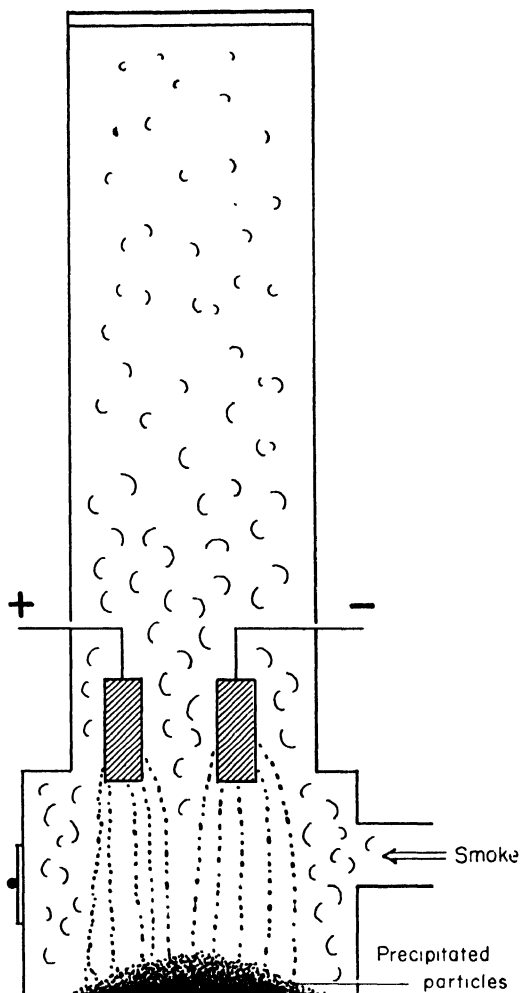


Fig. 41. The "smokeless chimney" (the Cottrell Process).

dispersed in glass. The color of the iris of the eye and other anatomic structures (e.g., skin) is best explained on a colloidal basis. As pointed out above, the color results from the absorption and reflection of light by the dispersed particles.

EMULSIONS

Emulsions are colloidal systems of liquids dispersed in liquids. When two immiscible liquids, such as oil and water, are shaken, a milky

fluid results; this is an emulsion. The agitation has dispersed the oil into globules of colloidal dimensions. Such an emulsion is referred to as an oil in water emulsion. If this emulsion is allowed to stand, it will soon separate into the original liquids from which it was made. Emulsions, however, can be made stable by the addition of a third substance called an *emulsifying agent*. An emulsifying agent acts—it seems—by forming a film over the surface of the dispersed globules. If to our oil in water emulsion mentioned above we add just a little soap, a *stable* emulsion

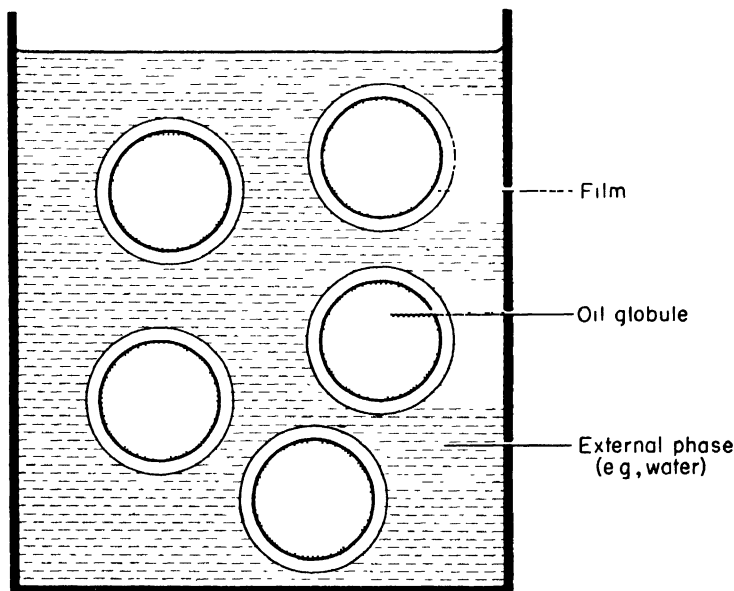


Fig. 42. Globules of an emulsion prepared by using an emulsifying agent.

results. The film evidently prevents the globules from running together to form larger globules (see Fig. 42).

Emulsions and emulsifying agents are of considerable theoretical and practical importance. The fats and oils contained in protoplasm are undoubtedly in the form of emulsions. Milk is an emulsion of butter fat dispersed in water, with *casein* as the emulsifying agent. The souring of milk is explained thus: Certain bacteria present in the milk act upon lactose to form lactic acid; the acid coagulates the casein, and the emulsion is thereby destroyed. Mayonnaise is a highly concentrated emulsion of vegetable oils dispersed in water, with egg yolk as the emulsifying agent. Countless products on the market are emulsions. Cod liver oil and mineral oil emulsions are prepared by the pharmacist in

order to increase palatability. Cresol, a commonly used disinfectant, would be of little value if it were not in the form of an emulsion. Lysol is a trade name for a soap emulsion of cresol.

During the process of digestion, emulsification plays an important role. In order for fats and oils to be properly digested by the enzymes within the intestine, they must be first emulsified. The fats and oils in the colloidal state—i.e., emulsified—are readily acted upon; *this is due to the greater surface area of the colloidal state*. The bile salts present in bile serve as the emulsifying agents. Any obstruction or dysfunction which interferes with the emulsification of fats and oils in the diet (e.g., jaundice, gallstones) is a nutritional insult.

Surface Active Agents. All emulsifying agents have one characteristic in common: *They reduce surface tension*. By surface tension of a liquid we mean—in simple but fairly accurate language—its tendency to assume a shape which gives the smallest surface area possible. For example, if a drop of alcohol and a drop of water are placed on a glass plate, there is considerable difference between the areas covered by the drops; alcohol, having *less* surface tension than water, covers a greater area. Therefore, when an emulsifying agent is added to a liquid, the liquid is more able to *spread* and *penetrate*.

In the last few years chemicals have been synthesized which possess tremendous powers of emulsification; i.e., they drastically lower surface tension. Such agents—commonly referred to as *surface active agents*—have revolutionized the cleaning industry. *Tide*, *Vel*, *Dreft*, *Fab*, *Cheer* and similar “soap” products contain surface active agents. Such products are commonly referred to as “detergents.”

Certain surface active chemicals have proven to be potent bacteriostatic and bactericidal agents. Their action is ascribed to their powers to penetrate pathogenic organisms. *Zephiran*, a popular surface active antiseptic and germicide, is capable of inhibiting bacterial metabolism at a dilution as great as 1 to 30,000. Unlike conventional antiseptics and disinfectants, agents such as *Zephiran* are devoid of irritating properties.

OTHER COLLOIDAL SYSTEMS

The following colloidal systems deserve only brief mention.

Liquid Aerosols. *Liquid aerosols are colloidal systems of liquids dispersed in gases*. Liquid aerosols include atmospheric fog, clouds and mists. Preparations referred to as “aerosols” are commonly used as disinfectants, deodorants and insecticides. A DDT aerosol, for example, is formed by allowing air pressure to force a solution of DDT through a very small valve; in this way, particles of the solution enter the air in a colloidal state. Aerosols have proved to be an effective and economical way of applying such agents.

Solid Emulsions. *Solid emulsions are colloidal systems of liquids dispersed in solids.* Water in paraffin wax and minerals with liquid inclusions (e.g., opal, pearl) are examples of this type of system.

Foams. *Foams are colloidal systems of gases dispersed in liquids.* Certain agents enhance foam formation. Licorice, for example, when added to a solution in which carbon dioxide gas is being evolved causes a copious heavy foam to form. This is the reason why licorice extract is used in the Foamite type of fire extinguisher. Usually foams are formed by vigorous agitation of a liquid. Anyone who has beaten egg whites has witnessed the beautiful foam which results.

Solid Foams. *Solid foams are colloidal systems of gases dispersed in solid.* Gaseous inclusions in minerals (pumice), lavas, hydrogen in iron and adsorbed gases are examples.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- _____ particles invisible
- _____ internal phase
- _____ a colloidal system
- _____ a solid in a liquid
- _____ gas in a liquid
- _____ liquid in a liquid
- _____ path of light
- _____ rapid zigzag motion
- _____ migration of colloidal particles
- _____ absorption of light by particles
- _____ separation of a crystalloid from a colloid
- _____ agitation
- _____ precipitation
- _____ milk
- _____ reduce surface tension

Column II

- 1. an example of condensation
- 2. brownian movement
- 3. produces color
- 4. Tyndall effect
- 5. soaps and detergents
- 6. a true solution
- 7. one state dispersed in another
- 8. a natural emulsion
- 9. a foam
- 10. a sol
- 11. an example of dispersion
- 12. dispersed phase
- 13. emulsion
- 14. dialysis
- 15. electrophoresis

On a basis of colloidal chemistry explain the following:

1. Why the iris of the eye is colored.
2. How bile aids in the digestion of fats.

3. Why aerosol insecticidal sprays are so effective.
4. Why protoplasm is viscous.
5. Why colloidal particles of a suspenoid do not settle out.
6. Why adding a pinch of salt to coffee enhances its clarity.
7. Why milk sours.
8. Why surface active disinfectants are superior to ordinary disinfectants.
9. How it is possible to separate a certain water-soluble hormone (such as adrenalin) from the gland.
10. Why gelatin swells when added to water.

CHAPTER 10

ORGANIC CHEMISTRY

INTRODUCTION

There are two types of compounds which constitute the earth: *organic* and *inorganic*. Organic compounds include all compounds which contain carbon; all other compounds are referred to as inorganic. In general terms, therefore, there are two great branches of chemistry: *organic, which is defined as the study of carbon and its compounds; and inorganic, which is defined as the study of all the other elements and their compounds.*

What is there about the element carbon that places it in a category by itself? Actually, carbon is the most unique of all the elements: *Carbon atoms have the ability to combine with one another an endless number of times, and in an endless number of ways.* This fact explains the huge number of carbon compounds found in the tissues of plants and animals, and in the products derived therefrom (e.g., petroleum, coal tar, wood). In addition to their number,* organic substances are also characterized by the extremely complex nature of their molecules; molecular weights in the vicinity of hundreds of thousands are common in compounds such as proteins and related substances. It is obvious, therefore, that the study of organic chemistry must be approached and handled in a manner slightly different from our previous studies. In order to effectively grasp the principles of organic chemistry, we must learn to *classify* and *generalize*; i.e., we must apply techniques similar to those employed in biology. The present chapter sets forth a synopsis of the cardinal concepts in a manner commensurate with this view.

Before we embark upon our journey throughout the heavens of carbon atoms, it will be instructive to compare our present definition of organic chemistry with the definition of the preceding century. At that time, organic chemistry was defined as *the chemistry of living things and their products*. From what has been said, this was a reasonable and logical definition. In the year 1828, however, the German chemist Wöhler completely changed the picture by an experiment which was as

* The number of organic compounds exceeds 250,000, compared to 27,000 inorganic compounds.

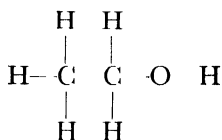
outstanding in its simplicity as in its farflung implications. Wöhler discovered that the chemical compound *ammonium cyanate* could be converted by heat into *urea*—a substance theretofore produced only in the tissues of animals and excreted in urine. *Thus, Wöhler demonstrated that it was possible to synthesize a natural product.* Other syntheses followed; today the organic chemist seems to be able to synthesize any compound of nature. Moreover, he can prepare substances foreign and, in many cases, superior to those of natural origin. Plastics, rubber, dyes and drugs are but a few examples of his ability. Organic chemistry is best defined, then, as simply the *study of carbon and its compounds.*

The importance of organic chemistry may be easily perceived from the above statements. There is not a single area of the biologic sciences which does not demand some knowledge of the basic principles. In the following chapter on biochemistry, i.e., the chemistry of life processes, an understanding of organic chemistry is a *sine qua non*. We shall do well, then, to assimilate thoroughly the concepts of the present chapter.

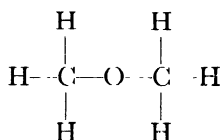
Nonelectrolytes. *In contrast to inorganic substances, organic compounds are nonelectrolytes.* This is to be expected since organic molecules are constituted by *covalent atoms*; i.e., no ions are available. In general, a substance which does not conduct an electric current is an organic substance. This test, plus the fact that *organic compounds char or burn upon heating*, enable us to identify swiftly organic substances.

In general, organic compounds react at a much *slower rate* than inorganic compounds; this is easily explained by their nonionic nature. It will be recalled that compounds which furnish ions react immediately. When a solution of salt is added to a solution of silver nitrate, for example, a copious white precipitate forms instantly. On the other hand, there are many organic reactions which require several hours to react completely. The covalent nature of the organic molecule, then, is a basic chemical difference.

Structural Formulas. The properties of an organic compound depend upon the *arrangement* of its atoms as well as the number and kinds of atoms in the molecule. This is epitomized by the striking fact that we often find two or more compounds to which the same ordinary, or *empirical*, formula must be assigned. For example, two very different compounds have the empirical formula C_2H_6O . The organic chemist has conclusive evidence that these different compounds are a result of different arrangements of the atoms in the molecules. For this reason—and many others—the *structural formula* is employed in organic chemistry. In the example cited, the two compounds have the following structures:

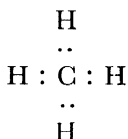


Ethyl alcohol
($\text{C}_2\text{H}_6\text{O}$)

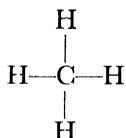


Dimethyl ether
($\text{C}_2\text{H}_6\text{O}$)

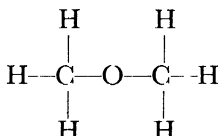
Carbon has a *covalence* of 4 in all its organic compounds; i.e., carbon always shares its outer 4 electrons. In the compound known as methane, CH_4 , 1 atom of carbon shares 4 pairs of electrons with the hydrogen atoms. From our earlier work, this may be represented thus:



More commonly, a line called a *bond* is used to represent a pair of shared electrons. The above formula is usually written thus:

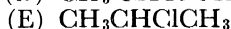
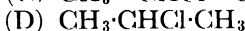
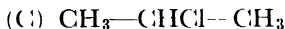
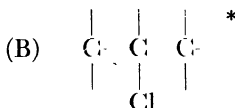
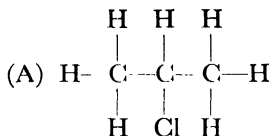


It is to be noted that the *number of bonds about any one atom is equal to the atom's valence*. In the following structural formula, note that this is the case:



In this formula every hydrogen atom is surrounded by 1 and only 1 bond; every carbon atom is surrounded by 4 and only 4 bonds; and the oxygen atom by 2 and only 2 bonds.

For the sake of time and convenience, structural formulas are usually abbreviated or condensed. Any such formula is acceptable so long as the complete structure is correctly indicated. The following structure, for example, is often written in the ways indicated:

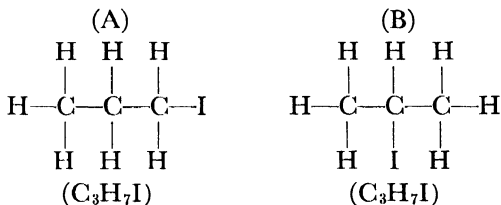


* Open bonds, by convention, denote hydrogen atoms.

The ability to write and interpret structural formulas is essential. The above facts in conjunction with others contained in this chapter will easily permit us to master the art.

Isomerism. Let us now direct our attention to those compounds which have the *same* empirical formula, but *different* properties. As stated before, this situation is common in organic chemistry. The term *isomerism* is applied to this condition; the compounds are referred to as *isomers*. Isomerism can be explained only on a basis of a *difference* in molecular structure. Let us look a little closer and see if we can deduce a little more information about this phenomenon.

There are two isomers with the empirical formula $\text{C}_3\text{H}_7\text{I}$. The following structures are the only possible arrangements which are different:



If we study these two structural formulas closely, we shall discover that the carbon atoms joined to the iodine atoms *differ* in respect to the carbon atoms about them. Thus, the carbon atom of compound A is joined to one group (C_2H_5), while the carbon atom of compound B is joined to two groups, i.e., two CH_3 's. *Whenever, therefore, an empirical formula can be written so as to yield more than one structural formula, isomerism exists.*

As the number of carbon atoms in the molecule increases, the number of possible isomers also increases. A compound with 15 carbon atoms, for example, could have more than 4000 isomers. Isomerism, then, is a

complicating factor in the study of organic compounds; in practice, however, only two or three isomers of any given formula are of importance.

Optical Isomerism. A peculiar type of isomerism is shown by many organic substances. Lactic acid will serve as a typical example. All three varieties of this acid possess the *same* physical and chemical properties—they *differ* only in regard to their effect upon *polarized light*; hence, they are said to be *optically active*. When polarized light is passed through each of the three acids the following happens: One kind turns the plane of polarized light to the *right* (this acid is called *dextro* or *d*-lactic acid); the other acid turns the plane of light to the *left* (this is *levo* or *l*-lactic acid); and the third has no effect upon polarized light—it is called *dl*-lactic acid.

Figure 43 demonstrates the way in which this phenomenon can be observed by the use of a *polarimeter*. When ordinary light is passed through a glass plate of special construction, such as a tourmaline plate, it emerges changed in this respect: The electromagnetic vibrations take place in only *one* plane, as opposed to ordinary light which vibrates in all planes; such light is said to be *polarized*. Now, when polarized light falls on another plate of the same construction as the first, it will completely pass through *only* if the second plate is in a certain position—specifically, only when the crystals of the two plates run in the same direction. Other positions will allow varying degrees of light to pass—all the way to a complete obstruction.

Let us place two such plates at the ends of a glass tube a few inches long; further, let us make one stationary (this plate is called the *polarizer*), and the other so that it rotates (this plate is called the *analyzer*). Now let us view a source of light with the eye at the analyzer, and rotate the analyzer so that maximum light is seen. With the analyzer in this position, an *optically active* compound (in solution if a solid) is placed into the tube. If the variety added is *d* or *l*, the light—as viewed with the eye at the analyzer—is *not* as bright as before; this is because the plane of light leaving the polarizer has been *turned* by the solution, with the result that it does not hit the analyzer at the proper angle for complete transfer. By rotating the analyzer, however, we can once again restore maximum brightness. By convention, if the adjustment is made by rotating to the *right*, the compound is in the *dextro* or *d* form; if the analyzer must be turned to the *left*, the compound is called the *levo* or *l* form. The *dl* form of a compound *does not* change the plane of light. Actually, the *dl* form is really a mixture of the *l* form and *d* form.

In practice it is desirable to know the exact or so-called *specific rotation* of an optically active compound. The specific rotation of a compound is defined as the number of degrees the analyzer must be

rotated for a solution containing 1 gm. of the compound per cc. in a polarimeter tube 1 dm. long at a specific temperature and at a specific intensity of light. For example, the *specific rotation*, $[\alpha]$, of a freshly prepared glucose solution is $+111^\circ$; i.e., the analyzer must be rotated to the *right* 111° for a solution of glucose under the conditions stated

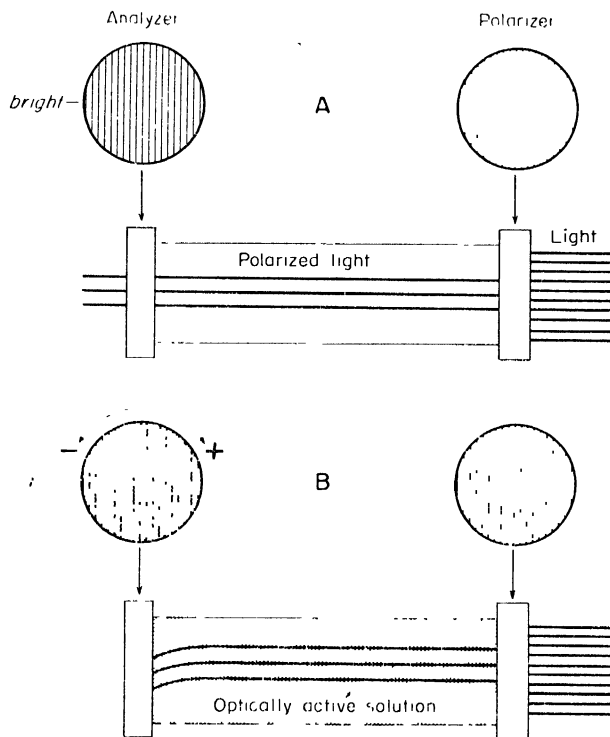


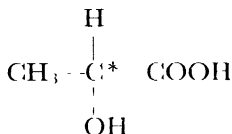
Fig. 43. Demonstration of *optical activity* by the use of a *polarimeter*. In *A*, the *analyzer* is adjusted for maximum light transfer. In *B*, an optically active compound has been added to the tube. Now, the analyzer must be rotated left (–) or right (+) in order to restore the former brightness. This is necessitated by the fact that the polarized light has been “turned” by the solution. (See text for details.)

above. If the specific rotation of a freshly prepared glucose solution were not 111° , it would mean that the solution was not pure. Thus, the polarimeter is an essential instrument in dealing with optically active compounds.

It was stated above that optical isomers are the same chemically and the same physically, save their effect upon polarized light. Of tremendous interest, however, is the fact that they are almost always *different phys-*

iologically. Optically active drugs, for example, are usually potent only in one form. *Alkaloids*—powerful drugs of natural origin—are mostly *levorotatory*.

In contrast to the first type of isomerism discussed (which we may refer to as structural isomerism), optical isomers have the *same* structure when written on a piece of paper. By the use of three-dimensional models, however, a difference can be demonstrated. For this reason, optical isomerism is sometimes referred to as *stereo-* or *spatial isomerism*. Of extreme practical importance was a finding by LeBel and van't Hoff. They showed that any substance which has 1 carbon atom attached to 4 different groups or atoms is optically active. This can be readily shown by the following structure of lactic acid:



Note that the carbon atom marked with an asterisk (a so-called *asymmetric* carbon atom) is attached to 4 different groups.

When an optically active compound is synthesized in the laboratory a *racemic* mixture is obtained; i.e., it is constituted by *equal* parts of the dextro and levo forms. The racemic form of a compound is designated as *dl*. In the case of medicinal substances, various techniques, which we shall not discuss here, are used to separate the *d* and *l* forms.

HYDROCARBONS

All organic compounds may be considered derivatives of the great class known as *hydrocarbons*. A *hydrocarbon* is an *organic compound which contains only carbon and hydrogen*. Hydrocarbons range in complexity from a few atoms per molecule to compounds whose molecules contain in the neighborhood of a hundred atoms. Hydrocarbons occur naturally in petroleum and coal tar. Actually, petroleum is nothing more than a mixture of hydrocarbons. In this section we shall discuss the various classes of hydrocarbons and the important members thereof.

There are two major categories of hydrocarbon compounds; i.e., any one hydrocarbon has chemical and physical properties which place it into one of two groups of similar substances. Thus, out of their vast number the organic chemist has demonstrated an unyielding devotion to obey certain rules and laws. It has been deduced from extensive studies that these two major categories are a result of the way in which the carbon atoms are joined in the hydrocarbon molecule. Conclusive evidence indicates that they are joined in *chains* with open ends, or in

rings without open ends. Hydrocarbons of the chain type are referred to as *aliphatic* hydrocarbons; hydrocarbons of the ring type are referred to as *cyclic* hydrocarbons. The cyclic hydrocarbons, in turn, are of two classes: *aromatic hydrocarbons* and *alicyclic hydrocarbons*.

Aliphatic Hydrocarbons

Petroleum. Petroleum is the vast natural source of the aliphatic hydrocarbons.* It is a dark-colored oily liquid composed of gaseous and

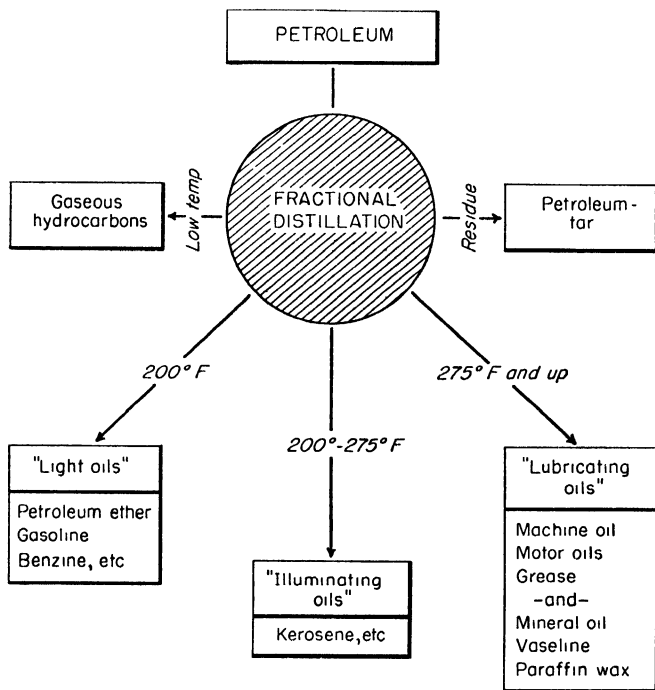


Fig. 44. Products of petroleum.

solid hydrocarbons dissolved in liquid hydrocarbons. By a process called *fractional distillation* the many vital constituents are separated. Fractional distillation is the process of separating a mixture into parts, or *fractions*, by distilling the mixture and collecting the parts of the distillate separately. This is possible by virtue of the different boiling points of the substances in the mixture. In addition to the pure hydrocarbons presented in the tables, petroleum yields an endless number of useful

* Petroleum is the final product in the degradation of organic matter, i.e., dead plants and animals.

products such as *gasoline*,* *kerosene*, *mineral oil*, *Vaseline*, *paraffin* and *lubricating oils* (see Fig. 44). These products are not single compounds, but *mixtures* of hydrocarbons which appear in certain fractions. The world production of petroleum is now over 2 billion barrels annually.

In order to simplify our study, it is convenient to arrange the aliphatic hydrocarbons in groups, or *series*. There are three important aliphatic series: *the methane series*, *the ethylene series* and *the acetylene series*.

Methane Series. The hydrocarbons of this series are often termed *paraffins* (paraffin is a mixture of solid hydrocarbons of this series). The table below gives the names, formulas and boiling points of the first ten members. Others are known as far up as 28 carbon atoms; the first 10, however, are the most important.

Methane Series

	Formula	Boiling Point (°C.)
Methane	CH ₄	-161
Ethane	C ₂ H ₆	- 88
Propane	C ₃ H ₈	- 44
Butane	C ₄ H ₁₀	-- 6
Pentane	C ₅ H ₁₂	36
Hexane	C ₆ H ₁₄	69
Heptane	C ₇ H ₁₆	98
Octane	C ₈ H ₁₈	124
Nonane	C ₉ H ₂₀	150
Decane	C ₁₀ H ₂₂	174

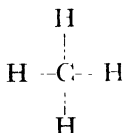
A glance at the table will disclose the singular fact that each member of the series differs from the one preceding it by the group of atoms, CH₂. Such a series of hydrocarbons is called a *homologous series*. Further, the formula for any member of the series is given by the general formula, C_nH_{2n+2}, in which "n" is the number of carbon atoms. In general, the members of a homologous series are similar in their chemical characteristics. Their physical properties show a regular gradation; i.e., their physical state (gas, liquid or solid) is a function of their molecular weight.

PROPERTIES. The hydrocarbons of this series are all *colorless* compounds. The first four members—methane, ethane, propane and butane

* Increased demands for gasoline (a mixture of hydrocarbons with carbon chains C₅ to C₁₂) prompted new methods for obtaining it. At the present time more than one-half our gasoline supply is obtained by a process called "cracking," where larger hydrocarbon molecules are broken down into simpler ones by heating under pressure.

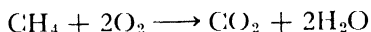
—are gases; those containing 5 to 16 carbon atoms are liquids; and those containing more than 16 carbon atoms are solids. *All members of this series are insoluble in water. Chemically, they are rather inert; strong acids and bases have little or no effect upon them. All of them burn, however, to form carbon dioxide and water.*

METHANE. The general properties of the paraffins are characterized by methane. Methane gas—also known as *marsh gas* and *fire damp*—is the simplest compound of carbon. It has the following structure:



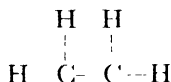
Methane constitutes from 90 to 95 per cent of natural gas. It is formed in marshes by the decay of organic matter under the water; bubbles of the gas are often seen rising from the bottom of stagnant pools. In the laboratory the gas is prepared by heating a mixture of sodium acetate, sodium hydroxide and calcium hydroxide.

Methane is a colorless, odorless gas, about one-half times as heavy as air. It is only slightly soluble in water. Chemically, methane is rather inert; it fails to react with most substances. In air, however, it burns with a very hot, pale blue flame, forming carbon dioxide and water:

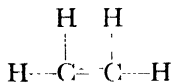


In the presence of sunlight, methane reacts with chlorine and bromine to form a series of products. These derivatives will be discussed later.

Ethylene Series. Ethylene is a hydrocarbon which has the formula C_2H_4 . If we attempt to write a structural formula for this compound, we find that the laws of valence seem to be violated, thus:



In this structural formula, each carbon atom is surrounded by 3 bonds instead of 4. Therefore, how can there be a compound with the empirical formula C_2H_4 ? The answer resides in the fact that there is a *double bond* between the two carbons, thus:



Ethylene is the first member of the so-called *ethylene series** of hydrocarbons. Each member, like ethylene, is characterized by the

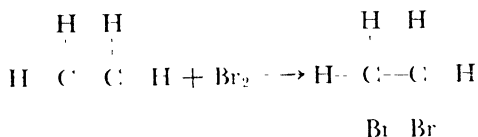
* Members of this series are also commonly termed *olefins*, due to their odoriferous character.

possession of a *double bond*. The general formula for hydrocarbons of this series is C_nH_{2n} . A few members of the series are listed below.

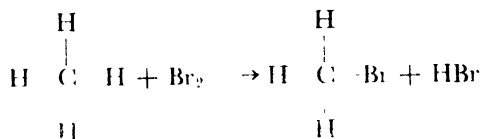
Ethylene Series

	Formula	Boiling Point ($^{\circ}C$.)
Ethylene (ethene)	C_2H_4	-104
Propylene (propene)	C_3H_6	-47
Butylene (butene)	C_4H_8	-1.4
Amylene (pentene)	C_5H_{10}	40
Hexylene (hexene)	C_6H_{12}	64
Heptylene (heptene)	C_7H_{14}	95

PROPERTIES. Like the methane series, the lower members are gases and the higher members are liquids or solids. Chemically, however, there is an important difference between the two series. In contrast to the paraffins, members of the ethylene series are *decidedly reactive*. This can be explained only on a basis of the *double bond*. When given the opportunity, it appears that the carbon atoms which share a double bond prefer to dissolve the relationship; i.e., a double bond imparts an *unstable* nature to a molecule. The halogens, for example, swiftly break the bond and *add* on to the molecule. Bromine reacts with ethylene as follows:



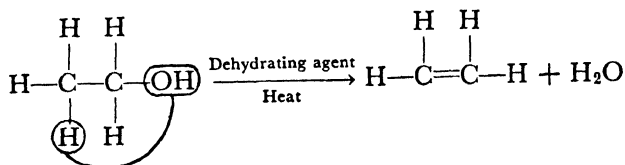
A hydrocarbon or any other organic compound which possesses a double bond is said to be *unsaturated*; i.e., it is capable of adding on atoms. The compound formed as a result of the addition is termed an *addition product*. Conversely, compounds which do not contain a double bond are said to be *saturated*. Saturated compounds react by *substitution*; i.e., atoms are exchanged for hydrogen. Bromine reacts with methane as follows:



The concept of the double bond is of vital import. We shall have occasion to refer to saturation and unsaturation throughout our study.

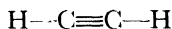
ETHYLENE. The general properties of the series are characterized by ethylene. Ethylene is a colorless gas which can be condensed to a liquid. It burns with a luminous flame, forming carbon dioxide and water. Its most characteristic property—as indicated above—is its power to unite (by addition) with other substances, particularly with the halogens.

Ethylene may be prepared by a number of methods. Of special interest is its preparation by the removal of the elements of water from ethyl alcohol (C_2H_5OH). This can be accomplished by the use of a suitable dehydrating agent such as sulfuric acid. The reaction is as follows:



Ethylene gas and its derivatives are very useful substances. Of singular interest is the fact that ethylene is a potent anesthetic. Its highly explosive nature, however, presents a serious disadvantage.

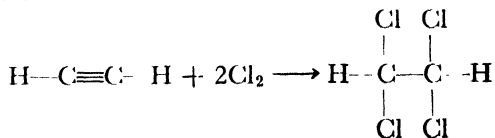
Acetylene Series. Acetylene gas (C_2H_2) is by far the most important member of a series whose general formula is C_nH_{2n-2} . Members of this series are unique in that they possess a *triple bond*. Acetylene has the following structure:



The first three members of the series are listed below:

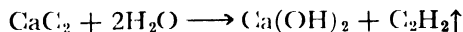
Ethyne (acetylene)	C_2H_2
Propyne	C_3H_4
Butyne	C_4H_6

The properties of acetylene are illustrative of its homologs. Physically, acetylene is colorless, possesses a garlic-like odor, and is sparingly soluble in water. Chemically, acetylene is marked by extreme activity. Thus, the *triple bond* imparts a more unstable character to a molecule than does the double bond. Acetylene combines readily with chlorine, forming an *addition* compound having the formula $C_2H_2Cl_4$. The reaction is as follows:



Since it takes 4 atoms of chlorine to saturate 1 molecule, we are presented with good evidence that acetylene has a triple bond.

Acetylene is readily prepared by dropping water onto powdered calcium carbide:



Calcium carbide is made in large quantities by heating a mixture of lime (CaO) and coke (C).

Commercially, acetylene has been used for cutting and welding metals, and as a source of illumination. Acetylene is also used in the manufacture of a number of organic compounds of industrial importance. Thus, it is possible to start with *lime* (calcium oxide) and *coke* (carbon)—simple and cheap raw materials—and synthesize complex substances.

Nomenclature. *The ability to name an organic compound properly is probably the most important practical aspect of organic chemistry.* In the early years of the study, naming was haphazard; indeed, the chemists themselves were often confused. As the number of compounds grew by leaps and bounds, it became quite evident that an accurate and explicit system of nomenclature was essential. Today almost all organic chemists throughout the world have agreed upon a basic system. It is evident, of course, that the “old” and the “new” are always coexistent. The name *chloroform*, for example, will probably continue in preference to the more accurate name, *trichloromethane*. In general, however, confusion has given way to order. It is hoped that the student will develop—in an elementary way—a “feel” for naming organic compounds. The aliphatic hydrocarbons are named as follows:

METHANE SERIES. The name for any member of the *methane* series has the suffix *-ane*. With the exception of the first four members, the first part of the name indicates the number of carbon atoms in the molecule. When one hydrogen atom is removed from any member of the methane series, the resulting group is called an *alkyl radical*; the radical is named by changing the final syllable of the hydrocarbon name from *-ane* to *-yl*:

Methane Series

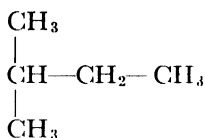
Hydrocarbon	Alkyl Radical
Methane	methyl- CH_3
Ethane	ethyl- C_2H_5
Propane	propyl- C_3H_7
Butane	butyl- C_4H_9
Pentane	pentyl- C_5H_{11}
etc.	

In order to name paraffin isomers, we must modify our rule. There are, for example, *three* pentanes. In order to have a different name for each of the three structures, the following convention is followed. First, structural formulas are written for the possible arrangements; second, the longest chain is numbered in such a manner that the side radicals are attached to the carbons of the lowest possible numbers; and third, we base the name for each compound on the longest chain. The naming of the three pentanes is done as follows:

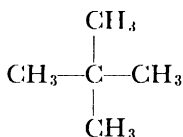


5 carbons in a continuous chain

Name: Normal pentane

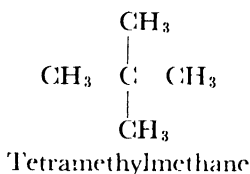
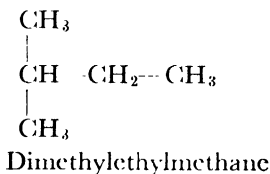


2-methyl butane



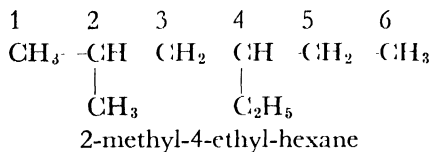
2,2-dimethyl propane

The above system of naming represents the preferred method—it can be applied to all aliphatic compounds. Since the three pentanes are relatively simple, however, they may also be named according to the older system, namely, as derivatives of methane:

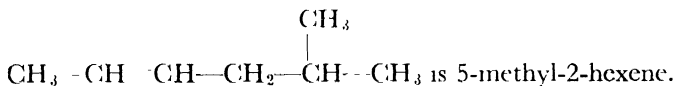


Such a system, i.e., naming a hydrocarbon or derivative on a basis of methane, is hardly applicable to complex substances. The following

compound, for example, if named according to this system would indeed present difficulties. It is easily named, however, by the preferred system:



ETHYLENE SERIES. The hydrocarbons of this series are named by replacing the suffix *-ane* of the paraffin hydrocarbon having the same number of carbon atoms by the suffix *-ylene* or *-ene*. Isomerism in this series is due not only to branching in the carbon chains, but also to changes in the position of the double bond. Isomeric members and derivatives are therefore named by numbering the compound in such a way that the smallest possible numbers are assigned to the *unsaturated* carbon atoms, thus:



ACETYLENE SERIES. The name of any homolog of this series is derived from that of the methane hydrocarbon which contains the same number of carbon atoms by replacing the suffix *-ane* by *-yne*. Thus, acetylene, C_2H_2 , is called *ethyne*; and $\text{CH}_3\text{C}\equiv\text{CH}$, *propyne*, and so on. The triple bond is located in the manner used for the olefins.

Aromatic Hydrocarbons

A vast amount of experimental evidence indicates that an astronomical number of organic substances are constituted by molecules which contain a nucleus of 1 or more carbon rings, each ring in turn containing 6 *unsaturated carbon atoms*. All hydrocarbons (and their derivatives) of such a constitution are referred to as *aromatic compounds*. The term aromatic has its origin in the fact that certain substances (e.g., oil of bitter almonds, vanilla and oil of wintergreen) are cyclic compounds. The possession of an odor is not characteristic, however, of all aromatic substances.

It is indeed a difficult task to find an adjective which embraces the significance of the chemistry of aromatic hydrocarbons and their derivatives. It is certainly an exact statement of truth to say that our lives have been revolutionized by discoveries in this area of organic chemistry. "Miracle drugs," modern insecticides (e.g., DDT), dyes, plastics and explosives are but a glimpse of the complete picture. Through the study

of complex aromatic structures found in living cells, the biologic chemist is getting ever closer to a reasonable explanation of physical life. The student of the biologic sciences will undoubtedly embellish his knowledge by an understanding of some of the basic principles.

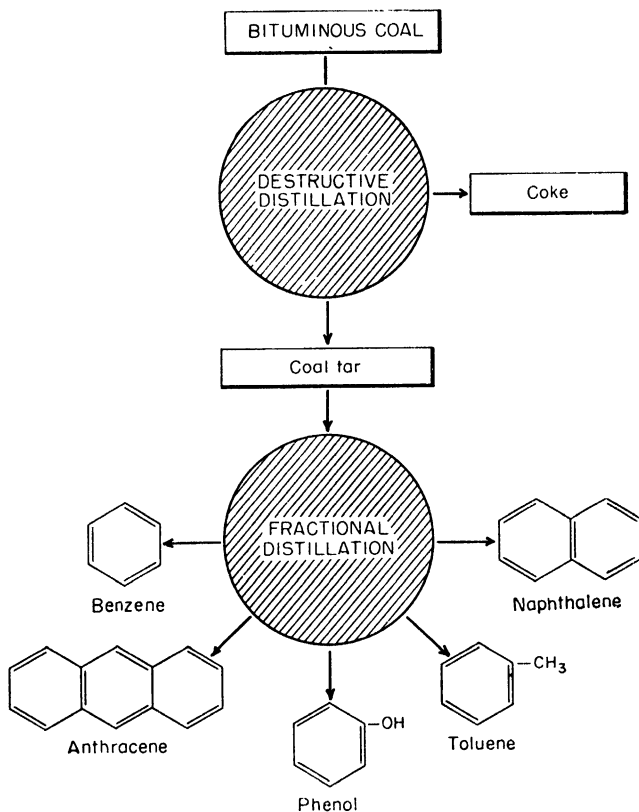


Fig. 45. Coal-tar derivatives.

All aromatic compounds may be derived from three basic hydrocarbons—*benzene*, *naphthalene* and *anthracene*. In this section we shall study the behavior and nomenclature of these three substances.

Benzene Series. Benzene,* C_6H_6 , is the most important member of a series—the so-called *benzene series*—whose general formula is C_nH_{2n-6} . The principal homologs are named in the following table:

* The word *benzene* is not to be confused with the word *benzine*. Benzine is a mixture of hydrocarbons derived from petroleum. (The words are pronounced the same.)

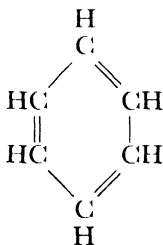
Benzene Series

	Formula
Benzene	C_6H_6
Toluene	C_7H_8
Xylene	C_8H_{10}
Mesitylene	C_9H_{12}
Cymene	$C_{10}H_{14}$

COAL TAR. Benzene, together with some of the other members of the series, is a product of the *destructive distillation* of bituminous coal; i.e., the coal is heated in the absence of air. First, combustible gases escape: then a viscous black liquid distills out, leaving a residue of coke in the retort. This black liquid, called *coal tar*, is probably the most valuable raw material of the chemical industry. When subjected to *fractional distillation*, it yields a conglomeration of aromatic substances; of these, *benzene*, *toluene*, *naphthalene*, *anthracene*, *phenol* and *cresol* are the most important. Each of these substances serves as the source material from which thousands of other useful compounds are prepared (Fig. 45). All compounds, whether obtained directly from coal tar or indirectly, are commonly referred to as "coal-tar derivatives."

PROPERTIES. The general properties of the series are reflected by those of benzene. Benzene is a colorless liquid boiling at 80° C. It has a peculiar, pleasant odor. Several of the other homologs have a similar odor. Benzene is insoluble in water, but soluble in alcohol and chloroform. It burns with a bright, luminous, smoky flame.

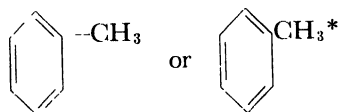
The ring structure of the benzene molecule is well established. The following structural formula is the only possible configuration consistent with experimental facts:



For the sake of convenience, the organic chemist usually abbreviates this structure as follows:

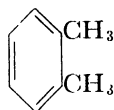


Toluene, with the empirical formula C_7H_8 , has the following structural formula:

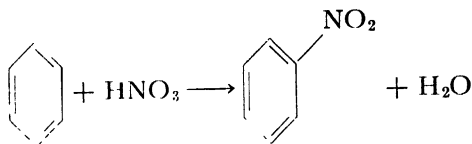


* For convenience, the bond attaching an atom or a group to a benzene ring is often omitted.

In other words, the toluene molecule is formed by replacing a hydrogen atom on the benzene ring with a methyl group (CH_3). The other members of the series may be considered in a similar manner. For example, xylene (C_8H_{10}) has this structure:



In contrast to the aliphatic hydrocarbons, benzene and its homologs react with a variety of common laboratory chemicals to form many highly useful substituted derivatives. With nitric acid, for example, benzene readily forms *nitrobenzene*—a source material from which several dyes and drugs are prepared:

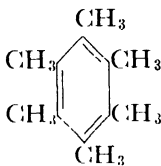


POLYMERIZATION. An interesting chemical phenomenon occurs when acetylene gas is passed through a tube heated to dull redness—*benzene is formed*. This fact is of fundamental importance: *It shows that a simple substance can unite with itself to produce a more complex molecule; this is called polymerization*. In this case, 3 molecules of acetylene (C_2H_2) unite to form 1 molecule of benzene (C_6H_6). Benzene, therefore, may be referred to as a *polymer* of acetylene.

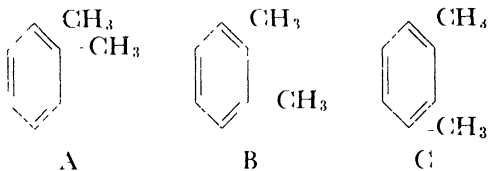
Nature is a master in the art of polymerization. Starch, proteins, glycogen and rubber are but a few of the many important polymers of the biologic world. Polymers such as these present the most complex substances known to the chemist. Rubber, for example, is a polymer of a substance called *isoprene* (C_5H_8). A rubber molecule is formed in the tissues of the rubber tree by the union, or polymerization, of a thousand or more isoprene molecules. The composition of rubber may be represented by the formula $(C_7H_8)_n$ in which n stands for a large

but indefinite number. This knowledge led to the synthesis of rubber from isoprene and similar substances. Polymerization will be further discussed under carbohydrates and proteins.

NOMENCLATURE. The first few members of the benzene series have common names ending in *-ene*. In order to name a more complex member, however, it is most convenient to consider the member as a derivative of benzene. For example, $C_{11}H_{18}$ is best named *hexamethylbenzene*:



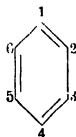
There are no isomers of benzene or toluene. Since all 6 carbon atoms of the benzene ring are equivalent, it makes no difference at which position *one* group is attached. Xylene, however, presents a different situation. For reasons which are quite obvious, viz., the distance between the attached groups, the following structures are *not* the same:



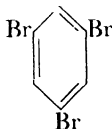
Formula A shows the two methyl groups on neighboring carbon atoms; formula B has 1 carbon atom separating the groups; and formula C, 2 carbon atoms between the groups. Isomer A is called *ortho* or *o-xylene*; isomer B, *meta* or *m-xylene*; and isomer C, *para* or *p-xylene*. The prefixes *ortho*, *meta* and *para* are employed not only for naming isomeric hydrocarbons, but also certain aromatic derivatives of the benzene series. For example, *p*-dichlorobenzene is the name for the following structure:



When more than two groups are attached to the benzene ring, however, we must employ numbers to locate their positions. The ring is numbered as follows:



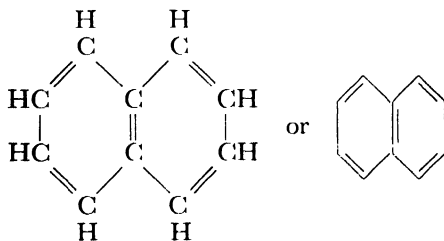
For example, 2,4,6-tribromobenzene is the name for the structure below:



When a hydrogen atom is removed (i.e., substituted by another atom) from a member of the benzene series, the resulting group is called an *aryl radical*; C_6H_5 is called *phenyl*, C_7H_7 is *tolyl*, and C_8H_9 is *xylyl*, and so on. The phenyl radical is the most common of the aromatic substances. It will be recalled that important radicals—*alkyl radicals*—are also derived from the methane series (e.g., methyl, ethyl, propyl, etc.). Radicals are useful in the naming of organic compounds; we shall frequently have occasion to use them.

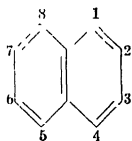
Naphthalene. Naphthalene ($C_{10}H_8$) is present to the extent of about 6 per cent in coal tar, from which it is obtained in large quantities. Naphthalene is a white, volatile solid with a characteristic penetrating odor (moth balls are nearly pure naphthalene). It is soluble in hot alcohol and in ether.

The relation of naphthalene to benzene has been discovered through a careful study of its chemical conduct. The facts can be best interpreted by assuming that the molecule of naphthalene is formed by the union of 2 *benzene residues*. The structural formula for naphthalene is as follows:

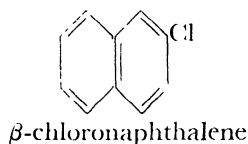
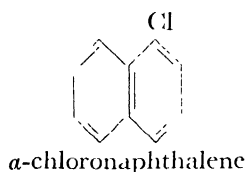


Naphthalene resembles benzene closely in its behavior with chemical reagents. Thus, derivatives are formed when it is treated with chlorine, bromine, nitric acid or sulfuric acid. These derivatives are valuable source materials from which important dyes and drugs are manufactured.

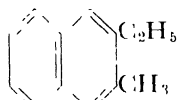
Owing to the presence of two rings, the opportunities for isomerism are great. Higher members of the class and their derivatives are named by numbering the carbon atoms as follows:



Monosubstitution products exist in *two forms*. The carbon atoms numbered 1, 4, 5 and 8 bear the same relation to the molecule. Compounds with an atom or radical in these positions are called *alpha* (α -) compounds. Compounds with an atom in position 2, 3, 6 or 7 are called *beta* (β) compounds. For example, α -chloronaphthalene and β -chloronaphthalene are the names for the following structures:

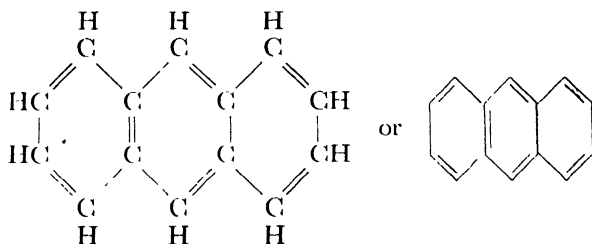


When two or more groups are present, however, numbers must be employed. For example, *2-ethyl-3-methyl-naphthalene* is the name for the following structure:



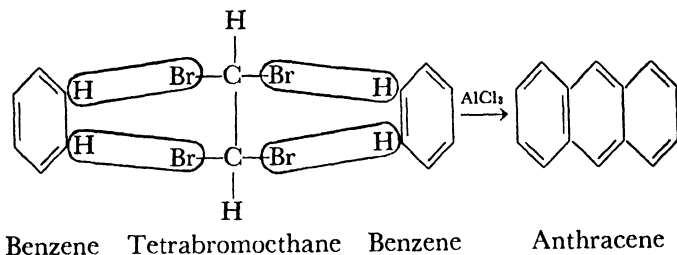
Anthracene. Anthracene ($C_{14}H_{10}$) is obtained from coal tar, in which it is present to the extent of less than 0.5 per cent. When pure it forms colorless monoclinic (needle-like) plates, showing a beautiful blue fluorescence.

The structure of anthracene is of singular interest. The following structure is arrived at as a result of a number of syntheses of the hydrocarbon:



Thus, we may consider the anthracene molecule as formed by the union of 3 *benzene residues*.

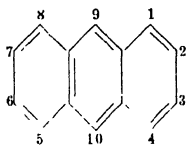
Perhaps the student at this point thinks that the organic chemist—with all his fancy structures—is “pulling his leg.” Although it is beyond the scope of this text to account for all the facts presented, the following reaction deserves an “elementary glance.” When benzene is heated with tetrabromoethane in the presence of aluminum chloride, *anthracene* is formed:



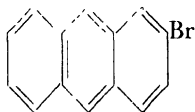
Thus, the manner in which a compound is synthesized often discloses its molecular structure. The student should realize that it takes a great deal of time and effort to arrive at the structure of a new compound. It is hoped that the above example gives an idea of the methods employed.

Anthracene is more reactive than benzene. Anthracene readily reacts with bromine, nitric acid and sulfuric acid at cold temperatures to form important derivatives. For example, *alizarin*—an important red dye—is manufactured from anthracene. This dye was formerly obtained from the root of the madder plant, which was grown in France on a large scale.

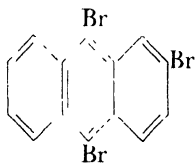
For the purpose of naming derivatives, the anthracene molecule is numbered as follows:



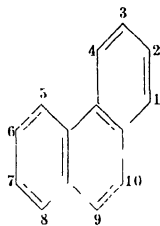
Monosubstitution products exist in *three forms*. The carbon atoms numbered 1, 4, 5 and 8 bear the same relation to the molecule. Compounds with a group in these positions are called *alpha* (α) compounds. Compounds with a group in position 2, 3, 6 or 7 are called *beta* (β) compounds. Positions 9 and 10 are called *gamma* (γ). For example, β -bromoanthracene has the following structure:



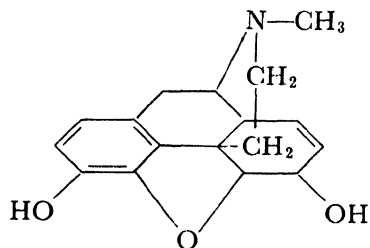
When two or more groups are present, however, the numbers must be used. 2,9,10-tribromoanthracene is the name for the following structure:



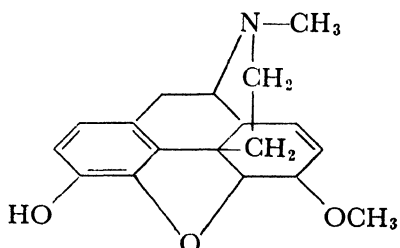
PHENANTHRENE. Phenanthrene ($C_{14}H_{10}$) is isomeric with anthracene. Its mode of synthesis indicates that its structure is as follows:



Phenanthrene is of special interest because *morphine* and *codeine* are phenanthrene derivatives. The structures for morphine and codeine are as follows:

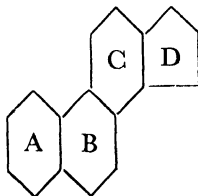


Morphine



Codeine

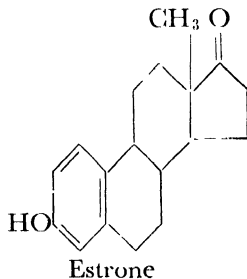
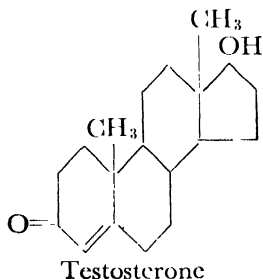
CYCLOPENTANOPERHYDROPHENANTHRENE. This relative of phenanthrene has the following structural formula:



Rings A, B and C constitute the phenanthrene portion of the molecule; since all the carbon atoms are saturated, we use the term *perhydrophenanthrene*. Ring D is composed of 5 saturated carbon atoms, and has the name *cyclopentane*. Although a rather bulky and unwieldy word, cyclopentanoperhydrophenanthrene may be easily pronounced when analyzed in the following manner: *cyclo-pentano-perhydro-phenanthrene*. For the sake of convenience, this substance and compounds derived from it are referred to as *steroids*.

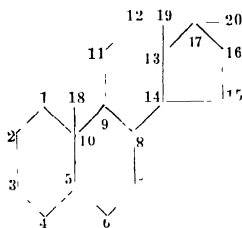
The so-called *steroid structure* constitutes one of the most interesting structures of organic chemistry. In the last few years the importance of steroids in the biologic areas has eclipsed many other events. For example, vitamin D, cholesterol,* the sex hormones, the adrenal hormones, the drug cortisone and many other vital substances are steroids. The successful synthesis of a steroid compound is just about the epitome of the organic laboratory. Drs. Kendall and Reichstein received the *Nobel Prize* for their contribution to this field of chemistry.

The following steroids should be of interest to the student: *testosterone* and *estrone*. Testosterone is a potent male hormone; estrone is a potent female hormone. Of paramount importance to the student of physiology is the fact that a *difference of one or two groups often completely changes* the biologic activity of a compound. Their structures are as follows:

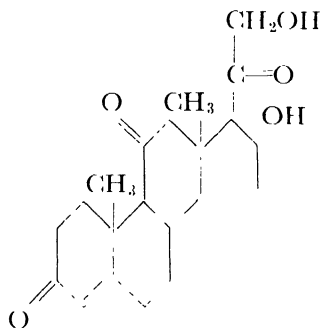


* Cholesterol is an example of a steroid alcohol. Steroid alcohols are referred to as *sterols*.

In order to facilitate the naming of steroid derivatives, the parent compound is numbered as follows:



The drug cortisone has the following structure and name:

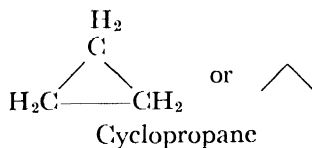


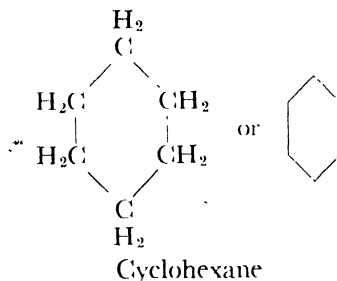
11-dehydro-17-hydroxycorticosterone

Alicyclic Hydrocarbons

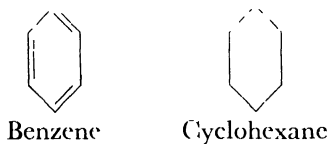
Alicyclic hydrocarbons are constituted by molecules containing *saturated* carbon atoms arranged in rings; this is in contrast to the unsaturated rings of the aromatic hydrocarbons. The chemical behavior of alicyclic compounds parallels that of the aliphatic substances.

The name of a compound of this class is derived by adding the prefix *cyclo-* to the name of the aliphatic hydrocarbon which contains the same number of carbon atoms. Thus, *cyclopropane* and *cyclohexane* have the following structures:





When using abbreviated ring symbols, we should make certain that we do not confuse the alicyclics with the *aromatics*. Benzene and cyclohexane, for example, should always be written thus:



Although many substances that occur in nature are members of this class (e.g., the *terpenes*, *camphors* and *naphthenes*), the alicyclics—at present—are of lesser importance than the aromatics.

Cyclopropane. Cyclopropane, $(\text{CH}_2)_3$, deserves special mention because it is the simplest alicyclic hydrocarbon. Moreover, it is steadily gaining popularity as a potent anesthetic gas. For this purpose, however, it suffers a grave disadvantage: *It is extremely explosive.*

OTHER CLASSES OF ORGANIC COMPOUNDS

As stated previously, all organic compounds may be considered as derived from hydrocarbons. These derivatives—regardless of their simplicity or complexity—may be easily classified on a basis of similar chemical properties. Similar chemical properties, however, result from the presence of a characteristic group, or radical. Actually, therefore, our classification is based on the presence of such a group. This is analogous to our classification of inorganic compounds. It will be recalled, for example, that all acids—regardless of the elements from which they are composed—liberate the hydrogen ion (H^+) in solution; i.e., acids are acids because of the H^+ ion. The following are the principal classes of organic compounds—i.e., in addition to the hydrocarbons:

1. Halogen derivatives
2. Alcohols

3. Phenols
4. Aldehydes
5. Ketones
6. Acids
7. Esters
8. Ethers
9. Amines
10. Heterocyclics
11. Metallic derivatives
12. Carbohydrates
13. Fats
14. Proteins

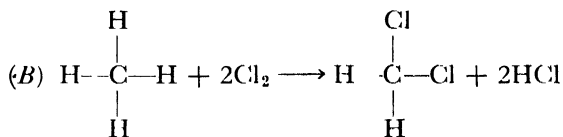
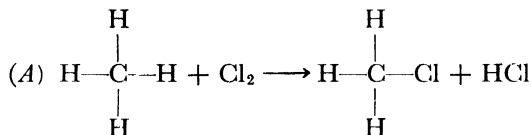
Each of the above classes is characterized by a certain chemical radical. It is only fair to state, however, that there are many organic substances which contain two—and sometimes three, but rarely four—groups, or radicals, of different classes. In this case, such a compound belongs to more than one class. Often, however, one radical is strong enough to overshadow the properties of the other radical or radicals.

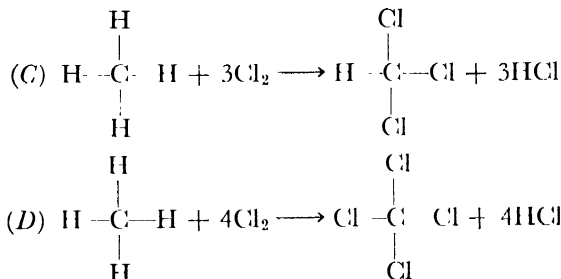
HALOGEN DERIVATIVES

A large number of compounds may be formed from hydrocarbons by the substitution of halogen elements (i.e., fluorine, chlorine, bromine and iodine) for hydrogen atoms. In the case of unsaturated hydrocarbons, *addition* takes place. Although it is possible to form such compounds through direct action of the halogen on the hydrocarbon, it is usually a much simpler matter to do this by other methods.

The following halogen derivatives will serve to illustrate this class and, in addition, indicate the value of certain members.

Chloromethanes. When chlorine reacts with methane (in the presence of sunlight) there are four possible derivatives, depending upon the conditions under which the reaction is carried out. The reactions are as follows:





These compounds and all other halogen derivatives are named on a basis of the *hydrocarbon* from which they were derived:

(A). CH_3Cl —monochloromethane (methyl chloride)

(B). CH_2Cl_2 —dichloromethane

(C). CHCl_3 —trichloromethane (chloroform)

(D). CCl_4 —tetrachloromethane (carbon tetrachloride)

Compounds of extensive value such as trichloromethane and tetrachloromethane are usually known under a more popular name—in this instance, *chloroform* and *carbon tetrachloride*, respectively.

CHLOROFORM (CHCl_3). Chloroform is a heavy, colorless, sweet smelling and noninflammable liquid possessing potent anesthetic properties. Although beset by toxic actions on heart and liver tissues, it still enjoys some use in this area. Chloroform is an excellent solvent for fats, oils and resins.

CARBON TETRACHLORIDE (CCl_4). Carbon tetrachloride is one of the most important industrial and commercial organic compounds. It is a noninflammable, colorless liquid with a low boiling point. Its chief property is its ability to dissolve grease and fat readily; thus it is a safe liquid for dry cleaning. It also is the only liquid employed to extinguish electrical fires. When sprayed on a fire, it vaporizes to form a heavy gas which excludes oxygen.

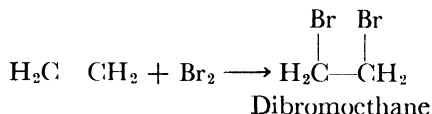
Iodomethanes. The most important iodine derivative of methane is triiodomethane, commonly known as *iodoform* (CHI_3). Iodoform is a yellow powder with an extremely characteristic odor (perhaps best described as "medicinal"). Iodoform still enjoys some use as an antiseptic dusting powder. Iodoform is readily prepared by the action of iodine and sodium hydroxide on ethyl alcohol. This reaction is often used as a *test* for ethyl alcohol.

Halogenated Aromatics. Just about any halogen derivative desired can be prepared from the aromatic hydrocarbons. The reaction of benzene with chlorine will serve as an example. Of the chlorobenzene derivatives, p-dichlorobenzene is of commercial importance. This compound has the following structure:



From our previous work with isomerism, we know that there are two other chlorobenzenes—*ortho* (o-) and *meta* (m-). Only the para form, however, possesses insecticidal properties.

Test for Saturation. Bromine and iodine are frequently employed in the laboratory to determine if a compound is saturated or unsaturated. It will be recalled that unsaturated compounds are much more reactive than saturated compounds. When, for example, a solution of bromine is added to an unsaturated compound, the reddish-brown color of the solution quickly disappears; i.e., an addition product is formed. Saturated substances react at a much slower rate and sometimes not at all. Ethylene reacts with bromine as follows:



Identification. Halogenated organic compounds may be identified in a rather crude—but fairly accurate—fashion in the following manner. A copper wire is dipped into the compound, and then held in the flame of a Bunsen burner. A positive test is indicated by a *green* flame.

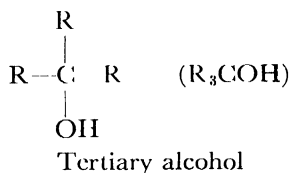
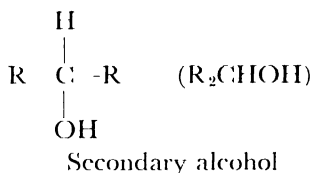
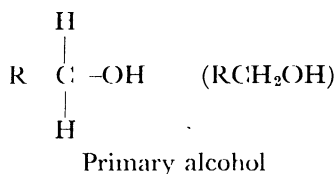
Generic Formula. Throughout our work with the various classes of organic compounds, we shall find it convenient to employ a general, or a so-called *generic formula*. The generic formula for halogenated derivatives may be given by RX , where R stands for an *alkyl* or *aryl* group, and X for the halogen element.

ALCOHOLS

Alcohols comprise a large and important class of organic compounds. An alcohol is a substitution product of a hydrocarbon in which a hydrogen atom of the hydrocarbon has been replaced by a *hydroxyl group* (OH). An alcohol may, therefore, be considered as an *organic hydroxide*, or *base*.

There are three classes of alcohols: *primary*, *secondary* and *tertiary*. A primary alcohol is an alcohol in which the hydroxyl group is attached to a carbon atom which, in turn, is attached to not more than 1 other carbon atom; a secondary alcohol is one in which the hydroxyl group is attached to a carbon atom which, in turn, is connected to 2 carbon

atoms; and a tertiary alcohol is one in which the carbon atom is attached to 3 other carbon atoms. Therefore, there are three generic formulas:

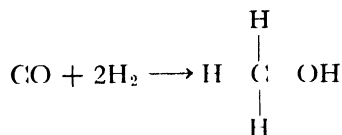


Although all alcohols share common properties, the behavior of any one alcohol depends to some degree upon whether it is primary, secondary or tertiary.

Alcohols are known which contain two, three, four, five or six hydroxyl groups; such alcohols are referred to as polyhydroxy alcohols.

The following alcohols are the most important of the entire class. Moreover, they will serve to illustrate the general behavior of this large group of compounds.

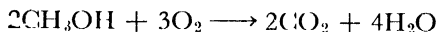
Methyl Alcohol. Methyl alcohol (CH_3OH), also known as *methanol* or *wood alcohol*, is the simplest alcohol possible. It is one of the volatile products formed when wood is subjected to destructive distillation. Under proper conditions carbon monoxide and hydrogen unite and form methyl alcohol:



This synthesis has been one of the great triumphs of modern organic chemistry.

Methyl alcohol is a colorless liquid which boils at 65°C . It mixes

with water in all proportions and is an excellent solvent. Many substances which are insoluble in other liquids are soluble in methyl alcohol. The alcohol burns with a pale blue flame which does not deposit soot:



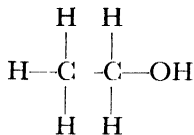
Chemically, methyl alcohol reacts with several substances. It reacts with acids, for example, to form an important group of compounds called *esters*. We shall discuss esters in a subsequent section.

Methyl alcohol is used extensively commercially as a solvent for shellac, in making varnish, and in the preparation of dyes and formaldehyde. In addition, it is a valuable solvent and reagent in the laboratory. Methyl alcohol is also used in biology as a preservative for specimens.

Of vital toxicologic interest is the fact that methyl alcohol is a potent poison, causing partial or complete blindness in small doses. Its inherent toxicity coupled with its availability makes methyl alcohol a dangerous article in the laboratory, industry and household. There are numerous poisonings among those who ingest methyl alcohol as a substitute for "alcohol" (i.e., grain alcohol). There are many such persons, however, who are not aware of the difference. Each year there are about 150 deaths resulting from this substance.

Methyl alcohol is not as depressant to the central nervous system as grain alcohol. It differs from ordinary grain alcohol also in that it is not completely oxidized in the body to carbon dioxide and water. As a result, intermediate products—*formaldehyde* and *formic acid*—are produced. It is thought that these products are the cause of the blindness.

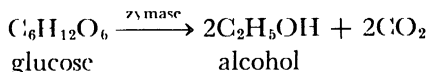
Ethyl Alcohol. Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), also known as *ethanol*, *grain alcohol* or "*alcohol*," is unquestionably the most infamous and notorious compound known to man. There seems to be no other substance which has enlisted as much comment from the sages of chemistry, biology and philosophy—past and present. Alcohol—at least its properties—has been known since the earliest period of written history—perhaps before. The ancient Egyptians, for example, were well aware of its spiritous and preservative properties. Ethyl alcohol is a primary alcohol with the following structure:



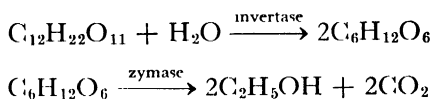
Ethyl alcohol is produced by the oldest chemical process known to man—*fermentation*. Fermentation is defined as the degradation of carbohydrates (i.e., sugars and starches) by organic catalysts called *enzymes*. The subject of carbohydrates and enzymes will be thoroughly

treated in the next chapter. For the present, let us just say that enzymes are complex chemical substances (of a protein nature) produced by *living cells*. In alcoholic fermentation, ethyl alcohol and carbon dioxide gas are the final products.

Alcoholic fermentation is carried out by adding yeast to a warm solution of glucose ($C_6H_{12}O_6$). The yeast contains an enzyme called *zymase* (produced by yeast cells) which brings about the following reaction:



Cane sugar ($C_{12}H_{22}O_{11}$) is also fermented by yeast. Since zymase can only act upon simple sugar, i.e., glucose, the yeast must contain some other enzyme which converts cane sugar (sucrose) to glucose. This enzyme is called *invertase*. The fermentation of cane sugar is as follows:



Starch, however, is the cheapest source material for producing ethyl alcohol and spiritous beverages. In this process malt (which is made from sprouting barley) is added to a mixture of some grain (source of starch) and water. An enzyme in the malt called *diastase* converts starch into *maltose*, an isomer of sucrose. Yeast is then added. The yeast acts upon the maltose in the manner described for sucrose. Alcohol is obtained from the mixture by fractional distillation. By distillation it is only possible to obtain 95 per cent alcohol.* When 100 per cent alcohol (*absolute alcohol*) is desired, it is necessary to treat the 95 per cent with a dehydrating agent such as lime. In recent years, a totally synthetic process of producing ethyl alcohol has been adopted in some areas. The synthetic process starts with ethylene and sulfuric acid.

Pure ethyl alcohol has a peculiar, pleasant odor. It boils at $78^\circ C$. It burns with a nonluminous flame which does not leave a deposit of soot. Its effects upon the body are a result of its depressant action upon the central nervous system. When taken in large doses it may cause death. Chemically, ethyl alcohol reacts with a number of different chemical reagents. The products formed contain the *ethyl radical* (C_2H_5). Later on we shall mention a few important ethyl esters.

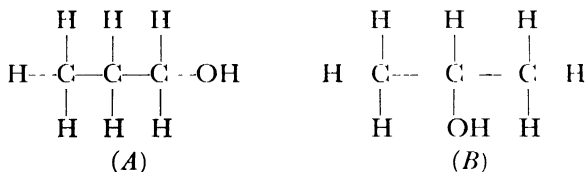
Millions of gallons of alcohol are used annually in various types of

* Alcoholic beverages are commonly rated by "proof." Proof is equal to twice the percentage reading. For example, 50 proof means 25 per cent alcohol.

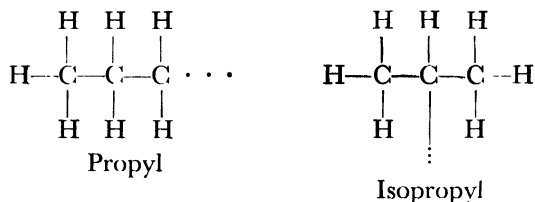
industry. As a solvent, ethyl alcohol stands next to water. There are numerous pharmaceutical preparations, e.g., tinctures, spirits and elixirs, which contain medicaments dissolved in alcohol. Of course, all spirituous beverages contain ethyl alcohol as the "active" constituent. In order to provide alcohol for industrial use at low cost (i.e., *tax-free*), the government permits the sale of denatured alcohol. Alcohol is denatured by adding to it substances, such as *methyl alcohol* or *pyridine*, which render the alcohol unfit for human consumption.

Alcohols of Propane. The alcohols of propane will serve to illustrate other facts about the class.

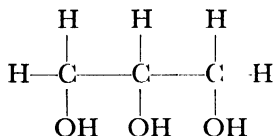
PROPYL ALCOHOLS. There are two alcohols with the empirical formula C_3H_7OH . The following structures are isomeric:



Compound A is called *propyl alcohol*; compound B is called *isopropyl alcohol*.* These alcohols have slightly different physical and chemical properties; for example, propyl alcohol boils at $98^\circ C.$, and isopropyl at $82^\circ C.$ It is to be noted that propyl alcohol is a primary alcohol, while isopropyl is a secondary alcohol. Derivatives of propyl and isopropyl alcohol contain the propyl (C_3H_7) and isopropyl radicals, respectively. The structures for these radicals are given below:



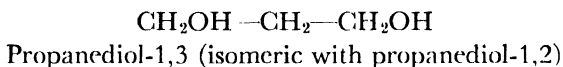
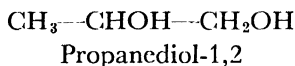
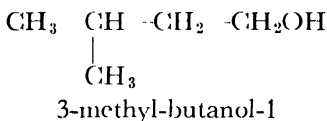
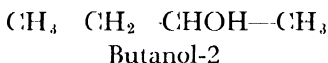
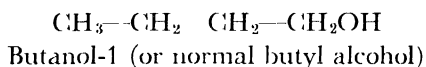
GLYCERIN. Glycerin ($C_3H_5(OH)_3$), also known as *glycerol*, is a trihydroxy derivative of propane. It has the following structure:



* The prefix *iso-* is frequently employed when there are two isomers of a given empirical formula. Thus, there are two butanes: normal *butane* and *isobutane*. When there are more than two isomers, however, numbering is used.

Glycerin is a heavy, colorless liquid, soluble in water and sweet-tasting. A sweet taste is characteristic of polyhydroxy alcohols. Glycerin is a by-product of the soap industry. Commercially, glycerin enjoys wide use. It is employed in the manufacture of nitroglycerin, and in the preparation of plastics, toilet articles and pharmaceutical preparations. Since glycerin is a constituent of practically all animal and vegetable fats and oils, it is of biologic importance. The chemistry of glycerin will be discussed in other sections.

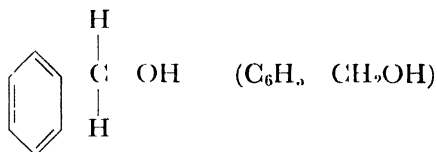
Nomenclature. Simple alcohols are named in the manner indicated above (e.g., *methyl alcohol*, *ethyl alcohol*, and so on). A more systematic and accurate way is as follows: The name of the alcohol is formed by replacing the final *e* in the name of the hydrocarbon from which the alcohol is derived by the ending *ol* (e.g., methyl alcohol is *methanol*, and ethyl alcohol is *ethanol*). When necessary, the position of the hydroxyl group is shown by adding to the name of the alcohol a number which indicates the position of the group in relation to the carbon atoms in the chain. Alcohols which contain two or more hydroxyl groups are named in a similar way. In this case, however, the number of hydroxyl groups is indicated by prefixing the syllables *di-*, *tri-*, and so on, to the suffix *-ol*. Alcohols with one hydroxyl group at the end, i.e., at the number 1 position, are often referred to as *normal*. The following examples are illustrative:



PHENOLS

The hydroxyl derivatives of the aromatic hydrocarbons are of two distinct classes: those in which the hydroxyl group is situated in a side chain; and those in which the hydroxyl group is linked *directly* to the ring. The former class closely resembles the aliphatic alcohols, while

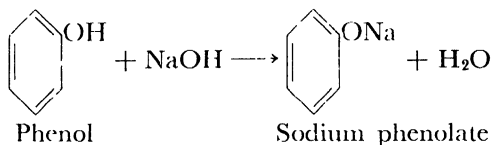
members of the latter class, which are called *phenols*, possess acid properties. Benzyl alcohol, for example, is a "regular" alcohol because the hydroxyl group is linked to the *side chain*. Its structure is as follows:



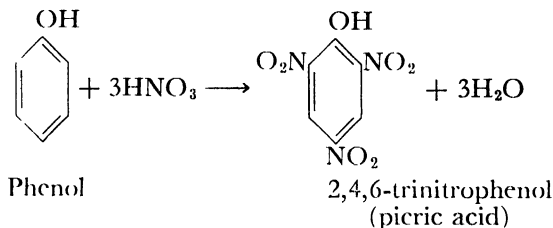
Actually, this alcohol may be considered as a substitution product of methyl alcohol, formed as the result of the replacement of 1 hydrogen atom by a phenyl radical. This section, then, is only concerned with phenols. The chemistry of this class may be well illustrated by a consideration of phenol and cresol.

Phenol. Phenol ($\text{C}_6\text{H}_5\text{OH}$), commonly known as *carbolic acid*, occurs in coal tar. It is a colorless substance which crystallizes in long needles which melt at 41°C . Phenol possesses a strong characteristic odor, described as "phenolic." Phenol dissolves in about 15 parts of water.

Phenol is quite reactive, and forms a number of important derivatives. Its acid properties are disclosed by the fact that it readily reacts with bases to form salts:



When treated with nitric acid it forms a yellow solid called *picric acid*. The reaction is as follows:



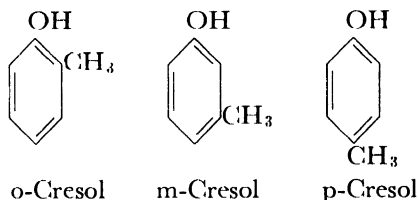
Picric acid, known chemically as 2,4,6-trinitrophenol, is used as an antiseptic, dye and explosive.

Phenol is one of the most important source materials obtained from

coal tar. Several of its derivatives, e.g., *picric acid* and *salicylic acid*, are of commercial value. It reacts with formaldehyde to form *Bakelite* and similar plastics. Although inferior to other antiseptics available at the present time, it continues to enjoy some use as a disinfectant and germicide. Of historical importance is the fact that phenol was the antiseptic used by Lister to herald "antiseptic surgery." Phenol is still the standard by which other antiseptics, disinfectants and germicides are evaluated; i.e., for every such agent a *phenol coefficient* is ascertained. A disinfectant with a phenol coefficient of 2, for example, means that it is twice as effective as phenol.

Phenol is of considerable toxicologic concern. Although less popular than in former years, it still remains high on the list of suicidal agents. Its toxic actions are those of a powerful corrosive.

Cresol. Whereas phenol is derived from benzene, cresol is derived from toluene. There are three isomeric cresols. Their structures are as follows:



They are all found along with other phenols in *creosote*. (Creosote is a mixture of chemical compounds contained in coal tar and the tars from pine and beechwood.) Although the isomers may be purchased separately, they appear on the market as a mixture. Unless otherwise specified, the term "cresol" refers to the mixture.

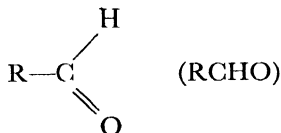
The properties of cresol resemble closely those of phenol. Cresol finds its most important use as a disinfectant and germicide. In this capacity it is superior to phenol. *Lysol* and similar products are essentially soap solutions of cresol. The soap is added to enhance the solubility of the cresol in water.

Other Phenols. Other important phenols include: *thymol*, *naphthols*, *catechol*, *resorcinol*, *hydroquinone* and *pyrogallol*.

Identification. The reactions of the phenols and their derivatives with *alkalis*, *ferric chloride* and *bromine water* are of particular value in their identification. Phenols react with alkalis to form soluble salts. Ferric chloride produces marked colorations in aqueous solution. With bromine water most phenols yield a precipitate of a brominated derivative.

ALDEHYDES

Aldehydes are derived from *primary alcohols by partial oxidation*. This fact is of great theoretical and practical importance. Thus, from a given alcohol, we can prepare the corresponding aldehyde. Aldehydes have the following generic formula:



The most common and characteristic members of the class are *formaldehyde* and *acetaldehyde*.

Formaldehyde. Formaldehyde ($\text{H}\cdot\text{CHO}$) is obtained through the oxidation of methyl alcohol. When methyl alcohol vapor and air are passed over a hot copper gauze, formaldehyde gas and water are formed:



Formaldehyde is the simplest aldehyde. It is a gas which is soluble in water, and has a powerful, irritating odor. The chemistry of formaldehyde is interesting. Formaldehyde is readily oxidized to *formic acid* and carbon dioxide. It is readily reduced by nascent hydrogen to methyl alcohol, thus:



With ammonia, formaldehyde reacts to form a complex substance called *hexamethylenetetramine*:



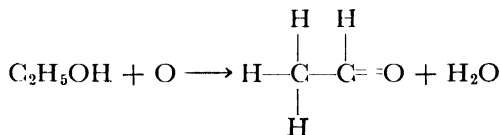
This compound is used in medicine under the name "methenamine" as a urinary antiseptic.

In the presence of a suitable catalyst, formaldehyde readily *polymerizes* to form a white solid called *metaformaldehyde*— $(\text{CH}_2\text{O})_x$. There is some evidence that the formation of starch in green plants (photosynthesis) involves a similar reaction. It has been suggested that formaldehyde is first formed from carbon dioxide and water (in the presence of chlorophyll and sunlight), and that the aldehyde then undergoes polymerization to produce carbohydrates.

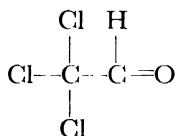
Formaldehyde comes on the market as "formalin," which is a 37 per cent aqueous solution of formaldehyde gas. The words "formaldehyde" and "formalin" are often used synonymously. At the present time formaldehyde seems to be the more popular term. Huge quantities of formaldehyde are used in the manufacture of certain dyes, plastics (e.g.,

Bakelite, *Formica*) and photographic films. In the biologic laboratory it is extensively used as a preservative for anatomic specimens. In the hospital it still enjoys some use as a disinfectant. Formaldehyde was formerly employed as a food preservative. This practice is now prohibited by law.

Acetaldehyde. Acetaldehyde (CH_3CHO) is prepared by the oxidation of ethyl alcohol. The oxidation is readily carried out by a mixture of sulfuric acid and potassium dichromate. The reaction is as follows:



Acetaldehyde, commonly called *acetic aldehyde*, or simply *aldehyde*, is a colorless liquid, boiling at 21°C . It mixes with water and alcohol in all proportions. Its odor is marked and characteristic. From the chemical point of view, the most characteristic property of aldehyde is its power to unite directly with other substances. Indeed, if left to itself, it readily changes into polymeric modifications; of these *paraldehyde* is the most important. The paraldehyde molecule is formed by the union of 3 aldehyde molecules; its formula is $(\text{CH}_3\text{CHO})_3$. Paraldehyde has been used for years as a *hypnotic*. Another interesting compound of acetaldehyde is *chloral*. Chloral is formed by the substitution of the 3 hydrogens of the methyl group with 3 chlorine atoms. Chloral has the following structure:

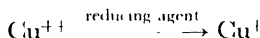


Chloral is a colorless liquid which boils at 98°C . When chloral and water are brought together, they unite to form a crystallized compound—*chloral hydrate*. In doses of 0.5 gm. to 2 gm., chloral hydrate produces a natural sleep; in larger doses it acts as an anesthetic.

Nomenclature. The simple aldehydes are usually named from the acids which they yield on oxidation; thus $\text{H}\cdot\text{CHO}$ is *formic aldehyde* or *formaldehyde*, and CH_3CHO is *acetic aldehyde* or *acetaldehyde*. In the more systematic method, the name of an aldehyde is formed by adding the suffix *-al* to the name of the hydrocarbon which contains the same number of carbon atoms. According to this system acetaldehyde is *ethanal*.

Identification. The ability of aldehydes to reduce other substances (i.e., they are reducing agents) is of analytical significance.

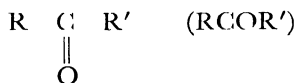
When an aldehyde or compound containing an aldehyde group is added to an *alkaline solution of a cupric salt*, a *red precipitate of cuprous oxide (CuO)* is formed. The reaction may be summarized as follows:



The reagent used is a clear, dark blue solution called *Fehling's solution*. It is prepared by adding *copper sulfate* to a solution which contains *sodium hydroxide* and *Rochelle salt* (sodium potassium tartrate).^{*} A similar, but more stable solution, is *Benedict's solution*. Benedict's solution has largely replaced Fehling's solution. The reaction, however, is the same.

KETONES

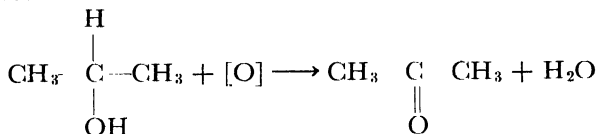
Ketones are closely allied to aldehydes. Whereas aldehydes are derived from *primary alcohols* by oxidation, ketones are derived from *secondary alcohols* by oxidation. The generic formula for ketones is as follows:



Note that the CO, or *carbonyl*, group is common to both aldehydes and ketones.

Although similar in structure, aldehydes and ketones differ in a few of their chemical properties. For example, aldehydes are *reducing agents* and ketones are not. This fact alone is of practical importance. The general properties of this class are well illustrated by *acetone*.

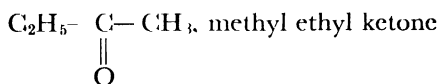
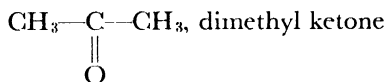
Acetone. Acetone ((CH₃)₂CO) is the first member of the class, and by far the most important. The formation of acetone as the result of the oxidation of isopropyl alcohol substantiates the generic formula given above:



Acetone is a liquid with a characteristic odor and a peppermint-like taste; it is miscible with water in all proportions. It boils at 56.1° C., and is inflammable. Acetone finds its greatest use as a solvent in a wide variety of industries. As a source material, acetone is used in the manufacture of chloroform, iodoform and various resins and plastics.

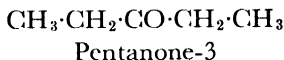
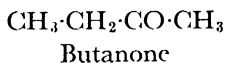
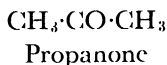
Nomenclature. Ketones can be named in accordance with the groups represented by R:

^{*} The Rochelle salt prevents the precipitation of cupric hydroxide.



etc.

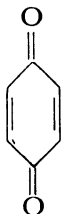
When both R's are the same, we have a *simple* ketone (e.g., acetone); when the R's are different, we have a *mixed* ketone (e.g., methyl-ethyl-ketone). To name complex ketones, it is preferable to employ the following system: Change the *-e* ending of the hydrocarbon with the same number of carbon atoms to *-one*, and indicate the position of the carbonyl group—when necessary—by numbering the longest chain thus:



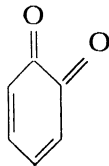
etc.

Identification. In contrast to aldehydes, ketones *do not* reduce Fehling's or Benedict's solution. They do, however, produce a color with *Schiff's* reagent on *standing* (aldehydes produce an *immediate* color). To establish the identity of a specific ketone, a derivative (an *oxime* or *phenylhydrazone*) is usually prepared from it.

Quinones. Quinones are aromatic compounds in which the carbonyl group (CO) is *part of the ring*. The CO group of an *aromatic ketone* is *not part of the ring*. The simplest member of this class is called *benzoquinone*. There are two isomers of this compound:



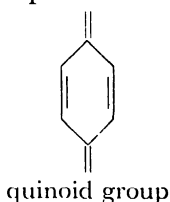
p-benzoquinone



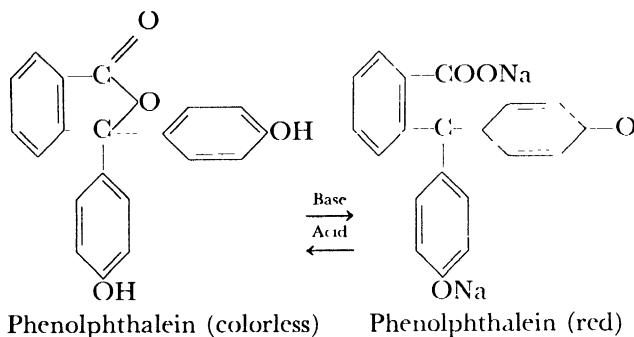
o-benzoquinone

No meta, or m-quinone, is known.

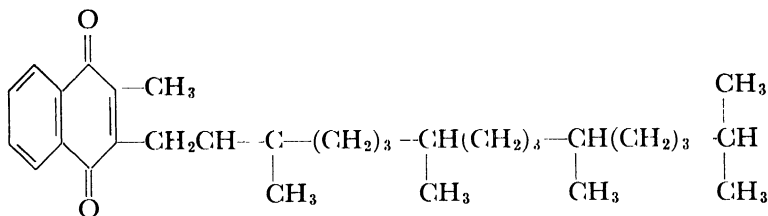
Quinones are of interest primarily because they are used to explain the color of certain dyes. The so-called *quinoid* structure is a *chromophore*, or color-producing group:



For example, the color change of the indicator *phenolphthalein* (colorless in acid; red in alkali) is explained on a basis of the quinoid chromophore. When phenolphthalein is in an acid solution, all 3 of its benzene rings have a *benzenoid* structure; in alkali, however, one of these benzenoid rings is changed to the *quinoid type*. This may be represented as follows:



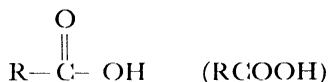
Several quinones are of commercial and pharmaceutical importance. Vitamin K, for example, a derivative of 1,4-naphthoquinone, has the following structure:



ACIDS

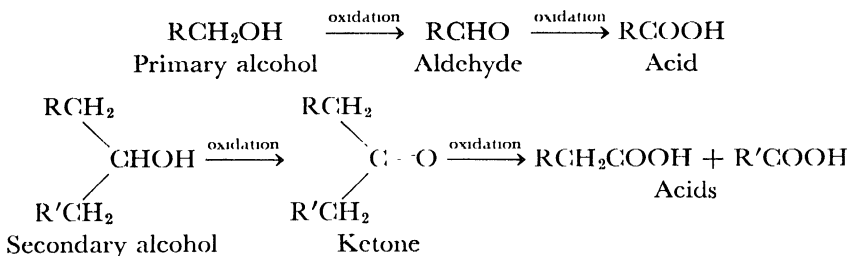
When primary and secondary alcohols are partially oxidized, aldehydes and ketones are produced, respectively. Aldehydes and ketones, however, are capable of being further oxidized to form products called

acids. Acids, therefore, result from the complete oxidation of alcohols; aldehydes and ketones are intermediate derivatives. The generic formula for an organic acid is as follows:



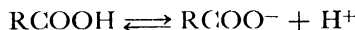
The —COOH group is called the *carboxyl radical*.

The relationship of alcohols, aldehydes, ketones and acids may be given as follows:



When tertiary alcohols are oxidized, a mixture of acids and ketones are obtained.

It was stated previously that organic compounds do not ionize. We must now qualify this statement to this extent: *Organic acids undergo a slight degree of ionization when placed in solution.* Thus, solutions of organic acids are weak electrolytes. The ionization of organic acids may be represented thus:



The presence of hydrogen ions, then, endows such compounds with acidic properties. For example, organic acids neutralize bases to form salts and water:



In a similar fashion, organic acids react with alcohols to form organic salts called *esters*. There are a large number of esters of importance.

Fatty Acid Series. Organic acids are present in the tissues of certain organisms or products derived from them. They occur in the form either of the free acid or of some derivative (salt or ester) of the acid. Like the hydrocarbons, they can be arranged in series. Of these series, the so-called *fatty acid series* is perhaps the most important. The term “fatty acid” has its origin in the fact that most fats are derivatives of acids belonging to this series. All members of the fatty acid series may be considered as derived from hydrocarbons of the *paraffin series*. A few of the most important acids of this series are given in the follow-

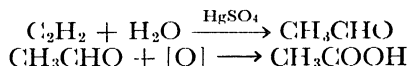
ing table. Note that these acids are monobasic; i.e., they contain only one carboxyl group.

Important Fatty Acids

Formic acid	HCOOH
Acetic acid	CH ₃ COOH
Butyric acid	C ₄ H ₇ COOH
Palmitic acid	C ₁₅ H ₃₁ COOH
Stearic acid	C ₁₇ H ₃₅ COOH

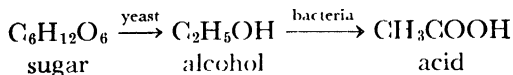
FORMIC ACID. Formic acid (HCOOH) is the simplest organic acid. It occurs in red ants, in stinging nettles, in the shoots of some of the varieties of pine, and elsewhere. Formic acid is a colorless liquid boiling at 99° C. It has an extremely penetrating odor. Chemically, it is a fairly strong acid, forming salts and esters called *formates*.

ACETIC ACID. Acetic acid (CH₃COOH) is one of our most important acids in commerce and in the laboratory. At one time it was prepared commercially by the distillation of wood. At present, however, it is being produced in huge quantities by a synthetic process. The process consists in combining acetylene with water via the catalytic action of mercuric sulfate to form acetaldehyde. The aldehyde is then easily oxidized to acetic acid. The equations are as follows:



Acetic acid is a clear, colorless liquid which boils at 118° C. It has a very penetrating, pleasant, acid odor and a sharp acid taste. The pure acid, which is solid at temperatures below 16° C., is known as *glacial* acetic acid. Chemically, acetic acid yields a large number of derivatives. Many of its salts and esters (called *acetates*) are widely used in the laboratory, industry, pharmacy and medicine.

A discussion of acetic acid would not be complete without a word about *vinegar*. Vinegar is an aqueous solution of acetic acid containing 3 to 6 per cent acid, a little alcohol and other substances in small quantities. It is produced by the fermentation of fruit juices (e.g., cider), which contain sugar. The sugar is first converted to ethyl alcohol (in the manner described earlier, i.e., by enzymes) and then oxidized to acetic acid by oxidizing bacteria (*Bacterium aceti*) present in the juice. The reactions may be summarized thus:



BUTYRIC ACID. Butyric acid (CH₃CH₂CH₂COOH) is present in rancid butter, muscle, sweat, cheese and feces. This acid is characterized chiefly by its disagreeable odor. A few of its esters are of biologic importance.

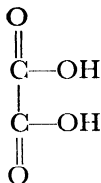
PALMITIC AND STEARIC ACIDS. Palmitic ($C_{15}H_{31}COOH$) and stearic ($C_{17}H_{33}COOH$) acids are of special interest because they are present as glyceryl esters (i.e., esters of glycerin) in the fats and oils of most animals and plants. In a later section we shall discuss these esters in detail.

NOMENCLATURE. The names of several of the acids of this series are derived from their origin (formic from "formica," butyric from *butter*, and so on). These acids may also be named by changing the ending *-e* of the hydrocarbons containing the same number of carbon atoms to *-oic*. Thus $H\cdot COOH$ is methanoic, CH_3COOH is ethanoic, and so on.

Acids of Other Series. There are many important acids of other series. These acids differ from those of the fatty acid series by having some radical (e.g., OH) in addition to a carboxyl group, or by being unsaturated. The following acids are worthy of mention.

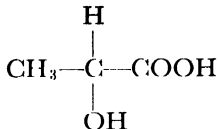
OLEIC ACID. Oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$) is an *unsaturated* acid. With hydrogen it is converted into the saturated stearic acid. Oleic acid is important because it is present—along with palmitic and stearic acids—as a glyceryl ester in fats and oils.

OXALIC ACID. Oxalic acid is a dicarboxy acid with the following structure:



Oxalic acid is present in the form of salts in a variety of plants. Rhubarb is rich in it. The urine contains small quantities of calcium oxalate. Oxalic acid is a strong acid. It is used in the laboratory, in the manufacture of dyes, in polishing metals and in bleaching and tanning. It is highly poisonous.

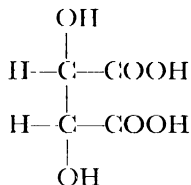
LACTIC ACID. Lactic acid ($CH_3CHOHCOOH$) has the following structure:



Of interest is the fact that this acid contains a hydroxyl group. The name lactic correctly suggests some relation to milk. The souring of milk is due to the formation of this acid from the action of certain bacteria (which produce enzymes) on milk sugar, or *lactose*. In the body, lactic acid is found in muscle tissue upon exercise.

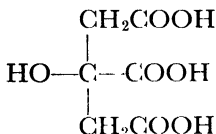
It will be recalled that lactic acid was given as an example of an *optical* isomer (*l*-lactic acid, *d*-lactic acid and *dl*-lactic acid). It will further be recalled that these three forms or varieties—like all optically active compounds—are identical in their properties except their action on polarized light.

TARTARIC ACID. Tartaric acid is a dihydroxy dicarboxylic acid. It has the following structure:



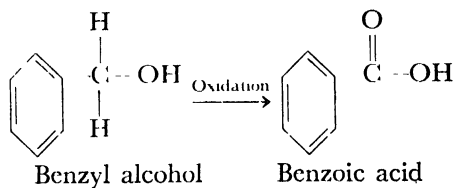
Tartaric acid occurs in many fruits, especially the grape, either in a free state or in the form of its salts. It is optically active. Some of its salts are popular compounds. Potassium acid tartrate (also known as *cream of tartar*) is a constituent of baking powders and is used in dyeing. Sodium potassium tartrate (commonly known as *Rochelle salt*) is a constituent of *Fehling's solution*, and is used in medicine as a cathartic. Potassium antimonyl tartrate (also known as *tartar emetic*) is used in medicine as an emetic.

CITRIC ACID. Citric acid has the following structure:



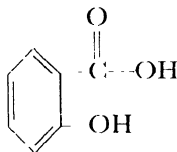
This acid occurs in the so-called citrus fruits, such as the lemon and grapefruit. It is a white solid, soluble in water. Citric acid is used in the manufacture of citrates, flavoring extracts, confectionary, soft drinks, and in dyeing and medicine. Magnesium citrate and sodium citrate are used extensively in medicine; the former is a laxative, and the latter prevents the coagulation of blood.

BENZOIC ACID. Benzoic acid is the simplest aromatic acid. It may be prepared in the laboratory by the oxidation of benzyl alcohol:



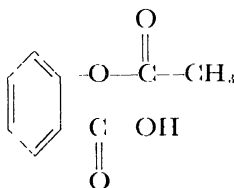
Benzoic acid occurs (as the free acid or ester) in gum benzoin, resins, balsam of Tolu, berries, and so on. The acid itself finds application as an antiseptic in medicine and in the manufacture of dyes. Its salts also enjoy wide use. Sodium benzoate is a common and safe food preservative. Benzyl benzoate is used in medicine. In addition to its salts, there are a number of other important derivatives.

SALICYLIC ACID. Salicylic acid is the simplest aromatic hydroxy acid. It has the following structure:



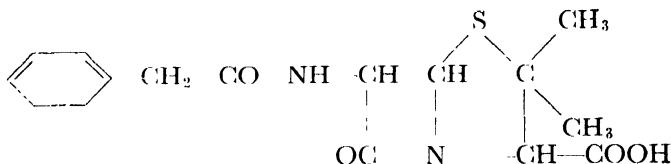
From our previous information, we can readily see that this acid may also be named o-hydroxybenzoic acid. Salicylic acid is found in the form of its methyl ester (*methyl salicylate*) in oil of wintergreen. It is prepared synthetically from phenol.

Salicylic acid and its salts and esters are just about our most common medicinal substances. Free salicylic acid is widely used as an antiseptic and fungistatic agent. Its most important derivative—*aspirin*—is without question the most popular drug in medicine. Aspirin has the following structure:



Chemically, aspirin is called *acetylsalicylic acid*. Other salicylates used in medicine include phenyl salicylate (*salol*) and methyl salicylate. Salicylates are also used in the manufacture of dyes.

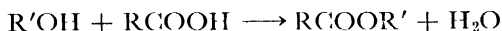
PENICILLIN. Of extreme interest and practical importance is the fact that penicillin is an organic acid; it has the structure shown below:



Penicillin is insoluble in water. Its alkali salts, which are extremely soluble, are employed when penicillin is to be administered by the intravenous route. Certain other salts, especially *procaine penicillin*, are *highly insoluble*; they are employed for intramuscular injections to prolong absorption, and thereby increase the duration of action.

ESTERS

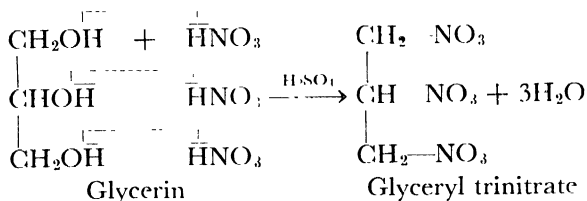
An ester is defined as an inorganic or organic acid in which the hydrogen of the carboxyl group has been replaced by some organic group (R). Esters are prepared by the interaction of an alcohol and an acid—this is called *esterification*. Esterification, then, is analogous to *neutralization* in inorganic chemistry. Esterification may be represented by the generic equation below:



There are a large number of natural and synthetic esters. In nature they are responsible for the characteristic odor of many fruits, flavors and flowers. Generally speaking, they all possess an agreeable odor. The esters made from acids and alcohols of low molecular weights are colorless, volatile liquids; the esters of high molecular weight acids and alcohols are thick liquids or solids. Most all esters are insoluble in water. Chemically, esters are neutral compounds which are decomposed upon heating with a dilute acid or base.

A great many esters are of commercial value. Although several are used as flavoring materials and in perfumes, the majority are employed for a variety of uses in industry, pharmacy and medicine. The following esters are of special interest and importance.

Esters of Inorganic Acids. **GLYCERYL TRINITRATE.** Glyceryl trinitrate, commonly called *nitroglycerin*, is prepared by the action of nitric acid on glycerin. In this reaction—and in all esterification reactions— H_2SO_4 is used as a dehydrating agent; such an agent hastens the speed of reaction.



Nitroglycerin is used in medicine as a *vasodilator* (especially in *angina pectoris*), and is the active constituent of *dynamite*.

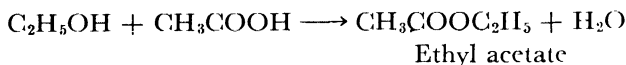
ETHYL NITRITE. Ethyl nitrite ($C_2H_5NO_2$) has an apple-like odor. It is prepared from ethyl alcohol and nitrous acid. An alcohol solution is used in medicine under the familiar name of "sweet spirit of nitre."

ISOAMYL NITRITE. Isoamyl nitrite ($C_5H_{11}NO_2$) is prepared from the reaction of nitrous acid on isoamyl alcohol. It is used in medicine as a vasodilator—especially (like nitroglycerin) in angina pectoris.

DIMETHYL SULFATE. Methyl alcohol reacts with sulfuric acid to form dimethyl sulfate ($(CH_3)_2SO_4$). This compound is extensively used in the organic laboratory (especially in the synthesis of other compounds) as a *methylating agent*, i.e., to introduce methyl groups into compounds. Diethyl sulfate, $(C_2H_5)_2SO_4$, is used in a similar manner as an *ethylating agent*.

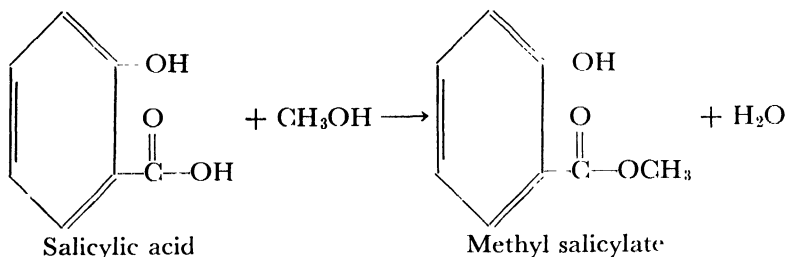
METHYL AND ETHYL CHLORIDES. Methyl chloride (CH_3Cl) and ethyl chloride (C_2H_5Cl) are the esters of hydrochloric acid and methyl and ethyl alcohols, respectively. Both of these agents have been used as local anesthetics; when sprayed upon the skin they evaporate rapidly, thereby cooling the tissues.

Esters of Organic Acids. **ETHYL ACETATE.** Ethyl acetate is prepared by the reaction between ethyl alcohol and acetic acid:



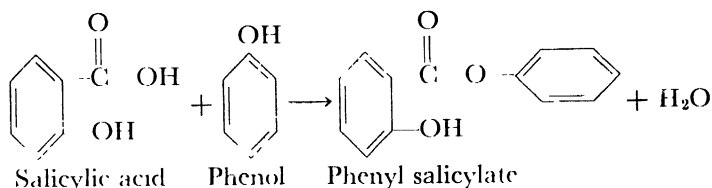
Ethyl acetate is one of our most important industrial solvents. In this capacity it is used in the manufacture of nitrocellulose, photographic films, resins and essences.

METHYL SALICYLATE. When methyl alcohol is heated with salicylic acid, methyl salicylate is formed:



Methyl salicylate is the chief constituent of oil of wintergreen and oil of birch. It is used in medicine as a *rubefacient* (in liniments and ointments), and as a substitute for the natural oil of wintergreen.

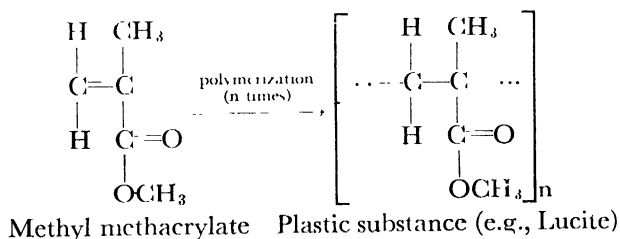
PHENYL SALICYLATE. Another ester of salicylic acid, phenyl salicylate (commonly called *salol*), is used in medicine as an intestinal antiseptic. It is prepared by heating salicylic acid and phenol, thus:



AROMATIC ESTERS. As pointed out at the beginning, a great many esters possess agreeable odors. The following esters are commonly employed as synthetic flavors:

<i>Ester</i>	<i>Flavor</i>
Isoamyl acetate	pear
Ethyl butyrate	pineapple
Isoamyl isovalerate	apple
Octyl acetate	orange
Ethyl formate	rum
Amyl butyrate	apricot

SYNTHETIC PLASTICS. Several synthetic plastics are derived from esters by polymerization. For example, *methyl methacrylate* undergoes polymerization to form a valuable group of plastic substances. This may be represented as follows:



Plexiglas and Lucite are important methacrylate plastics.

FATS AND OILS. All fats and oils of animal and plant origin are esters. Moreover, they are all derived from *glycerin*. A fat or oil is defined as an ester of *glycerin* and a *fatty acid*. We shall discuss these important esters as a separate class of organic compounds.

ETHERS

Ethers may be considered as alcohols in which the H of ROH is replaced by an R group. Ethers are really organic oxides. They have the following generic formula:

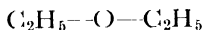


If the two R's represent the same group, the ether is referred to as a *simple* ether. If the two R's represent different groups, we have a so-called *mixed* ether. Thus, we have two generic formulas:

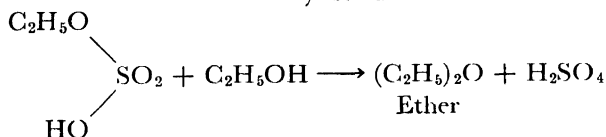
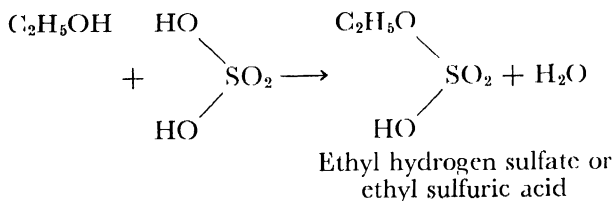


Ethers of low molecular weight are colorless, neutral liquids, and extremely volatile. All ethers—especially the lower members—are highly inflammable. Since they are highly inactive, they are extensively used as solvents for other organic substances. The following ethers are of particular importance.

Diethyl Ether. Diethyl ether (also known as *ether*, sulfuric ether and ethyl oxide) is our most important member of the class. It has the following structure:



Ether is prepared in great quantities by the reaction between *sulfuric acid* and *ethyl alcohol*. There are two steps in the reaction:



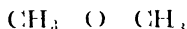
It can be seen that the sulfuric acid is regenerated and used over and over again.

Diethyl ether is a colorless, volatile liquid with a characteristic odor. It is highly inflammable and is explosive when mixed with air and ignited. Industrially, ether is unsurpassed as a solvent for a large number of organic substances. In this capacity, it is used in the manufacture of guncotton, collodion solutions and certain plastics. Because of its extreme volatility, it has been used as a refrigerant.

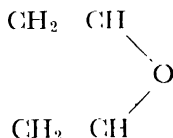
Of special interest, is of course, the fact that ether is one of our most important anesthetic agents. Although other agents have appeared on the scene, ether is still considered our standard anesthetic. Ether for this purpose must be highly purified.

Other Ethers. Many other ethers are of commercial importance. The following are widely used at the present time.

DIMETHYL ETHER. Dimethyl ether is used as a solvent. It has the following structure:

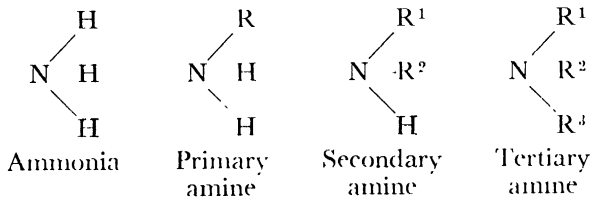


DIVINYL ETHER. Divinyl ether has rapidly gained popularity as a potent anesthetic. It has been successfully used in short surgical procedures. It has the following structure:

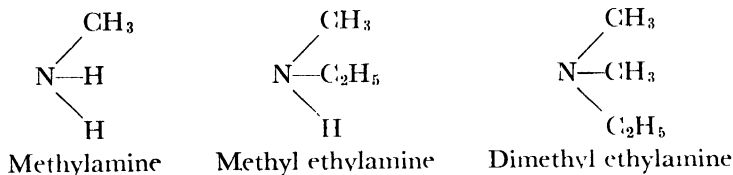


AMINES

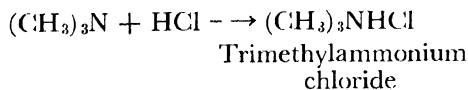
Amines are organic compounds which may be looked upon as derivatives of ammonia. Since ammonia has three replaceable hydrogens, we have three classes of amines—*primary*, *secondary* and *tertiary*. These facts may be summarized thus:



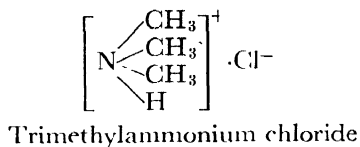
In primary amines, the —NH_2 is called an *amino group*; in secondary amines, the —NH is called an *imino group*. The following amines will serve to illustrate the manner in which amines are named:



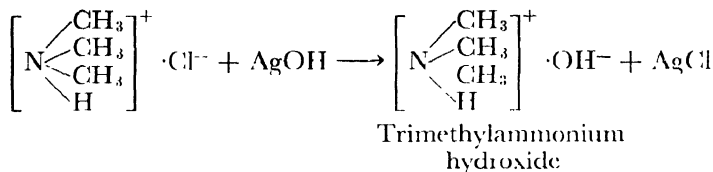
The most outstanding chemical characteristic of amines is their basic properties—they are more basic than ammonium hydroxide. By virtue of this property, they combine with acids to form *ammonium salts*. Trimethylamine, for example, reacts with hydrochloric acid to form *trimethylammonium chloride*:



Being a true salt, however, it furnishes ions in solution. For this reason, its structural formula is more correctly written thus:

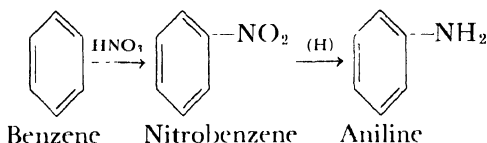


These organic ammonium compounds are known as *quaternary ammonium* salts. By treating quaternary salts with *silver hydroxide* (AgOH), *quaternary bases* are formed. Quaternary bases are related to ammonium hydroxide. For example, trimethylammonium chloride yields *trimethylammonium hydroxide*:



Amines are of paramount interest to the organic chemist, biochemist and physiologist. It is indeed a singular fact that the majority of our synthetic medicinals are amines. The following compounds have been chosen to illustrate the importance of this organic class.

Aniline. Aniline (chemically, *phenylamine*) is our most important amine. This is so because it is the source material for a large number of our most popular dyes and drugs. Aniline is prepared indirectly from coal tar; i.e., it is derived from benzene (present in coal tar) by the following reactions:



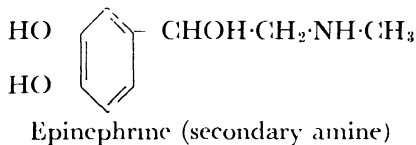
Aniline is a liquid with a characteristic odor which boils at 184°C . It is colorless when freshly distilled, but darkens on standing.

The value of aniline was first appreciated in 1856 when Perkin found that aniline could be oxidized with chromic acid to yield a violet dye—to which was given the name “mauve.” This was the first *coal-*

tar dye to be produced. Since then about 3000 coal-tar dyes have been synthesized.

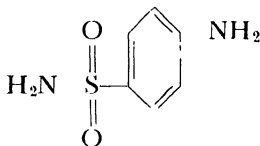
Physiologic Amines. The following amines are but a few of those which are employed in medicine. They clearly illustrate, however, how the organic chemist has revolutionized the practice of medicine.

EPINEPHRINE. Epinephrine—a hormone of the adrenal glands—has the following structure:

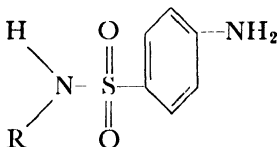


Epinephrine acts on many tissues in the body. It is most frequently used to relieve attacks of asthma and increase blood pressure. Epinephrine (also called *Adrenalin*) is obtained from adrenal extracts. It may, however, be synthesized in the laboratory. Several other agents of similar action—e.g., ephedrine, Benzedrine, and so on—have a similar structure.

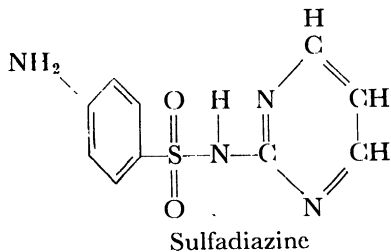
SULFONAMIDES. The efficacy of the sulfonamides (or “sulfa drugs”) in the treatment of infectious diseases is familiar to all. *Sulfanilamide* (chemically, p-aminobenzene-sulfonamide) was one of the first sulfa drugs used in medicine. It has the structure shown below:



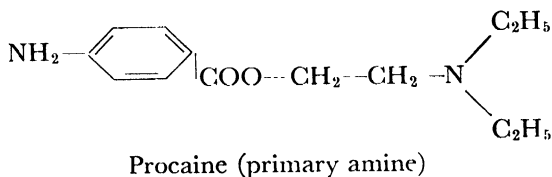
Sulfanilamide proved to be quite toxic to the kidneys and blood. This prompted the synthesis of a number of derivatives. Most derivatives are prepared by the replacement of a hydrogen from the —SONH₂ group by some organic group (R). The generic formula for the sulfonamides may be represented as follows:



Sulfadiazine, for example, a much less toxic agent than sulfanilamide, has the structure shown at top of page 216.

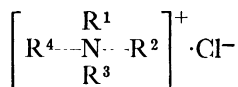


PROCAINE. Procaine or *Novocain* is also a familiar compound. Although hundreds of other local anesthetics have been synthesized, procaine is by far the most popular. Procaine has the following structure:

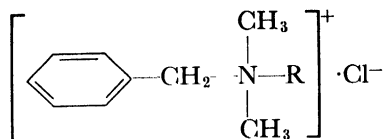


Several other important local anesthetics have a similar structure.

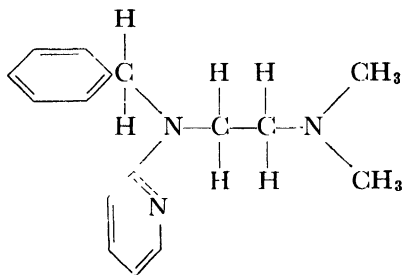
QUATERNARY ANTISEPTICS. Several quaternary salts are highly useful antiseptics. They are more potent and much less toxic and irritating than such conventional antiseptics as iodine and carbolic acid. Their generic formula may be represented thus:



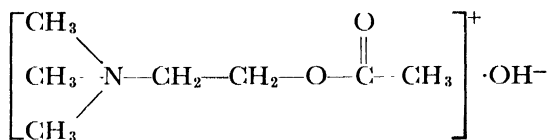
One popular agent of this class—Zephiran—has the following structure:



ANTIHISTAMINES. It has been postulated that an agent known as *histamine* (present within the cells of the body) is released by certain foreign proteinaceous substances (known as *allergens*) in certain individuals to produce the signs and symptoms of an allergy. This led to the synthesis of a large number of so-called *antihistamines*. Antihistamines—although not a cure—have brought dramatic relief to a variety of allergic conditions. One popular agent of this class—*Pyribenzamine*—has the structure shown at top of page 217.



ACETYLCHOLINE. Acetylcholine is of particular importance to the physiologist since it is liberated upon stimulation of the nerve endings of the parasympathetic and voluntary nervous systems. Acetylcholine is a *quaternary base*, and has the following structure:



The discovery of acetylcholine gave impetus to research concerning the relationship between quaternary compounds and the nervous system. As a result of this research, a large number of quaternary compounds have been introduced into medical therapeutics. Some of these agents augment the action of acetylcholine, and some inhibit acetylcholine. *Mecholyl*, *Doryl*, *Urecholine*, for example, act like acetylcholine; *tubocurarine* (obtained from a crude extract called *chuare*) is an inhibitor, and produces paralysis of voluntary, or skeletal, muscle.

HETEROCYCLIC COMPOUNDS

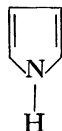
A great number of organic compounds are unique in that they contain rings in which elements other than carbon are also present. For this reason, such compounds are referred to as *heterocyclic*; aromatic and alicyclic compounds may therefore be referred to as *carbocyclic*. The majority of heterocyclic substances are derivatives of the following heterocyclic structures:



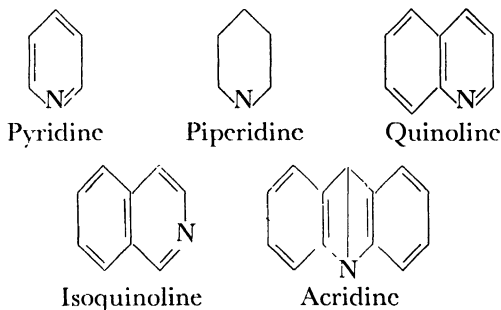
Thiophene



Furan



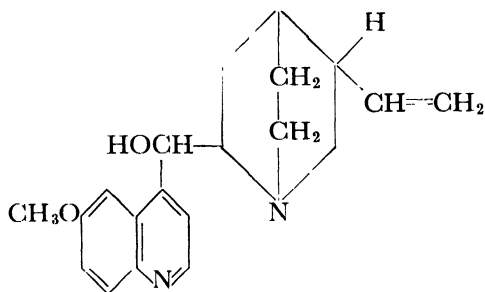
Pyrrole



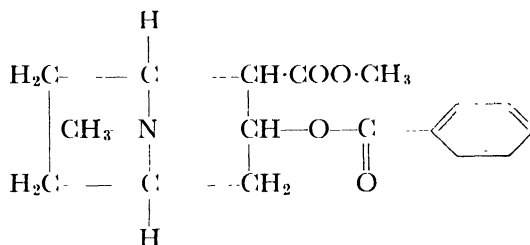
From the above structures, nature—and the organic chemist—have derived a variety of highly useful flavors, dyes, drugs and vitamins. Of special interest are the drugs of plant origin. Most of these drugs are heterocyclic compounds called *alkaloids*. Let us briefly discuss these substances. Also let us make a few statements concerning synthetic heterocyclic compounds.

Alkaloids. *Alkaloids are complex heterocyclic nitrogenous compounds of plant origin characterized by powerful physiologic activity.* Physically, they are white crystalline solids, insoluble in water, but soluble in alcohol, ether and chloroform. Alkaloids are optically active: *It is usually the levorotatory isomer which is physiologically active.* Chemically, alkaloids are characterized by their *basic* nature; i.e., they react with acids to form quaternary salts which are soluble in water. For this reason, alkaloids are usually employed in the form of salts. To aid in identification, so-called “alkaloidal reagents” are used to precipitate alkaloids from their aqueous solutions. The more popular reagents include: *tannic acid*, *potassium-mercuric iodide* and *picric acid*. The following compounds will serve to illustrate the importance of this class.

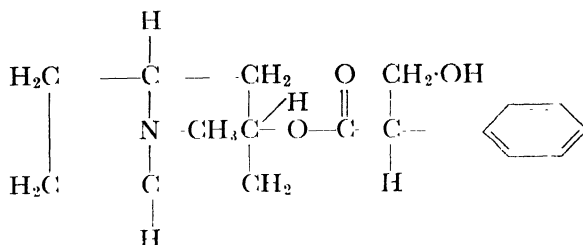
QUININE. Quinine is obtained from the bark of the *cinchona tree*. It is used in the treatment of malaria. Quinine—a derivative of quinoline—has the following structure:



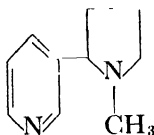
COCAINE. Cocaine is present in *coca leaves*. It was the first agent to be widely used as a local anesthetic. It has the structure shown below:



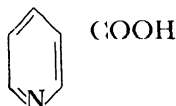
ATROPINE. Atropine is the active constituent of *belladonna* (deadly nightshade). Atropine is extensively used in medicine as an anti-spasmodic and mydriatic (dilating the pupil). It has the following structure:



NICOTINE. Nicotine is contained in tobacco leaves. Unlike most alkaloids, it is a *liquid*. Nicotine has the following structure:

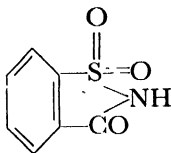


Nicotine is a highly poisonous substance. It is used as an insecticide. Upon oxidation nicotine yields a vitamin called *nicotinic acid*:



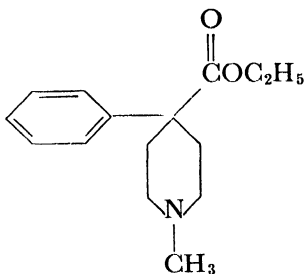
Synthetic Heterocyclic Compounds. The following compounds are illustrative of what the chemist has done in this area.

SACCHARIN. The synthesis of saccharin by Remsen was a milestone in the development of organic chemistry; above all, it removed the psychologic barrier between the chemist and nature. Saccharin may be represented as follows:

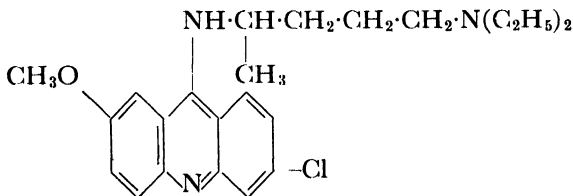


Saccharin, being about 500 times as sweet as cane sugar, is widely used as a sugar substitute. It has no nutritive value.

DEMEROL. Demerol has proven to be one of our most valuable analgesic agents. Although its analgesic action is close to that of morphine, its toxicity is greatly lower. Demerol is a synthetic derivative of piperidine with the following structure:

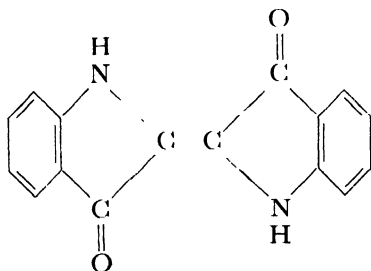


QUINACRINE. World War II prompted the synthesis of quinacrine (Atabrine) as a substitute for quinine. When given to our troops in the Pacific it proved to be a highly effective prophylactic agent against malaria. Since the war its usefulness in the management of certain forms of malaria has been established. Once again the chemist has demonstrated that he is a match for the chemical forces of nature. Quinacrine is a derivative of acridine with the structure below:

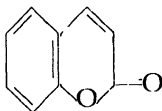


INDIGO. Like the spices of the West Indies, history was written by the efforts of man to grow and obtain indigo—one of the oldest and

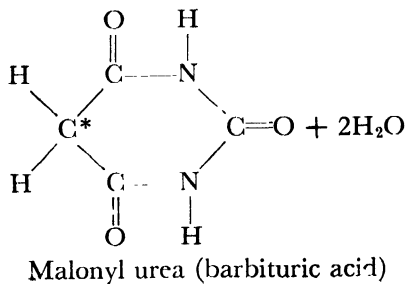
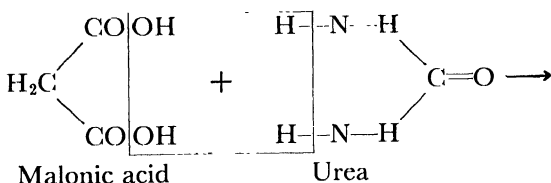
most popular vat dyes. Its synthesis in the organic laboratory by *Baeyer* stands as one of the great accomplishments of organic chemistry. Indigo has the structure shown below:



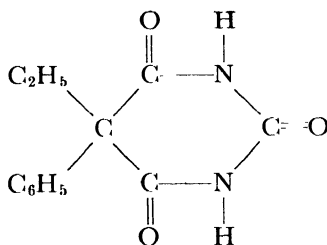
COUMARIN. Coumarin is the sweet-smelling constituent of the *tonka bean*. Its synthesis in the laboratory was a great boon to the tobacco, perfumery and allied industries, where it is extensively employed as a flavoring agent. It has the following structure:



MALONYL UREA. Malonic acid and urea react to form a heterocyclic compound called *malonyl urea*, or *barbituric acid*. The reaction is as follows:

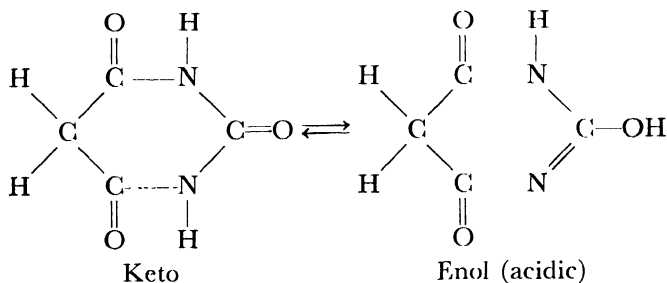


Malonyl urea has proved of tremendous value to the pharmaceutical industry; it is the basic nucleus of a medicinal class of compounds referred to as *barbiturates*. Depending upon the dose employed, the barbiturates produce all degrees of depression, ranging from sedation to anesthesia. The barbiturates have all but replaced other drugs of a similar pharmacologic action. The various barbiturate derivatives are synthesized by substituting alkyl radicals for the 2 hydrogens which are attached to the carbon atom marked with an asterisk (in the above formula). One of the most popular barbiturates, *phenobarbital* (chemically, phenylethylmalonylurea) has the structure below:

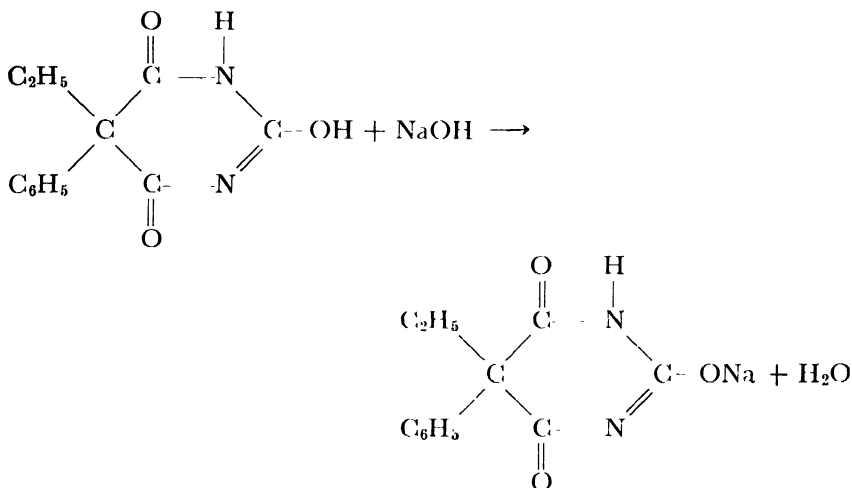


Phenobarbital (phenylethylmalonylurea)

All the barbiturates are *insoluble* in water, but *soluble* in water containing base. This suggests, and correctly so, that barbiturates form soluble alkali salts. It is for this reason that malonyl urea is called "*barbituric acid*," although no carboxyl group is present. The acidity is explained by the vacillation of one of the hydrogen atoms between one of the nitrogen atoms and the CO, or carbonyl group. This may be represented thus:



The so-called *enol* form above is acidic; i.e., it has a replaceable hydrogen. This is consistent with the statement made earlier (relative to carboic acid) that a hydroxyl group attached directly to a ring has acid properties. The sodium salt of phenobarbital is formed thus:



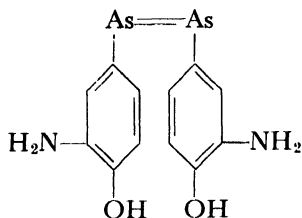
Phenobarbital sodium

Many other compounds are known which represent a mixture of the keto and enol in equilibrium. This phenomenon is called *tautomerism*.

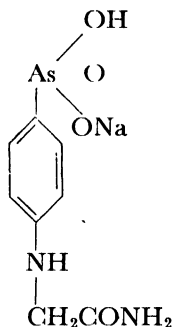
METALLIC DERIVATIVES OF ORGANIC COMPOUNDS

Several compounds used in medicine are organic compounds whose molecules contain one or more atoms of some metal—usually *arsenic*, *mercury* or *bismuth*. Almost all of these substances are employed as anti-infective agents. The following are the most important.

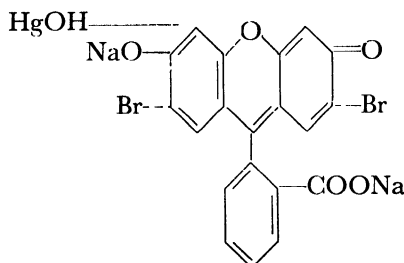
Arsphenamine. Arsphenamine, commonly known as *salvarsan* or “606,” was synthesized by Ehrlich and introduced by him for the treatment of *syphilis*. Although superseded by penicillin, arsphenamine deserves special mention because it gave birth to the concept of *chemotherapy*, i.e., the treatment of an infectious disease with a specific chemical substance. Arsphenamine (3,3'-diamino-4,4'-dihydroxyarsenobenzene) has the following structure:



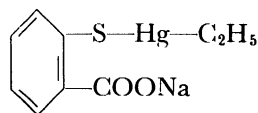
Tryparsamide. Tryparsamide has proved highly successful in the treatment of human *sleeping sickness*. Tryparsamide is an arsenic derivative of aniline with the following structure:



Mercurial Antiseptics. Several organic compounds containing mercury are used as antiseptics and disinfectants. *Mercurochrome* and *Merthiolate*, for example, have the structures shown below:

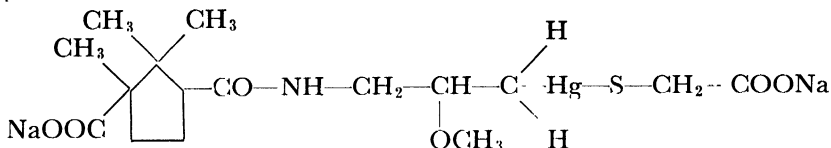


Mercurochrome



Merthiolate

Mercurial Diuretics. The most effective *diuretics* used in medicine are the so-called *mercurials*. One popular such agent—*Thiomerin*—has the following structure:

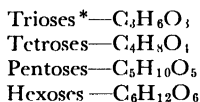


CARBOHYDRATES

Carbohydrates constitute a very large class of organic compounds whose members contain *carbon*, *hydrogen* and *oxygen* only, the hydrogen and oxygen being in the ratio of 2:1, respectively. Of chief interest to us is the fact that carbohydrates represent *one* of the *three* great classes of foodstuffs. In addition to their ability to sustain life, carbohydrates are essential raw materials of many industries.

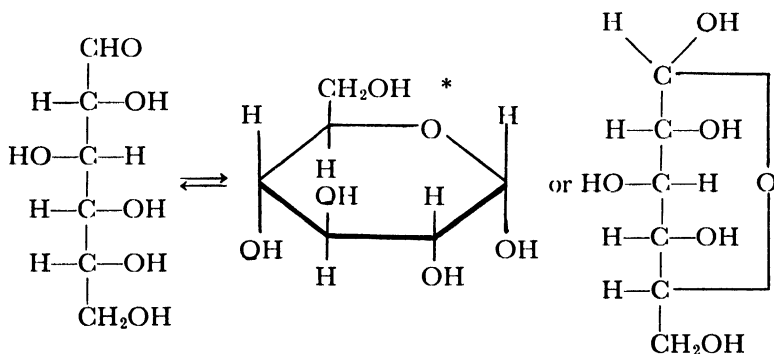
In very broad terms, carbohydrates may be placed into one of two categories of compounds: those that are crystalline and sweet, called *sugars*; and those that are tasteless and noncrystalline such as *starches*, *celluloses* (woody substances) and *similar substances*. Sugars are classified as *monosaccharides* and *disaccharides*; starches and celluloses are classed as *polysaccharides*.

Monosaccharides. Monosaccharides, or *simple sugars*, are carbohydrates which cannot be further hydrolyzed (i.e., broken down into simpler substances) with dilute acids. Monosaccharides are constituted by molecules which contain aldehyde or ketone groups linked directly to carbons containing hydroxyl groups. Monosaccharides are classified according to the number of carbon atoms; i.e., they may contain from 3 to 6 atoms per molecule. There are, therefore, 4 subclasses of monosaccharides:



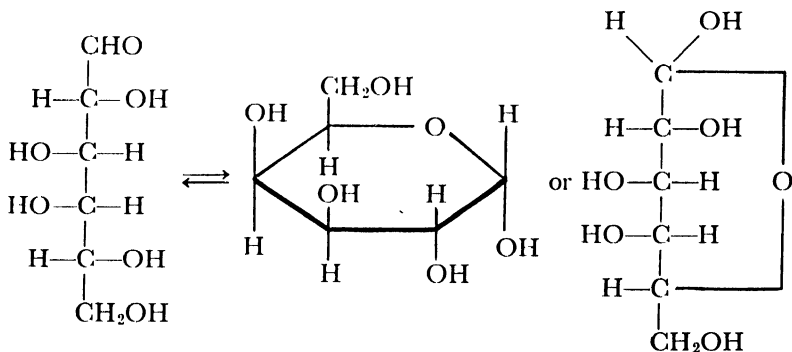
* The ending *-ose* generally refers to carbohydrates.

Of the above classes, the hexoses are by far the most outstanding monosaccharides. Among the hexoses, *glucose*, *fructose* and *galactose* are the most important members. These three hexoses (like all hexoses) have the same empirical formula, and are, therefore, *isomeric*. Their structural formulas are as follows. (Since there is evidence for both a *chain* and *ring* structure, both are given. It is quite probable that the chain and ring form coexist in equilibrium.)

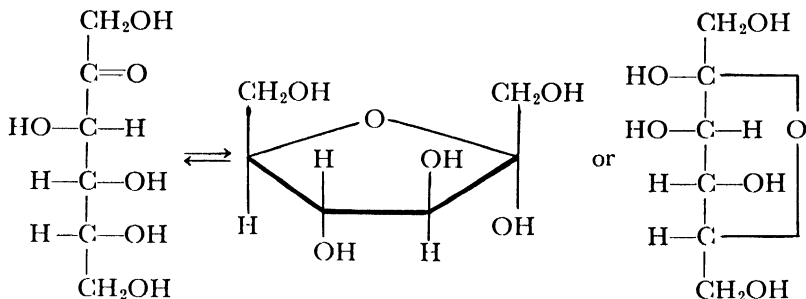


Glucose

* The ring is perpendicular to the plane of the paper, with the heavy lines facing out. The groups attached to the ring are perpendicular to the plane of the ring. The structure at the right is the older type ring.



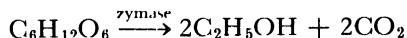
Galactose



Fructose

GLUCOSE. Glucose (also called *dextrose* or *grape sugar*) is one of the most important carbohydrates; physiologically, it is the *most* important. Glucose is present in the juice of many sweet fruits and in the blood of all animals. Commercially, it is prepared by the hydrolysis* of disaccharides and polysaccharides.

Physically, glucose is a sweet, white, crystalline solid, soluble in water. Glucose is optically active; dextro- or d-glucose is the common form. Chemically, glucose reacts with a number of compounds. Its chemical behavior is attributable mostly to the presence of the aldehyde or CHO group. For example, it produces a positive test with *Fehling's* or *Benedict's solution*. (At the present time Benedict's solution is used routinely to test for the presence of glucose in the urine.) As pointed out before, the enzyme *zymase* (present in yeast) converts glucose into alcohol and carbon dioxide (alcoholic fermentation):



* The term hydrolysis is applied to any reaction in which water takes part in the reaction.

In plant tissues glucose reacts with a number of diverse substances to form a valuable class of compounds called *glucosides*. Similar compounds of the other monosaccharides are generally called *glycosides*. Many glucosides and glycosides possess physiologic activity.

Glucose is used extensively in making candy, jellies, preserves, syrups, alcoholic beverages, and similar items. Its physiologic importance will be discussed under biologic chemistry. For now, let us say that glucose is the principal end product of carbohydrate digestion. It is common knowledge that glucose is used in medicine for *intravenous alimentation*, i.e., "feeding by vein."

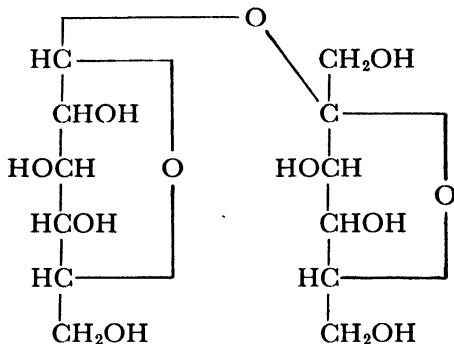
GALACTOSE. Galactose is obtained by the hydrolysis of *lactose*, or *milk sugar*. It reduces *Fehling's solution*, but is *slowly* fermented by yeast. Galactose is of concern primarily because it is one of the end products of digestion; i.e., it is absorbed into the blood along with glucose and fructose.

FRUCTOSE. Fructose (commonly called *levulose*) is present in honey. It is about 50 per cent sweeter than sucrose. It may also be obtained by the hydrolysis of cane sugar, or sucrose. Like the other two hexoses, it reduces *Fehling's solution*. Fructose may be distinguished, however, by a number of tests. Physically, chemically and physiologically fructose is much like glucose. Fructose is of extreme physiologic interest.

Disaccharides. Disaccharides are sugars which are synthesized in the tissues of plants from 2 monosaccharide molecules. The most important disaccharides are those formed from hexose molecules, viz., glucose, fructose and galactose. *Sucrose*, *lactose* and *maltose* are the most important disaccharides. All three are *isomeric*.

SUCROSE. Sucrose ($C_{12}H_{22}O_{11}$), or *cane sugar*, is physiologically the most important disaccharide. When an aqueous solution of sucrose is heated with dilute acid (hydrolyzed), it yields a mixture of *glucose* and *fructose*; this mixture is referred to as "invert sugar." The enzyme *sucrase* (present in the intestinal juice) brings about the same reaction. From this information, the chemist has suggested the structure shown at the top of page 228. Unlike the other common sugars—glucose, fructose, galactose, maltose and lactose—sucrose does not reduce *Fehling's solution*.

Sucrose is obtained from sugar cane and sugar beets. Essentially, the extraction process is carried out as follows: The juice is pressed from the cane or beets and separated from the insoluble fiber. Next the albuminous impurities in the juice are precipitated and filtered off. The filtrate is then evaporated at low temperatures under vacuum; *this causes the sugar to crystallize out*. The thick brown "mother liquor" remaining



Sucrose

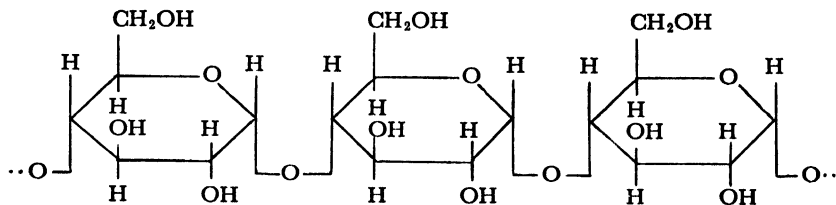
after crystallization is known as molasses. Molasses—which contains about 50 per cent sucrose—is used in making alcohol, table syrup and rum. When sucrose is heated above its melting point, a brown substance called *caramel* is formed. Caramel is commonly used to color foods.

LACTOSE. Lactose ($C_{12}H_{22}O_{11}$), or *milk sugar*, is present in milk to the extent of about 4 per cent. On acid or enzyme (*lactase*) hydrolysis, 1 molecule of lactose yields 1 molecule of *glucose* and 1 molecule of *galactose*. The souring of milk is due to the conversion of lactose to *lactic acid* by the action of certain enzymes in the milk. Lactose may be differentiated from many sugars by the fact that it is not fermented by ordinary yeast. Lactose is less sweet than sucrose and maltose. Lactose reduces *Fehling's solution*.

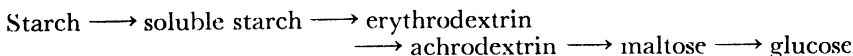
MALTOSE. Maltose ($C_{12}H_{22}O_{11}$), or *malt sugar*, is found in malt (malt is the sprouting grain of barley). When a solution of maltose is hydrolyzed by acids or by *maltase* (present in the small intestine), 1 molecule of maltose yields 2 molecules of *glucose*. Maltose is a reducing sugar.

Polysaccharides. Polysaccharides are *polymers* of the monosaccharides. This is proved by the fact that all polysaccharides may be hydrolyzed by acids and enzymes to monosaccharides. As stated previously, polysaccharides are noncrystalline, insoluble, tasteless substances. The following polysaccharides with the formula $(C_6H_{10}O_5)_x$ are the most important. (This formula means that these substances are formed from an indefinite number of hexose [usually glucose] molecules which have undergone polymerization.)

STARCH. Starch is a general term applied to a variety of similar polymers of glucose (e.g., cornstarch, potato starch, etc.). Starch with the empirical formula $(C_6H_{10}O_5)_x$ may be represented as follows:



Upon hydrolysis (by acids or enzymes) starch yields glucose as the final product. It is interesting to note, however, that several intermediate products are formed. The most important steps of the hydrolysis may be represented as follows:

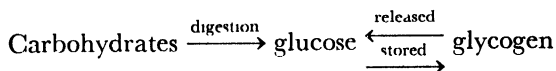


When boiled with water, starch granules swell and burst, forming a colloidal sol known as “starch paste.” The intense *blue* color which starch gives with *iodine* is highly characteristic, and of great analytical value.

Starches are widely distributed in the vegetable kingdom. They are synthesized from glucose formed in the process of photosynthesis. Starch is the principal carbohydrate food of plants and animals. Before it can be converted to energy, however, it must be converted (digested) to glucose. Starch, therefore, represents stored carbohydrate—or energy.

DEXTRIN. Dextrin $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ is the term applied to a variety of polymers obtained in the course of the hydrolysis of starch by enzymes; they are, therefore, less complex than starches. Dextrins which give a reddish-brown color with iodine are called *erythrodextrins*; those which do not give a color are called *achrodextrins*.

GLYCOGEN. Glycogen $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ —sometimes called “animal starch”—is found in animals, especially in the liver. Like the starches and dextrins, glycogen is a polymer of glucose; i.e., it yields glucose upon hydrolysis. When excess carbohydrate is taken into the body it is stored as glycogen. This may be represented thus:



Glycogen gives a *red* color with iodine.

INULIN. Inulin $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ is a polysaccharide found in the tubers of the Jerusalem artichoke and certain other plants. Unlike starch, it is

soluble in hot water, and gives a negative reaction with iodine. Inulin is unique in that it yields fructose when hydrolyzed.

CELLULOSE. All plant cells—in contrast to animal cells—contain a polysaccharide called cellulose ($C_6H_{10}O_5$). Cellulose is the chief constituent of the cell wall. (Cotton fiber is almost pure cellulose.) When hydrolyzed by acids, cellulose yields glucose. In general, however, cellulose is highly inert; for example, it is not acted upon by digestive enzymes.

Cellulose is of enormous industrial value—perhaps it is the most important single raw material available at the present time. In the form

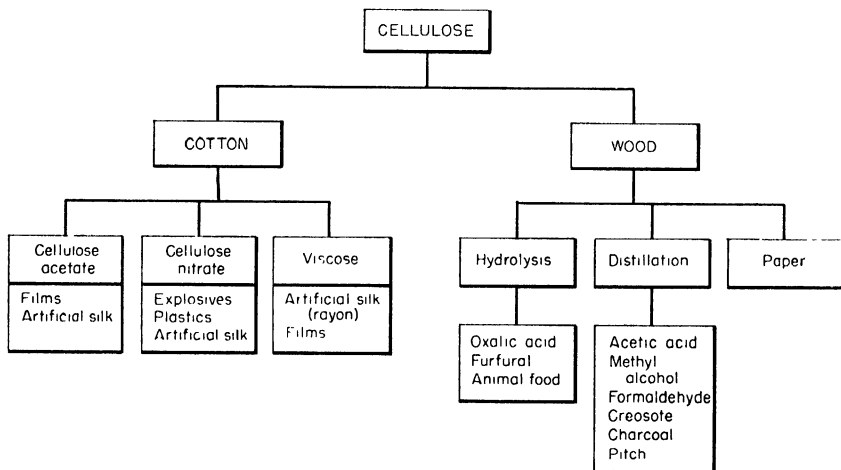


Fig. 46. Derivatives and products of cellulose.

of cotton and wood, cellulose is used in the manufacture of more than 50 different kinds of products; *rayon*, *lacquers*, *plastics*, *food*, *chemicals*, *explosives* and *paper* are but a few examples. Figure 46 presents in a diagrammatic manner some important cellulose products.

OTHER POLYSACCHARIDES OF CONCERN. Other polysaccharides of practical and theoretical importance include *gums*, *pectins* and *mucilages*. Gums (e.g., gum arabic, gum tragacanth) are carbohydrates combined with acids; mucilages are substances which form viscous liquids; and pectins are polysaccharides present in fruit. The gelatinization of fruit extracts is due to the action of pectin.

Molisch Test. All carbohydrates give the Molisch test. This simple and valuable test is performed by treating the substance under investigation with α -naphthol and concentrated H_2SO_4 . If the substance is a carbohydrate (or contains a carbohydrate) a *violet* color is produced.

Summary. From what has been briefly stated above, we can easily see that carbohydrates are of extreme interest to the organic chemist and biologist. The student will do well to understand and appreciate how they are related. Figure 47 succinctly presents the

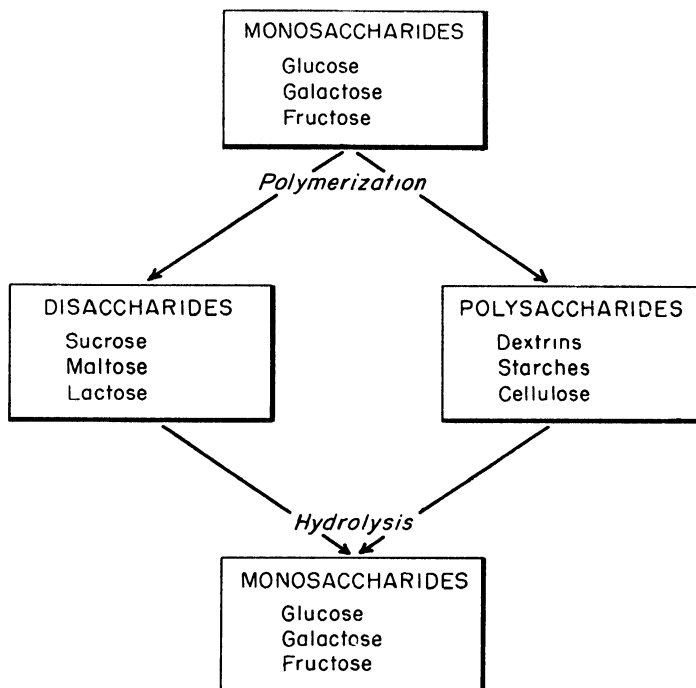


Fig. 47. Relationship of the principal carbohydrates.

cardinal facts relative to the classification of the most important carbohydrates.

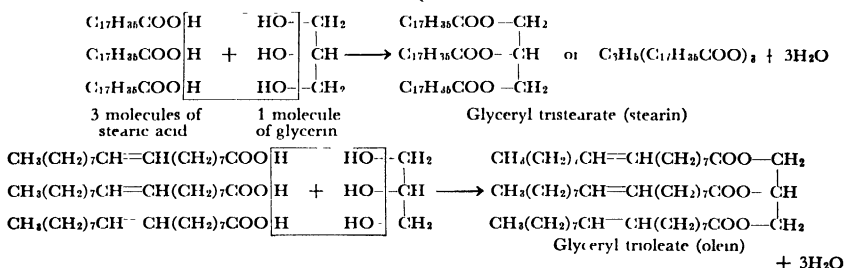
LIPIDS

Lipids include *fats*, *oils*, *waxes* and certain miscellaneous substances of biochemical and physiologic importance. These compounds are considered as a class by virtue of their "fatlike" physical and chemical properties. Sometimes the older term *fat* is employed synonymously with the term *lipid*.

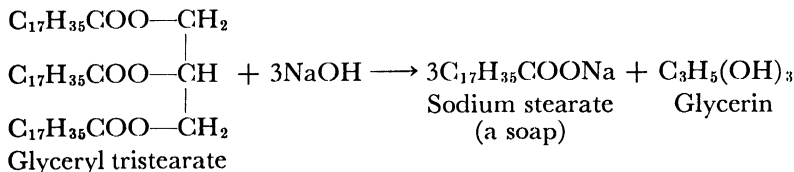
Fats and Oils. Fats are *glyceryl esters* of high molecular weight *saturated fatty acids*; oils are *glyceryl esters* of high molecular weight *unsaturated fatty acids*. This slight chemical difference accounts for their physical difference; i.e., fats are solid at ordinary temperatures, while

oils are liquid. There is, therefore, no great difference between the two types of compounds.

The glyceryl esters of stearic ($C_{17}H_{35}COOH$), palmitic ($C_{15}H_{31}COOH$) and oleic ($C_{17}H_{33}COOH$) acids constitute the bulk of all the fats in vegetable and animal tissues.* The biosyntheses of glyceryl tristearate (commonly called *stearin*)—a typical fat—and glyceryl trioleate (*olein*)—a typical oil—are as follows:



SAPONIFICATION. The hydrolysis of any ester employing alkali (i.e., NaOH or KOH) may be called *saponification*. Usually, however, the term is applied to the reaction between an *alkali* and a *fat* or *oil*. In this reaction, the sodium or potassium salt of a fatty acid—called a *soap*—and *glycerin* are formed. The following reaction is employed in the manufacture of soap:

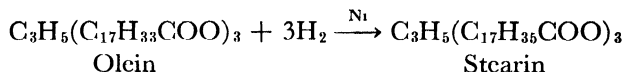


The kind of soap produced depends upon the type of fat or oil, and whether sodium or potassium hydroxide is used. Glycerin is a by-product of the process.

In the body, fats are hydrolyzed in a similar manner by the enzyme lipase. This will be discussed under digestion.

HYDROGENATION. Vegetable oils may be converted to fats by means of hydrogen and nickel (which acts as a catalyst); this process is called *hydrogenation*. What happens is this: The *unsaturated* glyceryl esters form addition products, or *saturated* esters. For example, olein (glyceryl trioleate)—a liquid—becomes stearin (glyceryl tristearate)—a solid. The reaction is as follows:

* In nature, a fat is almost always a mixture of fatty compounds; e.g., human fat contains the glyceryl esters of stearic, palmitic, oleic, butyric acids, and others.



The popular lard substitutes such as Crisco and Spry are prepared by the hydrogenation of cottonseed oil, peanut oil and other edible oils.

PROPERTIES. Fats and oils in the crude condition range in color from yellow to red. When refined, however, they are usually a pale yellow or colorless. All fats and oils are insoluble in water, but readily soluble in such organic solvents as ether, benzene and chloroform. The rancidity of fats results from any chemical action (hydrolysis or oxidation) which yields free fatty acid. The disagreeable odor of rancid butter, for example, is due to butyric acid (butter is chiefly glyceryl tributyrate).

ACROLEIN TEST. When fats and oils are strongly heated—alone or with a dehydrating agent such as KHSO_4 —a strong and penetrating odor is produced due to the formation of a compound called *acrolein*. Acrolein is derived from the glyceryl portion of the fat molecule. This reaction is used as a test for fats, oils and glycerin.

Another test—crude, but of some practical value—is to place a little fat or oil on a piece of paper; when held against a source of light, the spot is seen to be *translucent*.

Waxes. Waxes are the esters of high molecular weight alcohols (such as cetyl, $\text{C}_{16}\text{H}_{33}\text{OH}$, myricyl, $\text{C}_{30}\text{H}_{61}\text{OH}$, etc.) and fatty acids. Beeswax, for example, is *myricyl palmitate* ($\text{C}_{15}\text{H}_{31}\text{COOC}_{30}\text{H}_{61}$).

Waxes, like fat, are insoluble in water, but soluble in organic solvents, viz., ether, benzene, chloroform and carbon tetrachloride. Since they are not glyceryl esters, they may be differentiated from fats and oils by the *acrolein test*; i.e., they give a negative test. Waxes are widely distributed in the tissues of both plants and animals. The following waxes are of commercial importance.

<i>Wax</i>	<i>Source</i>	<i>Use</i>
Beeswax	Bee	Ointments, candles
Lanolin	Wool fat	Ointments, emulsions, etc.
Spermaceti	Head of sperm whale	Ointments, candles
Carnauba	Palm	Varnishes, candles

Other Lipids. There are many fatlike substances other than fats, oils and waxes of physiologic importance. These substances are impor-

tant because they are associated with certain types of tissue (e.g., nervous, muscle), and with certain biochemical reactions. Most such lipids may be placed into one of two categories: *phospholipids* or *cerebrosides*. Phospholipids are complex compounds whose molecules are constituted by a *fat*, *phosphoric acid* and a *quaternary base* (such as choline); cerebrosides contain a *fatty acid*, some *sugar* and some *amine*. *Lecithin* and *cephalin* (both phospholipids) deserve a word or two. Lecithin is now known to be an important agent in the transfer of fat throughout the body; any interference with its synthesis is now thought to play a part in a derangement known as a *fatty liver*. Cephalin (also kephalin) is a constituent of the blood concerned with the clotting mechanism.

PROTEINS

In some inconceivable fashion a complex class of compounds called proteins* (together with certain other substances) is tailored by the hands of nature into the substance of life—*protoplasm*. Some of the most brilliant investigations in the annals of science have been in the area of protein chemistry. Although the chemist is far from writing the prescription of life, he has elucidated a number of nature's puzzles. At the present time the protein chemist has a pretty good idea of how many key substances are put together. Recently, the synthesis of a protein hormone was announced. Just this fact alone indicates the wealth of information in the possession of the chemist. In this section, we shall learn those facts of protein chemistry which are essential to an adequate understanding of many physiologic processes.

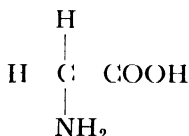
Amino Acids. It will be recalled from our discussion of carbohydrates that polysaccharides are hydrolyzed to monosaccharides; i.e., polysaccharides are *polymers* of monosaccharides. It has been known for some time that proteins are also *polymers*. As a matter of fact, polymerization is epitomized by the protein molecule. When proteins are hydrolyzed (by acids, alkalis or enzymes), *amino acids* are produced as the end products. Thus, proteins may be regarded as high polymers of amino acids. Some idea of the extent of polymerization can be gained from their molecular weight; for example, *hemoglobin* has a molecular weight of 68,000, and *globulin* (present in blood plasma), 104,000.

An amino acid is an acid in which a hydrogen atom has been replaced

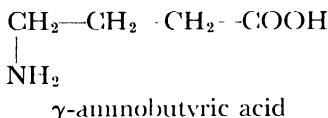
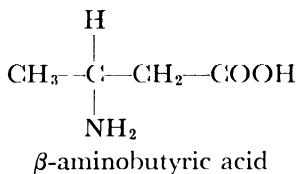
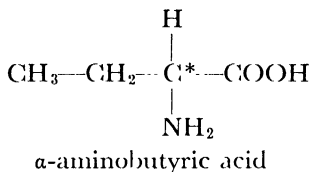
* Approximate elementary composition of most proteins.

Carbon	53%
Hydrogen . . .	7
Oxygen	23
Nitrogen . . .	16
Sulfur	1

by an *amino* (NH_2) group. *Glycine* (aminoacetic acid), the simplest amino acid, has the following structure:



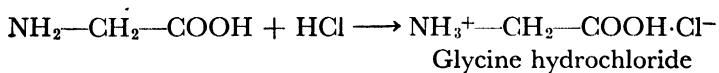
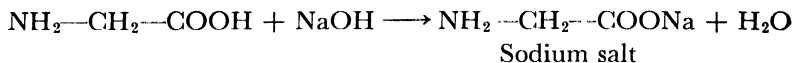
Amino acids are named according to the position of the NH_2 group. The following structures are named as indicated:



* The carbon atom adjacent to the carboxyl group is called alpha, the next beta, gamma, and so on.

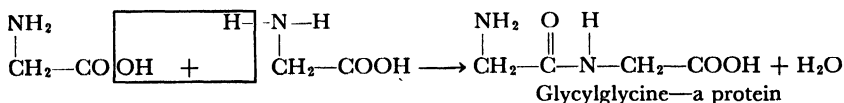
Since the α -amino acids are the ones derived from proteins, they are, physiologically, the most important.

Aside from the ability of amino acids to polymerize, they are also unique in that they are *amphoteric*; i.e., they react like acids toward bases, and like bases toward acids. For example, glycine reacts as follows:

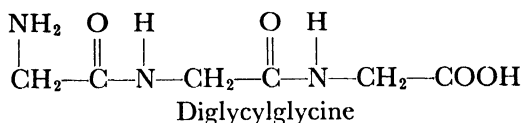


This amphoteric character is reflected by the protein molecule; thus, proteins are able to neutralize both acids and bases.

Structure. The simplest possible protein is glycylglycine—formed from two molecules of glycine in the following manner:

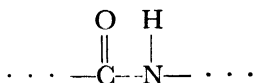


Glycylglycine, in turn, can combine with another molecule of glycine to form the following structure:

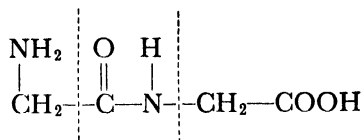


This structure can unite with another glycine molecule, and so on.

The above reactions give some idea of how protein molecules are constituted. Of course, polymers need not involve only one amino acid. Usually proteins are constituted by *several* different amino acids. It is to be noted that amino acids combine with one another in the following way: 1 hydrogen atom from the amino group of one acid unites with the hydroxyl group (from the carboxyl group) of the other acid; i.e., water is split out. As a result, the acid residues are held together by a so-called *peptide bridge*, i.e.:



Thus, glycylglycine contains one peptide bridge:



Simple proteins (proteins whose exact structures are known) are referred to as *polypeptides*. Glycylglycine is a *dipeptide*, diglycylglycine a *tripeptide*, and so on.

The hydrolysis of protein substances has yielded about 25 amino acids. Those of greatest physiologic importance are presented in the table as follows:

*Essential Amino Acids**

Isoleucine
Leucine
Lysine
Methionine
Phenylalanine
Threonine
Tryptophane
Valine

* Since these amino acids cannot be synthesized in the body, they must be furnished in the diet; i.e., they are *essential*.

Classification. The fact that amino acids polymerize an infinite and indefinite number of times plus the fact that an infinite number of combinations are possible (natural proteins average about 15 different amino acids) correctly suggest a huge number of compounds. It is essential, therefore, that we have some reasonable method of classification. Although by no means perfect, the following classes are of aid in our study. Since chemical properties alone are inadequate as sole criteria, physical and biologic properties are also considered. Only the more important classes are given.*

ALBUMINS. Probably the best example of an albuminous protein is egg white (which is principally *ovalbumin*). Albumins are widely distributed in animal tissues. Serum albumin is a vital constituent of the blood. Albumins are *soluble in water* and *coagulated by heat*.

GLOBULINS. Globulins look like albumins. They are *insoluble in water*, and *coagulated by heat*. The immunity factors in the blood have been shown to be associated with a particular kind of globulin—*gamma globulin*.

PROTAMINES. Protamines are relatively simple proteins, i.e., they yield only 4 or 5 amino acids on hydrolysis. They are unique in that they are found in the heads of mature spermatozoa. One variety of protamine (from salmon) is used in the preparation of *protamine zinc insulin*.

ALBUMINOIDS. Albuminoids are characterized by their extreme insolubility in chemical reagents. It is natural, therefore, that they should be found in the body's connective tissues. Keratin and collagen are important examples.

* Another classification places a protein into one of 3 groups—*simple, conjugated* or *derived*. Simple proteins are those which are hydrolyzed to *amino acids only*; conjugated proteins are those hydrolyzed to amino acids *plus a nonprotein substance*; derived proteins are natural proteins which have been altered by some physical or chemical process. The protein classes mentioned in the text fall into these 3 groups.

NUCLEOPROTEINS. Nucleoproteins are extremely complex combinations of *proteins* and *nucleic acids*. Nucleoproteins are characterized by the fact that they are found in the nuclei of cells.

GLYCOPROTEINS. Glycoproteins are protein substances which yield a sugar upon hydrolysis. Mucin—present in the mucous secretions of the body—is a glycoprotein.

PHOSPHOPROTEINS. Phosphoproteins contain phosphorus. They are very similar to nucleoproteins. Casein in milk is a phosphoprotein.

CHROMOPROTEINS. Chromoproteins, as the name indicates, are colored. Upon hydrolysis they yield a protein and a pigment. For example, hemoglobin (present in the red cells of the blood) yields the protein, *globin*, and the pigment, *heme*; heme contains *iron*. Chlorophyll, the green pigment of plants, and heme differ only in the metal present—chlorophyll contains *magnesium*.

Products of Hydrolysis. When any protein is subjected to hydrolysis (either by acids, bases or enzymes), it yields amino acids as the final products. Before the amino acid stage is reached, however, there are many intermediate products formed which possess singular properties. For our purpose let us say that a protein upon hydrolysis passes through the following intermediates. (Of course, each stage represents a less complex molecule than the one preceding it.)

Proteins $\longrightarrow$ metaproteins $\longrightarrow$ proteoses $\longrightarrow$ peptones
 $\longrightarrow$ polypeptides $\longrightarrow$ amino acids

When we discuss digestion in the following chapter, we shall refer to the hydrolysis of protein substances.

Properties. Physically, proteins are characterized by the fact that they are destroyed or “denatured” by heat. This is usually manifested by a change of color and solubility. For example, egg white, which is colorless and soluble in water, is changed to a white insoluble mass. Anyone who has ever fried an egg has observed this phenomenon. Heat kills cells because the proteins of the protoplasm are denatured. Proteins are not soluble in strong alcohol or in solutions of salts such as ammonium sulfate. This fact is often taken advantage of when it is desired to separate a protein from other substances.

Alkaloidal reagents (e.g., tannic acid, picric acid) and the salts of heavy metals (lead, mercury, silver, copper) react with proteins to form precipitates. This action of heavy metals is thought to account for their antiseptic and disinfecting properties—i.e., they react with the protoplasm of the bacterial cell, thereby destroying it.

Color Tests. There are a number of color tests used as an aid in the identification of protein substances. These tests in conjunction

with the chemical and physical properties cited above will usually establish the identity of a protein. Probably the two most popular tests are the *biuret* and *xanthoproteic*.

BIURET. When a protein is mixed with a concentrated solution of *sodium hydroxide* and a drop or two of dilute *copper sulfate* solution, a *violet* or *pink* color results. This reaction is thought to be due to the peptide bridge.

XANTHOPROTEIC. When a protein is heated with *concentrated nitric acid* a *yellow* color is produced. Upon the addition of an excess of *ammonium hydroxide* the yellow color is changed to an *orange* color.

RETROSPECT

Throughout the chapter we have constantly and consistently pointed out *relationships* and made *general* statements; in other words, we have exerted every effort to see the subject of organic chemistry as a whole.

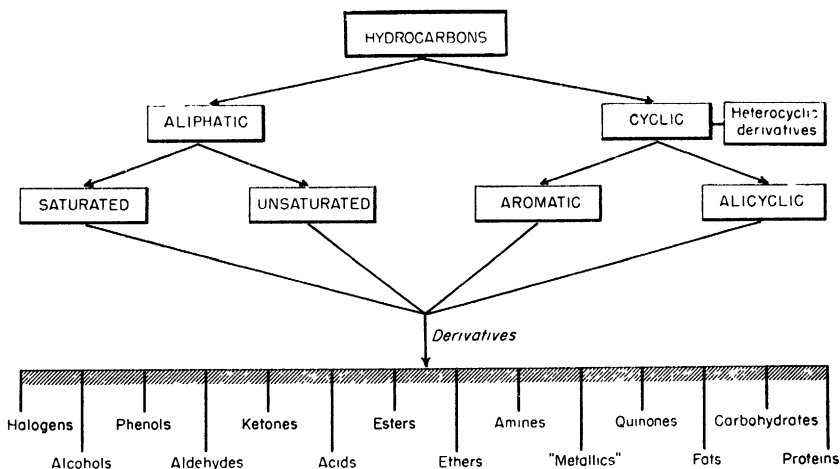
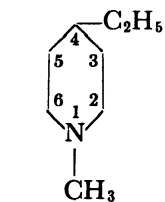
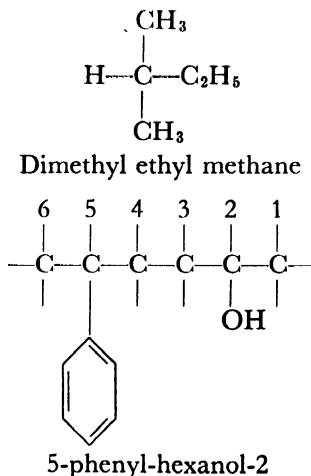


Fig. 48. Relationship of the principal organic classes.

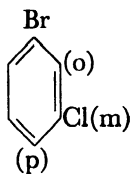
Only in this way can such a subject be understood and appreciated. As a final act toward this goal, let us refer to the following figures: Figure 48 presents an outline of the various organic classes we have studied; Figure 49 illustrates (in the way of review) the manner in which a few simple and complex organic compounds are named; and Figure 50 illustrates the complete synthesis of an organic compound. Those of us who are able—in a *general* way—to derive some degree of meaning

from these figures may have reason to believe that they have successfully digested the contents of this chapter.

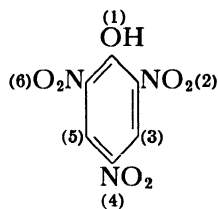
Although organic chemistry is unquestionably a complex study, the interest it provokes through its vital teachings empowers the student with a healthy and successful attitude.



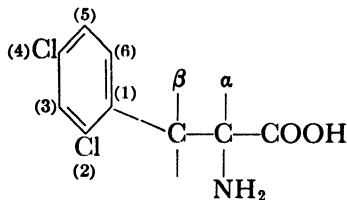
1-methyl-4-ethyl-piperidine



m-bromochloro-benzene



1-hydroxy-2,4,6-trinitro-benzene or, 2,4,6-trinitrophenol



α -amino- β -2,4-dichlorophenylpropionic acid

Fig. 49. The above names are illustrative of the method employed in the naming of simple and complex organic compounds.

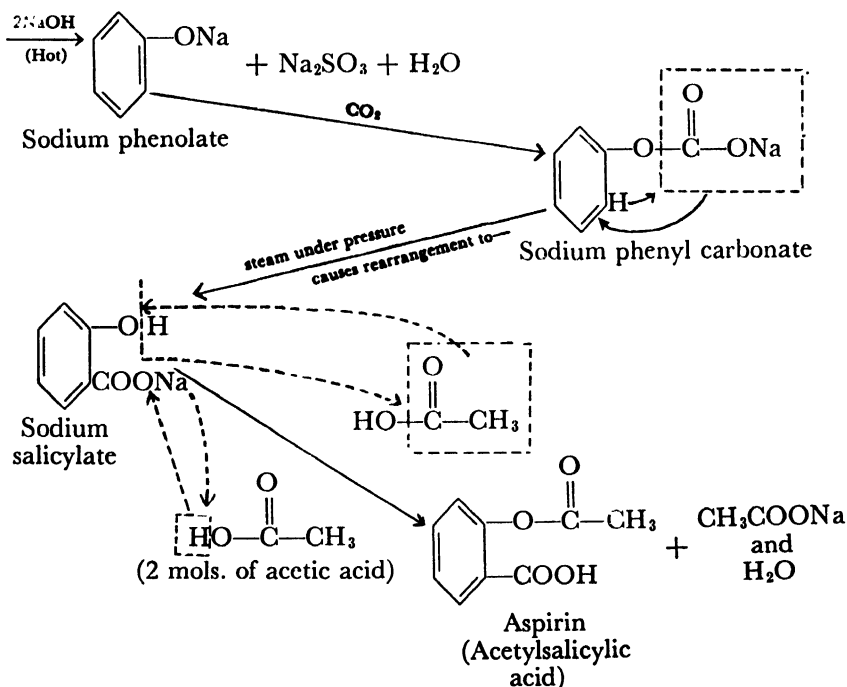
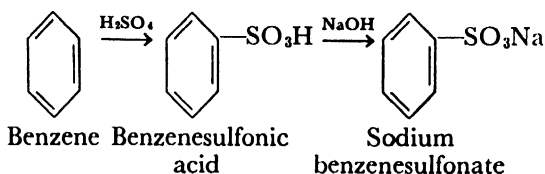
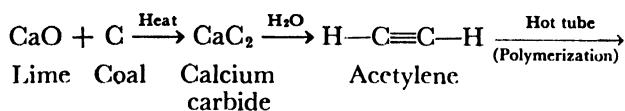


Fig. 50. The above synthesis is intended to show that the chemist can synthesize complex and useful compounds from simple inexpensive substances.

QUESTIONS

I. Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

A.

Column I

- _____ a characteristic property of carbon atoms
- _____ isomers
- _____ structural formula
- _____ empirical formula
- _____ charring
- _____ covalence
- _____ conduct a current
- _____ the synthesis of urea
- _____ bond
- _____ 4

Column II

- 1. "a graphic" formula
- 2. valence of carbon
- 3. same empirical formula
- 4. sharing of electrons
- 5. ability to unite with each other
- 6. only tells us the number of atoms
- 7. a line which denotes a shared pair of electrons
- 8. electrovalent compounds
- 9. due to the presence of carbon
- 10. demonstrated that man could mimic nature

B.

- _____ fractional distillation
- _____ methane series
- _____ one double bond
- _____ acetylene series
- _____ "aromatic" substances
- _____ a saturated ring
- _____ 2 fused benzene rings
- _____ anthracene
- _____ steroid structure
- _____ coal tar
- _____ petroleum
- _____ substitution
- _____ addition
- _____ carbon and hydrogen only
- _____ a member of a hydrocarbon series

- 1. separation of a mixture's constituents
- 2. homolog
- 3. naphthalene
- 4. a complex mixture of hydrocarbons of natural origin
- 5. 3 fused benzene rings
- 6. also called paraffin series
- 7. hydrocarbons
- 8. derived by destructive distillation
- 9. ethylene series
- 10. a reaction of a saturated compound
- 11. triple bond
- 12. a reaction of unsaturated compounds
- 13. alicyclic
- 14. cyclopentanoperhydrophenanthrene
- 15. benzene and its derivatives

C.

Column I

- - - ROH
- - - phenol
- - - esterification
- CO₂ and alcohol produced
- - - R—O—R
- - - fatty acids
- - - acetic acid
- - - partial oxidation of an alcohol
- - - a ketone
- - - polymers of amino acids
- starches
- sugars
- - - monosaccharide
- - - glycerin
- - - a positive Biuret test
- - - chloroform
- - - carbonyl group
- - - alkaloïds
- - - pyridine
- - - aniline

Column II

1. formed by the oxidation of acet-aldehyde
2. an alcohol
3. proteins
4. an important amine
5. a polyhydroxy alcohol
6. galactose
7. carbolic acid
8. an ether
9. a heterocyclic ring
10. characteristic group of ketones and aldehydes
11. acid plus alcohol
12. insoluble polymers of monosac-charides
13. a violet or pink color
14. fermentation
15. a halogen derivative
16. heterocyclic medicinal agents
17. stearic and palmitic
18. crystalline and soluble in water
19. RCHO produced
20. produced by the oxidation of a secondary alcohol

II.

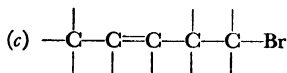
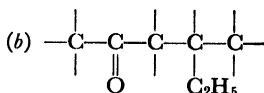
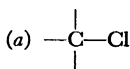
1. Using Cl₂ gas, CH₄ gas and AgOH, show how it is possible to synthesize methyl alcohol (CH₃OH).
2. When ethyl iodide, methyl iodide and sodium metal are reacted together, propane gas is formed. Account for this fact by using structural formulas.
3. Write the equation for the reaction between propylene and bromine water (Br₂).
4. What is the name and formula of the product formed when butanal is oxidized?
5. What is the name and formula of the product formed when propanol is partially oxidized?
6. When HCl is added to aniline (a liquid), a white crystalline solid forms. What is the structural formula for this product?
7. When tincture of iodine is added to olive oil, the color disappears. Explain.
8. When an acid is added to a solution of soap, a white precipitate forms. Explain.

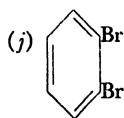
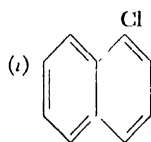
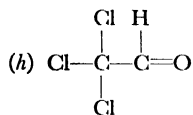
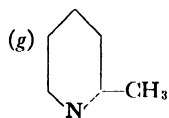
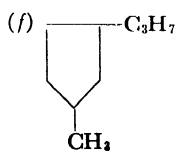
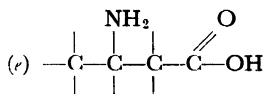
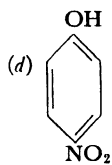
9. Why is lye (sodium hydroxide) effective in removing grease?
10. Morphine is very insoluble in water. When a drop of HCl is added, however, a solution is readily formed. Explain.
11. A nurse was ordered to obtain penicillin—for intravenous injection—from the pharmacist. She noted that the ampule given her was labeled penicillin *sodium*. Explain.
12. From naphthalene, nitric acid, zinc and hydrochloric acid, the chemist is able to synthesize α -naphthylamine. Using structural formulas, write the reactions involved. (Refer to synthesis of aniline.)
13. Glycerin is sweet tasting. On a basis of its formula, offer an explanation.
14. In an emergency, egg white (albumin) may be used as an antidote for acid and alkali poisons. Explain.
15. A few drops of HCl were added to a solution of sucrose, and the resulting mixture boiled for a few minutes. Although sucrose does not give a positive Benedict's test, the above mixture did. Explain.

III. Write structural formulas for the following organic compounds:

1. dibromomethane
2. 3-chloro-butanal
3. 3-methyl-pentanol-1
4. propanoic acid
5. ethyl-butyl ketone
6. dipropyl ether
7. aminoacetic acid
8. β -hydroxybutyric acid
9. propanone
10. p-dichlorobenzene
11. sodium acetate
12. 2,4-dichlorophenylacetic acid
13. β -naphthol
14. 2,4,6-trinitrobenzene (nitro = NO_2)
15. 2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane. (*bis* means two.)
16. hexachlorocyclohexane
17. 1-ethyl-3-methyl-pyridine
18. α -diethylaminoethyl-p-aminobenzoate
19. 1-phenyl-1-(2-pyridyl)-3-dimethylaminopropane
20. ethyl benzoate

IV. Write the names for the following structures (in some cases there are two acceptable names):





CHAPTER 11

BIOCHEMISTRY

Biochemistry is a marriage of the various branches of chemistry—especially organic—and biology; it may be defined, therefore, as the *chemistry of life*. In this chapter we shall direct our attention to the chemistry of the various physiologic systems of the human body. In general, of course, our study will apply to all plant and animal tissues.

PROTOPLASM

The difference between something that is living and something that is dead will probably always appear as a mystery, even to the most brilliant of minds. This is not to say that the scientist will never be able to explain what life is, but rather that he will not be able to comprehend what he has explained. For example, the astronomer can explain the nature of the universe to an unbelievable degree of detail, yet he views the myriad of stars above his head with the same wonderment as the savage. As a matter of fact, the biochemist and the astronomer have a great deal in common: They are both dealing with something infinitely distant from their powers of visualization. Scientifically, therefore, it seems prudent to think of life—i.e., protoplasm—as a concentrated universe of physical and chemical forces operating under the direction of energies derived from their unique synthesis. This statement represents the best attempt of the author to convey, in a *practical* way, the thoughts of the biochemist.

Now let us consider protoplasm on a pure physical and chemical basis. Protoplasm is the “stuff” of life. Specifically, it is the term used to describe the material which constitutes the living cell—plant or animal. The composition of protoplasm is not a mystery; as a matter of fact, we know a great deal about its constituents. Protoplasm is a *viscous, colloidal sol which contains proteins, carbohydrates, lipids, salts and enzymes dispersed or dissolved in water—the chief constituent* (see Fig. 51). That protoplasm is not a simple mixture of these substances is demonstrated by the fact that it carries on *metabolism*; i.e., it consumes oxygen and liberates carbon dioxide and energy. If metabolism stops, our mixture is no longer protoplasm because it is “dead.” The composition of the “living mixture” and the “dead mixture,” however, is the

same. We must assume, therefore, that the constituents of protoplasm are put together by the hands of nature in an extremely delicate manner. With these facts at hand, the chemist is forced to believe that *chemical structure* is one of the chief secrets of protoplasm.

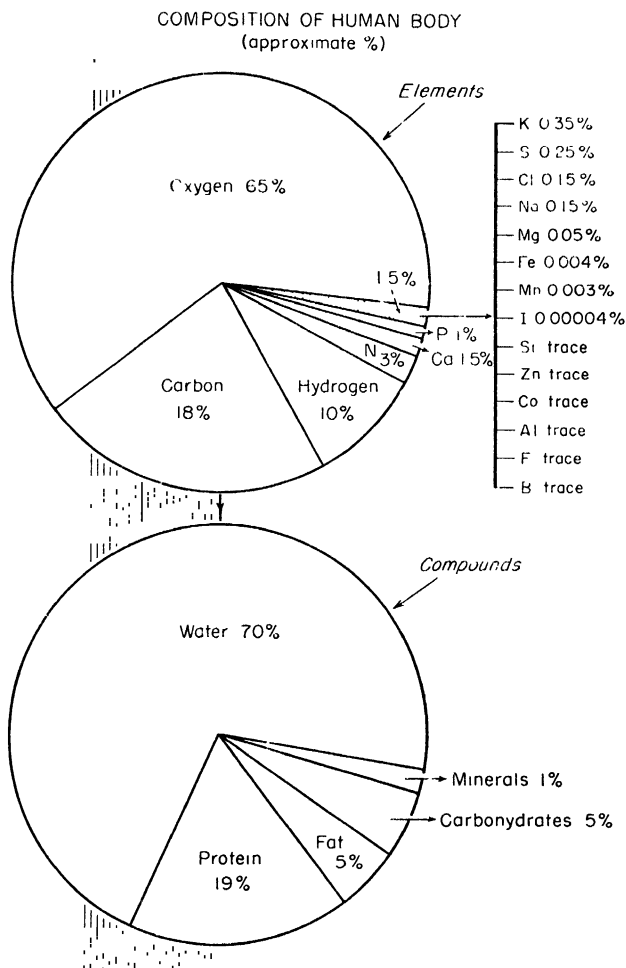


Fig. 51.

For a moment, let us look at one of life's simplest forms—the *ameba*. The *ameba* is a one-celled animal seen only with the aid of the microscope. Size, however, does not interfere with the fundamental manifestations of life; the little *ameba* carries on all the physiologic processes of

higher animals. There is an important and interesting physiologic difference, however: In higher animals we have "specialized protoplasm," i.e., one type of cell to perform each of life's physiologic functions. The physiology and biochemistry of higher forms, therefore, are most logically studied on a basis of the tissues which constitute the various systems.

Enzymes. The complex chemical reactions within (and without) the cells of the body are made possible by a class of catalytic substances called *enzymes*. Thus, an enzyme may be defined as an *organic catalyst*. It is now known that all forms of life depend upon these agents for their existence. Yeast cells, for example, derive their energy through the agency of the enzyme, *zymase*. Zymase converts glucose into alcohol, carbon dioxide and energy.

A number of enzymes have been isolated in the pure crystalline state. Extensive biochemical research has shown that they are *proteins* or proteins joined on to other groups.

Enzymes are also characterized by their extreme *potency* and *specificity*. A few grains of trypsin, for example, will easily convert a pound or two of meat (protein) into amino acids, whereas this enzyme has no action on carbohydrates. Enzymes are very sensitive to their environment, especially to *pH* and temperature changes. The enzyme ptyalin, for example, will not act in a basic medium; trypsin, on the other hand, requires a basic medium. As for temperature, they function best at body heat.

At the present time enzymes are named by adding the suffix *-ase* to a stem derived from the substance (called a "substrate") acted upon. For example, *maltase* converts *maltose* to glucose. Old names, however, such as pepsin, ptyalin and trypsin, are still used. Enzymes may be classified on a basis of the *types* of substrates. For example, the term *carbohydrase* could be applied to all enzymes which act upon carbohydrates. Thus, maltase would be a carbohydrase. The following classes of enzymes, together with representative members, are of physiologic importance. At appropriate places, the individual members will be discussed.

ESTERASES. Esterases are enzymes which hydrolyze organic esters. Examples: *pancreatic lipase* and *phosphatases*.

PROTEINASES. Proteinases hydrolyze proteins to amino acids and intermediate products. Examples: *pepsin*, *trypsin*, *rennin* and *papain*.

PEPTIDASES. Peptidases hydrolyze polypeptides to amino acids. Examples: *aminopolypeptidase*, *carboxypolypeptidase* and *dipeptidase* (erepsin).

PHOSPHORYLASES. Phosphorylases bring about the hydrolysis and synthesis of polysaccharides.

CARBOHYDRASES. Carbohydrases hydrolyze carbohydrates to simpler products: Polysaccharides and disaccharides are converted to monosaccharides. Examples: *sucrase*, *maltase*, *lactase*, *ptyalin*, *pancreatic amylase*.

OXIDASES. Oxidases play a vital role in so-called biologic oxidations, i.e., the utilization of oxygen within the cell. This subject will be discussed later. Important oxidases include: *catalase*, *dehydrogenase*, *peroxidase* and *cytochrome oxidase*.

ESSENTIALS OF LIFE

In order for protoplasm to survive, grow and reproduce itself, it must be supplied with the following chemical substances, or *nutrients*: *carbohydrates*, *fats*, *proteins*, *minerals*, *vitamins*, *water* and *oxygen*.

Water. Water is the basic constituent of protoplasm; all the other constituents are either *dispersed* (in a colloidal fashion) or *dissolved* in it. The bulk of plant and animal tissues, therefore, is due to water. Such vegetables as tomatoes and cucumbers are almost 100 per cent water; animal tissues contain in the vicinity of 70 per cent water.

The water of the body is said to be present in two compartments: *intracellular* and *extracellular*. Intracellular water refers to the water within the cell; extracellular water refers to the water outside the cells—specifically, in the *blood*, *lymph* and *tissue fluid* (Fig. 52). It is now generally accepted and appreciated that the balance—the so-called *water balance*—between these two compartments, and within the extracellular compartment, is one of the most critical situations in physiology. This is so because just about every physical and chemical action within our tissues indirectly affects the *equilibrium* (balance) between the locations mentioned above. For example, *edema* (the accumulation of water in the tissues) and *dehydration* (the loss of intracellular water) attend a large number of pathologic states. In general, any condition which upsets the *composition* (especially of *metallic ions* and *protein*) or the *pressure* (*osmotic*, *hydrostatic*, etc.,) of blood will bring about a shift of water.

Minerals. In nutrition the term *minerals* refers to the salts (usually inorganic) of essential *metals* and *nonmetals*, viz., K, Na, Ca, Mg, Fe, Cu, S, P, F, Cl, I, SO₄, HCO₃. A well-balanced diet supplies an ample amount of such substances. Metallic and nonmetallic ions are present within the cells (i.e., dissolved in intracellular water), and in all the fluids of the extracellular compartment. Although present in relatively small amounts, they play important roles in the distribution of the body's water, the action of enzymes and the formation of bones and teeth.

The cells of the body are particularly sensitive to the *ratio* between

the ionic concentrations (viz., Na^+ , K^+ , Ca^{++}). Any single ion is *toxic* to cells, but this toxicity is antagonized by the presence of others—*ion antagonism*. In order for the body's tissues to function properly, therefore, the *ionic balance* (commonly referred to as *electrolytic balance*)

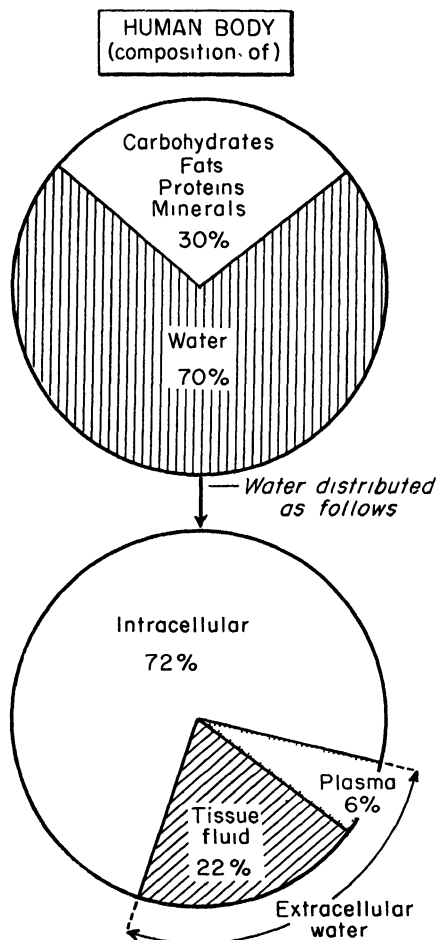


Fig. 52.

must be maintained. Extensive research has indicated that a great many pathologic manifestations are directly due to a shift in the ionic concentrations. Already the principles of electrolyte balance are being employed in medicine. It is now realized that practically all patients—especially those at “low ebb”—are benefited by the intravenous adminis-

tration of electrolyte solutions (NaCl , KCl , CaCl_2) that have been carefully calculated to meet the ionic needs of the patient's body. Figure 53 shows the ionic concentrations of the various fluids of the body.

Oxygen. Oxygen is needed for the oxidation of fuels within the cell to furnish energy for life's functions. Our present information on

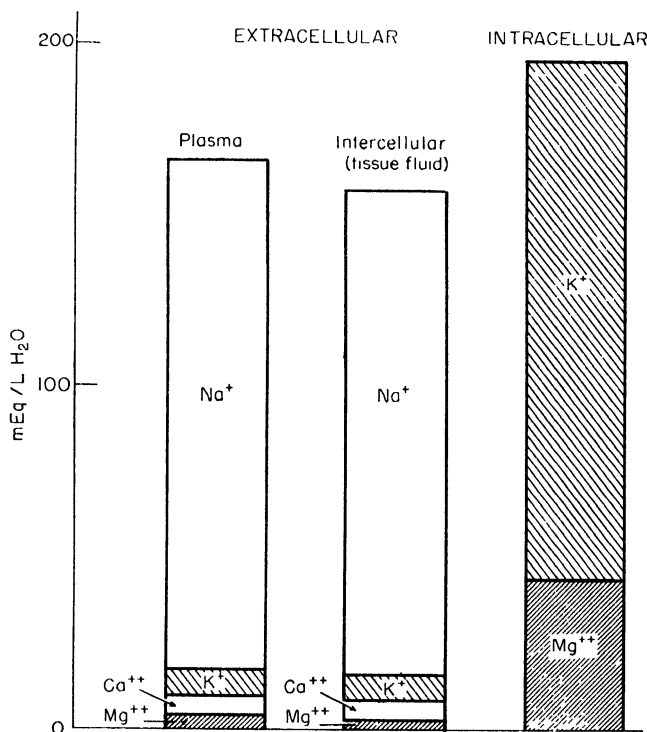


Fig. 53. Ionic concentrations of the body's intracellular and extracellular compartments. Concentrations are expressed as *milliequivalents* per liter (mEq./L.H₂O). 1 milliequivalent of any element is equal to .001 of its *equivalent weight*. The equivalent weight (Eq. w.), in turn, is equal to an element's *atomic weight* divided by its *valence*. Thus, 1 mEq. of Ca^{++} is equal to $\frac{40}{2} \times 0.001$, or 0.02 gm. (Modified from Gamble, J. L.: *Chemical Anatomy, Physiology and Pathology of Extracellular Fluid*, Ed. 5. Cambridge, Mass., Harvard University Press, 1949.)

this subject definitely shows that this is not a conventional type of "burning." As a matter of fact, the way in which energy is gained by the cell has proven to be one of nature's most uncanny and cunning chemical tricks. The important details will be given under the topic of respiration.

Vitamins. Since the beginning of the century it has been realized that certain nutritional factors other than water, minerals, carbohy-

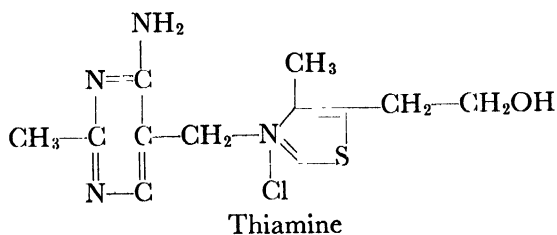
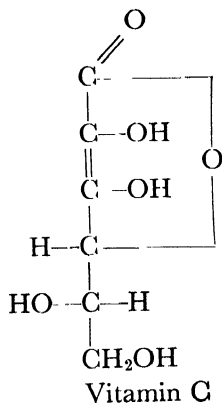
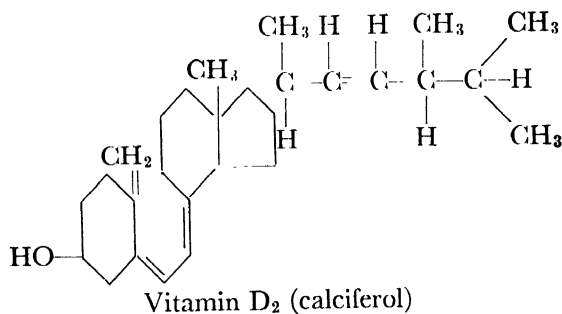
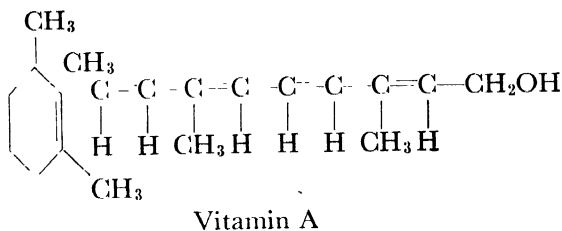


Fig. 54. Chemical structure of some vitamins.

drates, fats and proteins are essential to animal and human life. Concrete ideas, however, were not available until Hopkins in 1906 demonstrated that normal foods do contain *accessory factors*. In 1911 Funk, who believed that these accessory factors were organic *amines* (i.e., containing the NH_2 group), suggested the term *vitamine*. Further work by many investigators disclosed that the amino group was not character-

Table of Vitamins

<i>Group*</i>	<i>Other Common Name</i>	<i>Important Natural Source</i>	<i>Deficiency State</i>
Fat-soluble:			
Vitamin A	—	Fish-liver oils	Night blindness, xerophthalmia, keratinization of skin
Vitamin D	—	Fish-liver oils	Defective bone formation (e.g., rickets)
Vitamin E	—	Leafy vegetables	Sterility and muscular dystrophy in animals
Vitamin K	—	Leafy vegetables	Tendency to abnormal bleeding
Water-soluble:			
Vitamin B Complex†			
B ₁	Thiamine	Yeast, rice polishings	Polyneuritis, beri-beri
B ₂	Riboflavin	Milk, eggs	Cheilosis, seborrhea
B ₆	Pyridoxine	Yeast, liver	A dermatitis
B ₁₂	—	Liver	Pernicious anemia
Nicotinamide	Niacinamide	Liver, lean meat	Pellagra
Pantothenic acid	—	Liver, yeast, peas	Dermatitis in chicks
Biotin	—	Liver, kidney, yeast	Alopecia in rats
Choline	—	Egg yolk, brain	Fatty liver in dogs
Inositol	—	Heart muscle	Alopecia in animals
p-Aminobenzoic acid	PABA	Liver, yeast	Gray hair in rats
Folic acid	—	Liver	Retarded growth, certain anemias
Vitamin C	Ascorbic acid	Citrus fruits	Scurvy

* In each group there are usually two or more substances which possess vitamin activity. For example, there are at least 6 chemical substances which deserve the designation "Vitamin A."

† So named because its members (B₁ through folic acid) have a common source—viz., liver and yeast.

istic. In 1920 Drummond proposed a compromise, using *vitamin* without the final *e*.

The role that vitamins play in the welfare of man represents one of the most significant contributions of the chemist. It is now known—with mathematical precision—how much of most vitamins we must ingest in order to be healthy and free from the several *deficiency diseases*. The mechanisms by which the various vitamins perform their miracles were long wrapped in a shroud of mystery. Today the biochemist is able to offer an almost complete explanation. In general it may be said—with some degree of accuracy—that vitamins are the *regulators* of the chemical reactions within the cell. Specifically, they are concerned with the action of the cell's enzymes. Most vitamins of the B complex, for example, are known to function as enzyme helpers, or *coenzymes*.

All the vitamins have been isolated in the pure state. This has led to the determination of their chemical structure, and finally to their synthesis in the laboratory. The chemical structures of some of the vitamins are shown in Figure 54. Physically, the vitamins are often categorized according to their solubility in water or fat. The so-called *water-soluble vitamins* include vitamin C and members of the B complex group; the rest—A, D, K and E—are *fat-soluble*.

The names of the vitamins, their occurrence and a brief statement of their deficiency states are presented in the table on page 253.

Fats, Carbohydrates and Proteins. In order to be of use, fats, carbohydrates and proteins must be digested. The chemical aspects of this process are described under *digestion*. The digestive derivatives of carbohydrates are used by the cell to furnish *energy*; fats supply energy and form *adipose* (fatty) *tissue*; proteins are employed to *synthesize new protoplasm*, i.e., to repair and build tissue.

DIGESTION

Vitamins, minerals, water and oxygen are able to enter a cell directly; fats, carbohydrates (except monosaccharides) and proteins are not able to do so. In order for these substances to be absorbed and assimilated (i.e., synthesized into protoplasm), they must be *digested*, i.e., split into smaller soluble molecules. Thus, proteins are hydrolyzed to *amino acids*; carbohydrates are hydrolyzed to *glucose*, *fructose* and *galactose*; and fats are hydrolyzed to *fatty acids* and *glycerin*. The digestion of these substances is carried out in the mouth, stomach and small intestine through the agency of digestive *enzymes* secreted by a number of glands along the way (Fig. 55). The details of the digestive process are presented below.

The Mouth. The chief function of the mouth in the digestive process is mastication (chewing). Mastication reduces the size of the

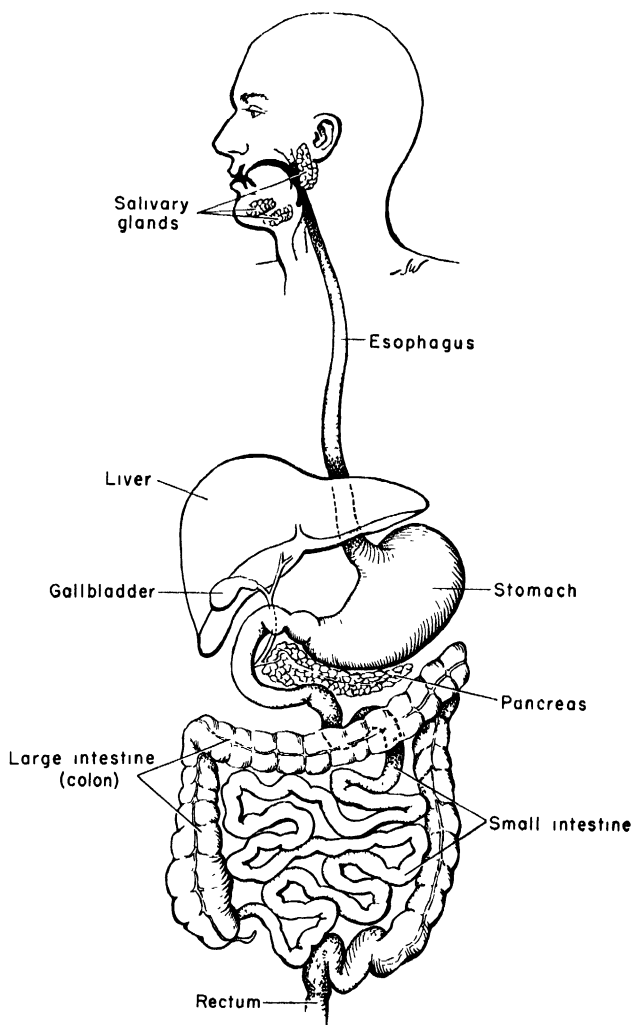


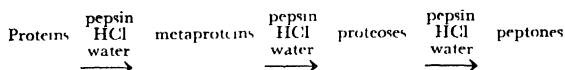
Fig. 55. The digestive system.

food particles for ease in swallowing, and facilitates enzyme attack throughout the alimentary canal. Mastication, of course, would be impossible without the moistening and lubricating effects of saliva. Saliva is secreted into the mouth by the sublingual, submaxillary and parotid glands (the so-called *salivary glands*). It contains mucin, salts, water and the enzyme *ptyalin*. Saliva has a *pH* between 6 and 7. The only chemical action in the mouth is the hydrolysis of starch by ptyalin.

Ptyalin converts starch first into *dextrins*, and then into *maltose*. This action is slight, however, because most of us swallow our food long before the time required for complete digestion. Fortunately, starch is completely digested in the small intestine.

The Stomach. The stomach acts as a storage place for food, and as a partial digester of proteins. These functions, however, are not indispensable; following total gastrectomy a patient seems to be able to take care of his food fairly well, aside from the fact he usually is not able to eat as much as before. Chemical digestion is performed by the so-called *gastric juice*. This juice consists of *water, salts, enzymes, mucin and hydrochloric acid*. Due to the presence of hydrochloric acid, it is highly acid. During fasting, the *pH* is about 3.5; following stimulation of secretion by food, the juice has a *pH* of about 1. Of interest is the fact that this juice is secreted by three types of cells. The *parietal cells* (located in the fundus and body of the stomach) secrete the *HCl*; the *mucous cells* (located throughout the stomach) secrete mucin; and the *mucogenic cells* (also found throughout) secrete the enzymes.

Most texts state that there are three enzymes present in the juice: *pepsin, rennin* and *gastric lipase*. It is quite safe to say that gastric lipase is unimportant. Rennin is equally unimportant in the highly acid stomach of the adult. In the less acid stomach of the infant, however, rennin is important in clotting milk. The chief chemical action of the juice, then, is due to the action of pepsin. It is now known that pepsin is secreted in an inactive form called *pepsinogen*,* and that pepsinogen is converted to *pepsin* in the presence of *HCl*. Moreover, pepsin itself requires an acid medium. This can easily be demonstrated in the laboratory. Pepsin is a *proteinase*; it converts proteins to *metaproteins*, soluble *proteoses* and *peptones*—intermediate products of protein hydrolysis:



As food leaves the stomach—in the form of a semiliquid called *chyme*—the proteins are at various stages of digestion. It is highly doubtful that all the proteins of an average meal are converted to peptones; indeed, some may leave unaltered.

A word should be said about *mucin*. Mucin—the characteristic constituent of mucus (found throughout the alimentary canal)—performs an important function in the stomach: It protects the gastric and duodenal mucosae from mechanical erosion and neutralizes acid. (For these reasons gastric mucin has been used in the treatment of peptic ulcer.)

* The inactive form of an enzyme is referred to as a *zymogen*.

The Small Intestine. It should be quite clear by now that salivary and gastric digestion contribute little in the way of chemical action. Thus, it is possible for carbohydrates, fats and proteins to enter the duodenum in an unaltered condition. The mechanical action of the mouth, stomach, saliva and gastric juice, of course, is unquestionably important; together they reduce the meal to a consistency (chyme) easily attacked by intestinal enzymes. The small intestine has two functions: the *digestion* of carbohydrates, fats and proteins; and the *absorption* of the products of digestion, vitamins, mineral salts and water. Absorption is made possible by its extensive length (20 ft.), and by its unique architecture (*villi*); both of these factors afford a tremendous surface area.

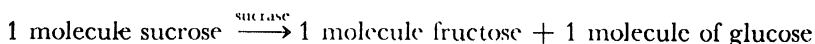
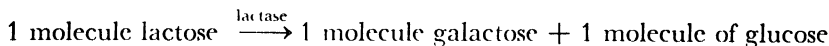
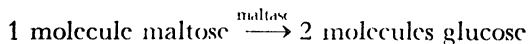
The digestive juice in the intestine is formed from the secretions of the *liver* (bile), *pancreas* and the *intestine* itself. These secretions have the following composition:

Pancreatic Juice:	Intestinal Juice:
Trypsinogen	Enterokinase
Lipase (steapsin)	Erepsin
Amylase (amyllopsin)	Sucrase
Bile*	Maltase
Bile salts	Lactase
Bile pigments	Mucin
Mineral salts	
Mucin	
Cholesterol	

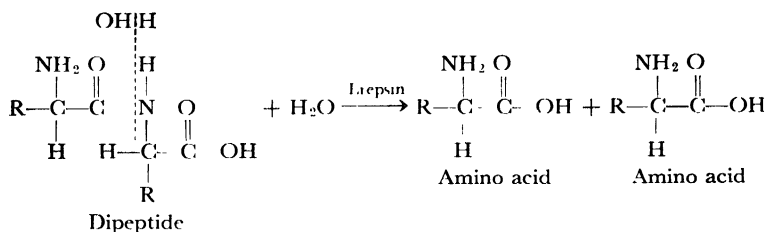
The above enzymes—unlike pepsin—require an alkaline medium in order to act properly. Alkalinity is assured by the buffering action of bile salts, and by the *pH* (8.5) of the pancreatic juice. The specific enzymes and their substrates are discussed under the following headings.

STARCH. Starch and dextrins are hydrolyzed by pancreatic *amylase* to *maltose*.

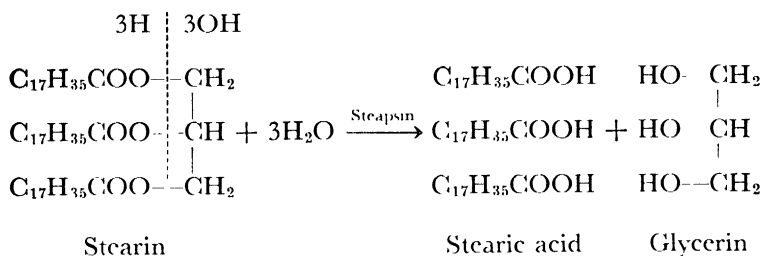
MALTOSE, SUCROSE AND LACTOSE. These three disaccharides (maltose being present as an intermediate in the hydrolysis of starch) are hydrolyzed as follows:



* Bile is *manufactured* in the liver and *stored* in the gallbladder.



FATS. Fats are hydrolyzed by *pancreatic lipase (steapsin)* to fatty acids and glycerin. Stearin—glyceryl tristearate—is hydrolyzed as follows:



The equation above illustrates the digestion of all fats. It will be noted that *1 molecule of fat yields 3 molecules of a fatty acid and 1 molecule of glycerin.*

Bile is a valuable adjunct in the digestion of fats. The function of bile, by means of bile salts, is to *emulsify* fats in water, thus increasing the surface area for attack by lipase.

Large Intestine. The chief functions of the large intestine are: *storage* of feces until defecation, and *water absorption* to prevent loss. Water absorption reduces the feces (indigestible food, bacteria, desquamated cells, etc.) to their typical consistency.

It is normal for bacteria to be present in considerable numbers in the colon, where conditions are favorable for their growth. Bacteria play a useful role in the *synthesis of certain vitamins* (e.g., vitamin K) and in the decomposition of substances (e.g., cellulose) which have escaped attack by the digestive juices. Unfortunately, however, certain types of bacteria secrete enzymes that can decompose monosaccharides and amino acids into harmful substances. Carbohydrates are broken down into *acids* (viz., *butyric, lactic, acetic*) and *gases* (*hydrogen, methane and carbon dioxide*). The action of bacteria on amino acids yields such substances as *histamine, phenol, indole* and *skatole*. These substances are very toxic if absorbed in considerable amounts. Fortunately, the body is protected against this type of insult by the detoxifying action of

the liver. For example, indole is changed to the nontoxic *indican*, which is excreted by the kidneys.

The formation of feces completes the digestive process. Figure 56 recapitulates the entire sequence of events.

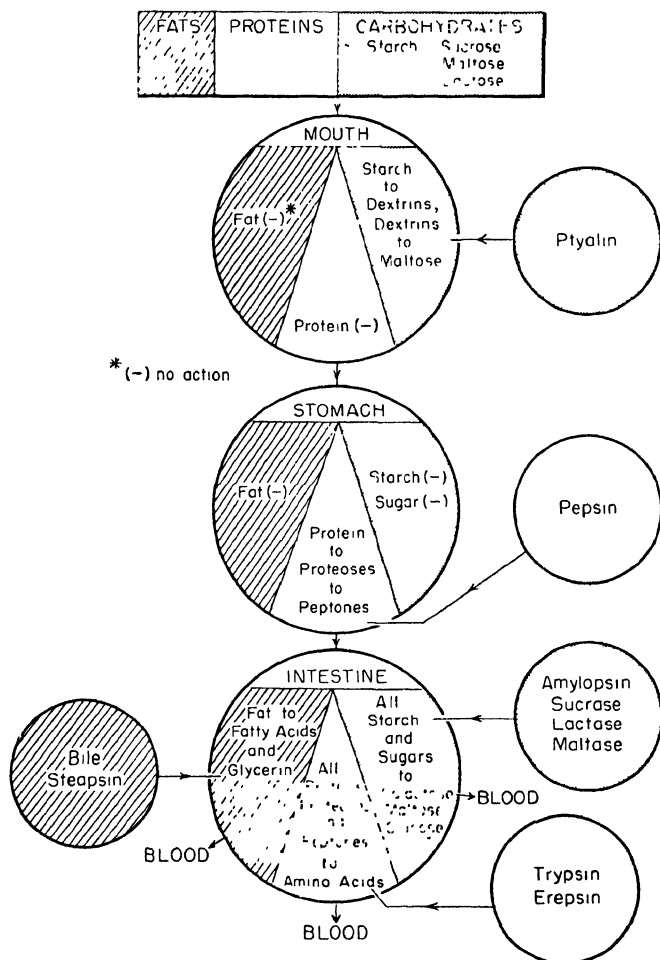


Fig. 56. A summary of digestion.

Absorption. The absorption of the soluble end products of digestion occurs throughout the mucosa of the small intestine. Amino acids, glucose, fructose and galactose are absorbed into the capillaries of the villi (Fig. 57). Concerning the absorption of fats, there has always

been a little difference of opinion. Recent information suggests that *bile salts* form a *soluble complex* with the insoluble fatty acids, thereby permitting them to penetrate the villi. Inside the villi the complex releases its fatty acid, which then unites with glycerin (being soluble glycerin passes into the villi unaided) to form fat. Once fat has been resynthesized inside the villus it is taken into the lacteals, and eventually enters the blood stream via the lymph.*

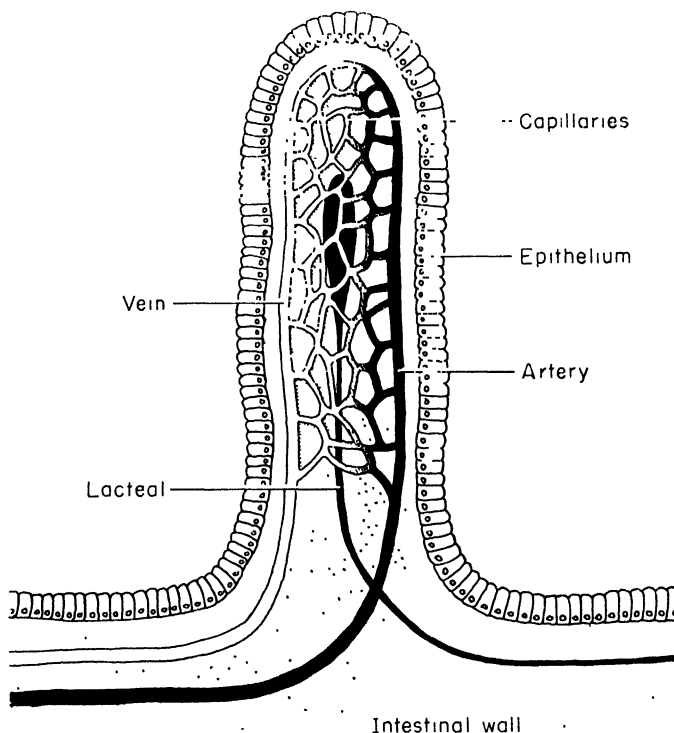


Fig. 57. Structure of the villus.

The mechanism of absorption involves more than the physical forces of diffusion and osmosis; it is probably an *active secretion* by the cells of the mucosa. This is supported by experimental evidence that certain closely related substances are absorbed at *different* rates. For example, glucose is absorbed much more rapidly than fructose.

Once the nutrients are absorbed into the blood they are transported to the body's tissues, where they diffuse through the thin capillary walls

* A certain amount of fat is taken directly into the blood via the villi capillaries.

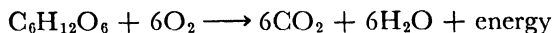
into the fluid surrounding the cells (*tissue fluid*). The nutrients then pass through the cell's *selective* membrane. Here again, it seems to be more than a simple case of diffusion or osmosis; the cell membrane seems "to know" what it wants to let in and out. For example, how else can we explain the fact that certain optical isomers are *physiologically different*? The cell membrane, then, functions on a basis of its ability to accommodate some structures and exclude others. In addition, recent work in this area indicates that the membrane expends energy in the transport process.

INTRAVENOUS ALIMENTATION. Food by vein is now a standard procedure in medical practice. Solutions are available which supply all the essential nutrients in a balanced form. Carbohydrate is administered as *glucose*, *fructose** or *invert sugar*; protein is given as *amino acids* (prepared by hydrolyzing "whole proteins," i.e., those that contain all the essential amino acids, such as casein, with digestive enzymes); electrolytes (viz., NaCl, KCl and CaCl₂) and vitamins are given in simple solution. These various solutions are given singly or combined.

Metabolism. *Metabolism may be defined as all the chemical changes which take place within the tissues.* Metabolism may be subdivided into *anabolism* and *catabolism*. Anabolism refers to all chemical changes which participate in the *synthesis* of protoplasm (*assimilation*), or other vital substances; catabolism refers to all chemical changes which involve the *degradation* of cellular constituents, yielding *waste products* and *energy*. In this section we are interested in the metabolism of the digestive products. The main points are briefly stated below.

CARBOHYDRATES. As we already know, carbohydrates make their way into the body in the form of the monosaccharides *glucose*, *fructose* and *galactose*. When the blood passes through the liver these three sugars—when present in excess amounts—are stored as the polysaccharide *glycogen* (C₆H₁₀O₅)_x (*glycogenesis*), which can be reconverted into glucose (*glycogenolysis*) and given up to the blood as needed. In this way, the glucose concentration of the blood remains constant.

The chief function of glucose in the tissues is to supply *energy*. This involves the oxidation of glucose to carbon dioxide and water. The reaction may be stated as follows:



Actually, the above reaction is only a summary of an extremely complex process. A rather complete analysis of the intermediate steps will be given under *cellular respiration*.

* It now appears that fructose, or levulose, is more easily absorbed *from the blood* than glucose. This means that fructose solutions—in the same period of time—deliver more calories than glucose solutions.

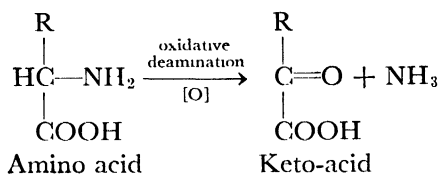
Unfortunately for those of us who have a tendency to put on weight, *excess glucose can be converted into fat*. Although this fact has long been recognized, the chemistry of the transformation has only recently been elucidated. It is believed that certain of the metabolic products derived from glucose (during its oxidation) are converted into *fatty acids*, and that these fatty acids combine with *glycerin*—*formed by the reduction of glucose*—to yield fats, which are stored in the fatty deposits of the body.

FATS. The liver is essential to the metabolism of fats. The fats which are absorbed into the blood from our food must be changed into a type which is able to enter the cell. A good portion of fat is transformed into *phospholipids* (via the liver), which the cells seem to absorb selectively from the blood. Fats (fatty acids) are also present in the blood as esters of *cholesterol*.

Once fats have been taken into cells, they may be oxidized to yield energy, or stored as fatty tissues. The oxidation of fats, like the oxidation of glucose, is not a simple process. The essential details will be presented when we consider cellular respiration.

PROTEINS. Proteins are taken into the blood as amino acids. Following absorption by the tissues they serve chiefly as the building blocks of *protoplasm*, *enzymes*, *hormones* and *blood proteins*. In excess amounts, however, amino acids undergo catabolic reactions, yielding *glucose** (and indirectly fat) *energy* and *nitrogenous waste products*, viz., *urea*.

The first of these catabolic reactions—*oxidative deamination*—is carried out in the liver. Deamination means the splitting off of amino groups. This process may be represented as follows:



It will be noted that the amino group has been replaced by oxygen, yielding a *keto-acid*. These keto-acids may be oxidized (yielding energy) in the tissues or converted into glucose, either for immediate use or storage. The amino groups are converted to *ammonia*, which is subsequently utilized by the liver in the synthesis of *urea* ($\text{NH}_2-\text{CO}-\text{NH}_2$). Urea appears in the urine as the chief nitrogenous waste product.

The metabolism of carbohydrates, fats and proteins is shown diagrammatically in Figure 58.

* The formation of glucose from proteins is called *gluconeogenesis*.

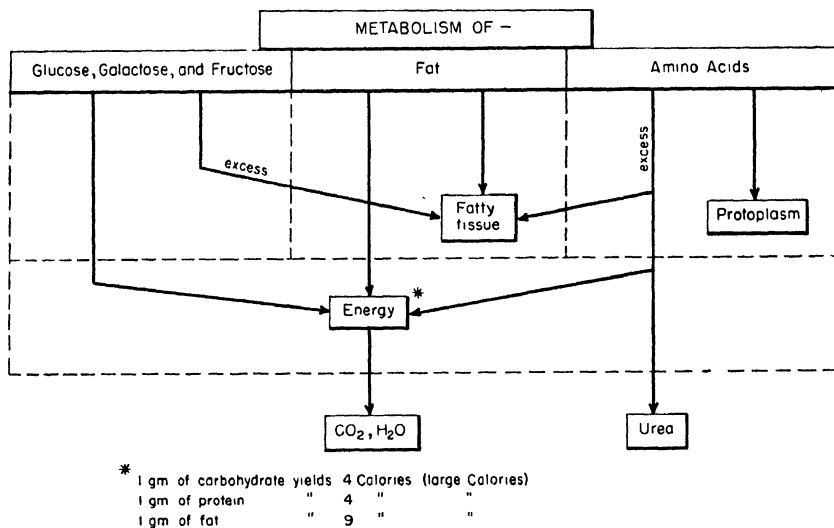


Fig. 58.

BLOOD (CIRCULATORY SYSTEM)

The unity of the organism is maintained by the circulation of a liquid tissue referred to as blood. There are other vital liquids in the body, however, in addition to blood; these include *tissue fluid*, *lymph*, *cerebro-spinal fluid*, *synovial fluid*, *aqueous humor* and *fluids of the ear* (endo-lymph and perilymph). It is important to realize, though, that all of these fluids are directly or indirectly derived from blood. For example, tissue fluid is a direct filtrate of blood, while lymph is derived from tissue fluid. In this section, we shall discuss the chemistry of blood, tissue fluid and lymph.

Blood is a viscous fluid composed of 45 per cent cells and 55 per cent plasma.* The cellular elements include *erythrocytes*, *leukocytes* and *platelets*, or *thrombocytes*. The liquid portion, or plasma, is a complex aqueous solution of *proteins*, *hormones*, *vitamins*, *lipids*, *gases*, *waste products* (viz., *urea*) and *inorganic salts*. An analysis of blood discloses the percentages presented in the table on page 265.

Blood performs a variety of vital tasks: It supplies the cells with the essentials of life; removes waste products; carries hormones; regulates the concentration of ions; regulates the osmotic pressure, temperature and gas tensions of tissue fluid; forms tissue fluid; aids in the defense against infection via leukocytes and antibodies. Of concern to us, how-

* By volume.

Composition of Blood

Blood cells		Erythrocytes
(40–50 % by volume)		Leukocytes
		Thrombocytes (platelets)
Plasma.....		Water, 90 %
(50–60 % by volume)		Inorganic salts, 0.9 %:
		Cations: Anions:
		Na ⁺ Cl ⁻
		K ⁺ of CO ₃ ⁻
		Ca ⁺⁺ HCO ₃ ⁻
		Mg ⁺⁺ SO ₄ ⁻
		Fe ⁺⁺ PO ₄ ⁻
		I ⁻
		Proteins, 7–9 %
		(viz., albumin, globulin, fibrinogen)
		Nonprotein nitrogenous substances:
		Urea
		Uric acid
		Creatinine
		NH ₄ ⁺ salts
		Amino acids
		Phosphatides
		Glucose, 0.1 %
		Fat
		Gases (O ₂ , CO ₂ , N)
		Special substances:
		Enzymes
		Antibodies
		Hormones

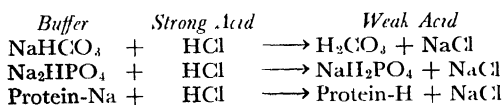
ever, are the important biochemical aspects of blood. The following topics are perhaps those of chief interest to the student of physiology.

Hydrogen Ion Concentration. Human protoplasm is killed unless its hydrogen ion concentration, or *pH*, remains between 7.2 and 6.7; nervous tissue is especially sensitive to a change in *pH*. There are two or three tissues, however, which can withstand a higher or lower *pH*. For example, the cells of the urinary tract can be subjected to urine of *pH* 4.8 to 8; and the gastric and duodenal mucosae are bathed with HCl of *pH* 1, although these are undoubtedly protected by a coating of mucus. A shift in the *pH* probably produces its deleterious effects by creating an unfavorable environment for cellular enzymes, thus interfering with the cell's chemistry; and by denaturing proteins, i.e., causing them to swell. The *pH* of protoplasm is maintained by the *tissue fluid* which, in turn, is maintained by the *blood* through various independent biochemical and physiologic mechanisms: *blood buffers, respiration,*

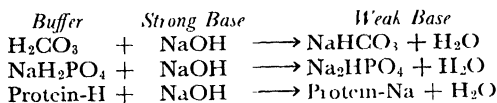
kidneys and alimentary tract. Blood itself has a *pH* of 7.43 to 7.4 (arterial), and 7.4 to 7.35 (venous).

BUFFERS. A buffered solution is a solution which—within reasonable limits—resists a change in *pH*. A buffer neutralizes strong acids and bases by the formation of *weaker* ones. The blood buffers include *bicarbonates*, *phosphates* (especially their Na salts) and *proteins** (viz., albumin, globulin and hemoglobin). The action of blood toward acids and bases may be represented as follows:

Against Acids (e.g., HCl)



Against Bases (e.g., NaOH)



There are several pathologic conditions in which an abnormal amount of acid substances escape into the blood. Usually the buffers (especially bicarbonate) are able to neutralize this excess acidity at a *constant pH*. Sometimes, however, the blood's buffer system is taxed beyond its powers, and death results if the *pH* goes below 6.9. An increase in the acidity of the blood is called *acidemia*, or *acidosis*. If the buffer system is able to cope with the situation without a change in *pH*, the term *compensated acidemia* is used; if there is a change in *pH*, it is called *uncompensated acidemia*.

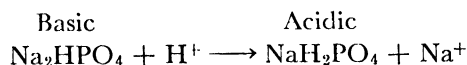
A decrease in the hydrogen ion concentration of the blood (i.e., an increase in *pH*) is called *alkalemia*, or *alkalosis*. Like acidemia, it may be *compensated* or *uncompensated*. Since the metabolic waste products of protoplasm are usually acidic, alkalemia is not as common as acidemia. There are several conditions, however, which will provoke alkalosis. The chronic ingestion of NaHCO_3 , for example, can bring about this condition. Death results at a *pH* above 7.8.

RESPIRATION. Respiration controls the *pH* of the blood via CO_2 . When the CO_2 tension of the blood is increased, respiratory receptors (in the *medulla*, *aortic arch* and *carotid sinus*) are *stimulated* by the gas itself, and by H^+ ions of carbonic acid ($\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$); as a result, CO_2 gas is blown off, thus compensating for an acidemia. This explains why exercise increases our rate and depth of breathing. Con-

* Proteins are *amphoteric*; i.e., they neutralize both acids and bases.

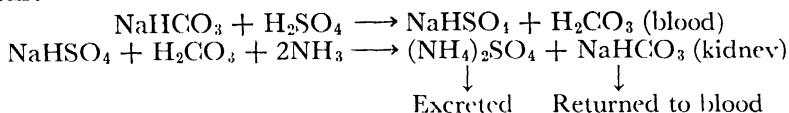
versely, when the blood is in a state of alkalemia there is a depression of respiration, causing a retention of CO_2 and H_2CO_3 .

KIDNEY. The kidney plays a vital role in the regulation of the hydrogen ion. Renal failure can easily produce a fatal acidosis. The kidney functions in this capacity by protecting the buffer capacity of the blood, especially the Na phosphates. In acidemia, the Na_2HPO_4 (a basic salt) of the blood is used to aid in the neutralization of the H^+ ion, thus:



In other words, there is a shift in the type of phosphate salt, from Na_2HPO_4 —the basic variety—to NaH_2PO_4 —the acid variety. If this were to continue, the blood would reach an uncompensated acidemia. The kidney remedies the situation by *excreting* the acid salt into the urine, and *reabsorbing* the alkaline salt back into the blood. In this way the ratio of Na_2HPO_4 to NaH_2PO_4 is kept constant.

In addition, the kidney forms ammonia to replace the alkaline metals, Na and K, which have been used to neutralize acids in the blood. If this were not done, the blood would be deprived of its most valuable buffers: NaHCO_3 and KHCO_3 . This may be represented by the following equations:



In the first reaction above, NaHCO_3 of the blood neutralizes H_2SO_4 to form the salt NaHSO_4 . The second reaction shows that when the blood passes through the kidney, the sodium atom of the salt is replaced by ammonia and reabsorbed into the blood as NaHCO_3 .

In alkalemia, the kidney acts in a reverse manner: It excretes the basic phosphate (Na_2HPO_4) instead of the acid phosphate (NaH_2PO_4), and Na and K salts instead of NH_4 salts.

THE ALIMENTARY TRACT. The cells of the stomach and intestine play an important role in regulating the pH by having the power of excreting acid (HCl) and alkaline juices (containing NaHCO_3), respectively. In severe acidemia, for example, the blood's acidity stimulates the emetic center directly, with the resulting loss of gastric HCl, thereby assisting in the restoration of pH. In cases of protracted emesis not due to acidemia, alkalemia may be produced. Likewise, diarrhea may cause an acidemia by a loss of alkaline intestinal juices. Excessive emesis and diarrhea, therefore, demand measures which will correct the shift in the blood's pH.

The concert of factors which regulate the body's pH are presented diagrammatically in Figure 59.

Clotting. Clotting prevents the escape of blood from the body. Intense investigations have disclosed that the clotting process is by no means simple; as a matter of fact, several theories have been offered to explain the series of chemical events involved. Most of these theories,

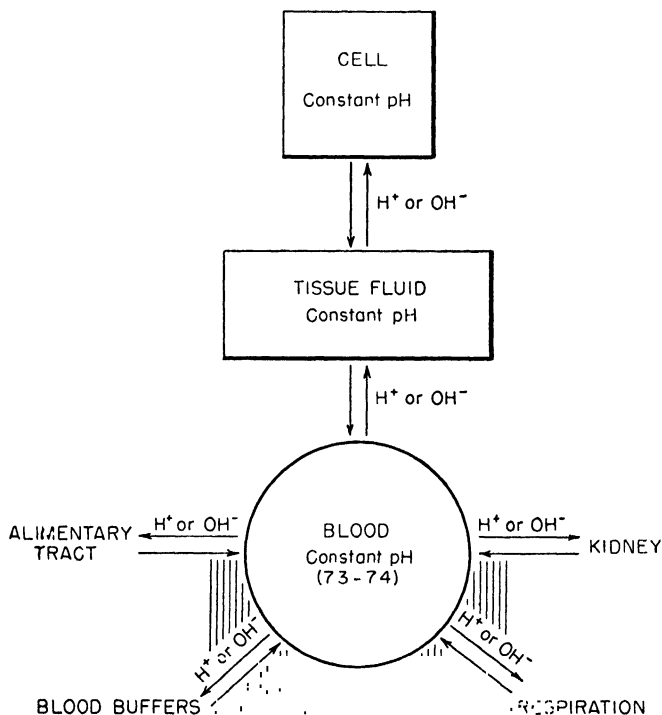


Fig. 59. Mechanisms by which the body maintains its pH of cells, blood and tissue fluid.

however, agree on the fundamental steps. The following explanation is presented as a summary of contemporary thought.

When tissue cells and thrombocytes are injured (thrombocytes are injured by passing over a foreign surface), an enzyme called *thrombokinase* is released. Thrombokinase then acts upon a substance in the plasma, called *prothrombin*, to form an enzyme called *thrombin*. This reaction, however, takes place only in the presence of calcium ion (Ca^{++}). Once thrombin is formed, it converts a soluble protein in the plasma, called *fibrinogen*, to *fibrin*. Fibrin separates from the blood as an insoluble mass of microscopic threads or fibers. In this way a mesh-

work is formed which catches and holds the cellular elements. This mass of fibrin and cells then contracts to form a *clot*. When exposed to air, the clot hardens and forms a tight seal (scab), thereby preventing the escape of blood. When blood is allowed to clot in a vessel, a clear aqueous liquid remains after the clot has formed; this liquid is called *serum*. Serum may, therefore, be defined as *plasma minus fibrinogen*.

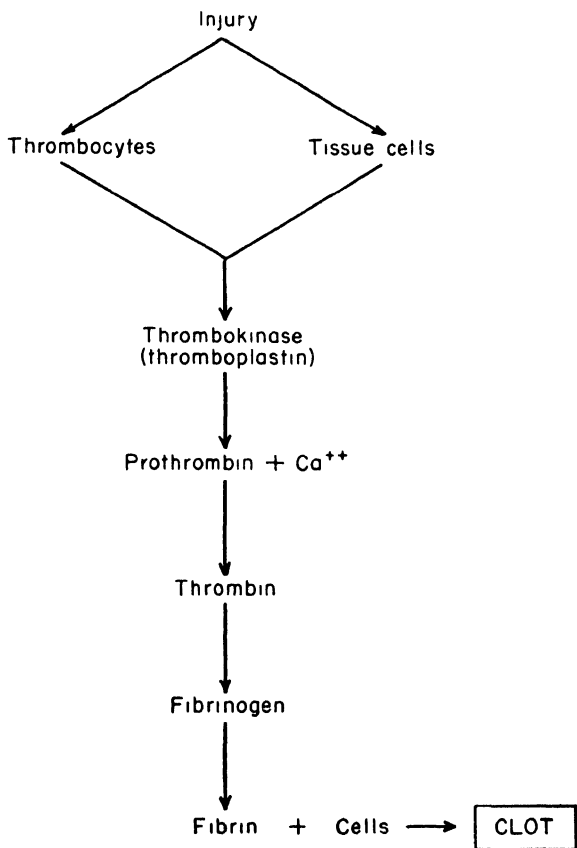


Fig. 60. Events involved in the coagulation of blood.

The sequence of chemical steps involved in the clotting mechanism may be summarized as in Figure 60. It should be evident that clotting can be prevented by any substance which is inhibitory to any participant.

CALCIUM. The role of calcium ion in the process is readily demonstrated by the fact that *sodium citrate* prevents clotting. Sodium citrate reacts with calcium to form *insoluble calcium citrate*; in this way,

Ca^{++} ions are *removed* from the plasma. Other salts, such as *oxalates*, will also prevent clotting by forming calcium precipitates. When blood is removed from the body for storage (in blood banks), a little sodium citrate is added to insure against clot formation.

PROTHROMBIN. Prothrombin is the inactive form of the enzyme thrombin. It is now known that prothrombin is synthesized in the liver, and further, that vitamin K is involved in the synthesis. Any injury to the liver, or anything which inhibits the utilization of vitamin K, will naturally inhibit clotting through a diminution of circulating prothrombin.

In medical practice, a drug called *Dicumarol* is employed as an anticoagulant either therapeutically to prevent enlargement of *thrombi*, or prophylactically to prevent postoperative thrombosis. It is thought that Dicumarol acts by diminishing the rate of prothrombin synthesis in the liver.

THROMBIN. Thrombin is a protein enzyme catalyzing the conversion of *soluble* fibrinogen to *insoluble* fibrin. Another anticoagulant used in medicine, called *heparin*, is thought to act by either interfering with the formation of thrombin, or by inhibiting its action. The presence of heparin in the circulating blood—and other inhibitory substances—has indicated that the clotting process is not simple. For example, heparin, which inhibits thrombin, is in turn inhibited by another substance. As a matter of fact, the more that we learn about the biochemistry of clotting, the more complex the picture becomes. The outline presented in Figure 60 is probably accurate in a general sense.

FIBRINOGEN. Fibrinogen is one of the soluble protein constituents of plasma. It is formed in the liver and may be low (thus interfering with clotting) in subjects with severe hepatic damage.

THROMBOKINASE. Thrombokinase, or *thromboplastin*, is a phospholipid found in the thrombocytes (platelets) and tissue cells. When cells are damaged or when thrombocytes come into contact with a foreign surface (damaged tissues, glass, gauze, etc.), this enzyme is released. The cause of hemophilia has been suggested as being due to an *excess stability* of platelets.

Osmotic Pressure. The osmotic pressure of human cells, tissue fluid and blood plasma is equivalent to a 0.9 per cent solution of NaCl (such a solution is commonly referred to as *normal saline*). This pressure is due to *salts* (electrolytes), *soluble organic compounds* and *proteins*. It should be obvious that optimal cellular performance demands a constant pressure. The body, therefore, makes every effort to regulate the osmotic pressure of the blood and the various fluids derived from blood.

TONICITY. Solutions which have the same osmotic pressure are said to be *isotonic*. For example, blood plasma is isotonic with a 0.9 per cent solution of NaCl or a 5 per cent solution of glucose. For solutions which have different osmotic pressures (*anisotonic*), the terms *hypertonic* and *hypotonic* are used. Thus, a 10 per cent glucose solution would be—relative to blood plasma—*hypertonic*; a 2 per cent solution would be *hypotonic*.

When solutions are added to the blood stream, they should never be *hypotonic*. Hypotonic solutions cause red cells to swell and burst (*hemolysis*). Hemolysis is evidenced by the release of hemoglobin from within the cell, turning the solution red. Hypertonic solutions shrink (*crenate*), but may not destroy cells; thus, *small* amounts can be added to

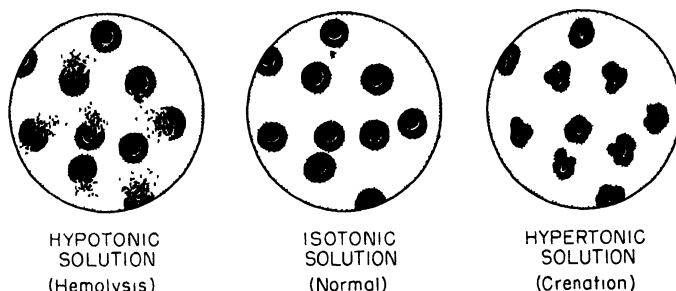


Fig. 61. The effects of hypotonic and hypertonic solutions on red cells of the blood.

the blood stream. The relation of isotonic, hypotonic and hypertonic solutions to blood may be readily demonstrated in the laboratory (Fig. 61).

Oncotic Pressure. Plasma proteins play a vital role because of the fact that they (normally) *do not* pass through the capillary wall. Hence, forced to remain in the blood stream, they tend to *hold* water; this affinity of protein for water is called *oncotic pressure*. Oncotic pressure is one of the determinant factors in the normal formation and reabsorption of tissue fluid: Tissue fluid is formed at the arteriolar end of the capillary where the hydrostatic pressure of the blood is *greater* than the oncotic pressure (22 mm. Hg); it is reabsorbed at the venular end where the hydrostatic pressure is *less* than the oncotic pressure. Oncotic pressure, then, is one of the body's chief mechanisms for maintaining the volumes of the blood and tissue fluid. A loss of proteins from the blood, for example, causes a *loss* of blood volume and a *gain* of tissue volume (edema).

Transport of CO₂ and O₂. The chemistry of the blood's physiology relative to the carrying of CO₂ and O₂ is an integral and in-

separable part of the respiratory process. For this reason, the subject will be discussed under the respiratory system.

Blood Fractions. Whole blood and plasma have been employed for quite a few years in replacement therapy. Very recently, synthetic substances (high molecular weight polymers) have been used with salutary results to restore blood volume following hemorrhage or shock. All of these methods, however, suffer important disadvantages; blood (especially whole blood) is not plentiful and, as yet, no substance has been synthesized which can replace blood. These facts provoked Dr. Cohn (a physical chemist) and his associates at Harvard to attack the problem in another way. They reasoned that in most cases the use of whole blood or plasma is wasteful because certain *fractions* (e.g., albumin, globulin, etc.) of the blood are just as effective. Blood albumin, for example, is as effective in maintaining blood volume as plasma. One pint of blood, therefore, could serve the needs of more than one patient, each patient receiving the applicable fraction.

The fractionation of blood presented huge problems. This was the question: How can one separate a mixture of a hundred or more *similar* chemical entities (present in small amounts) without destroying their properties? Cohn and his workers supplied the answer by devising an extremely complex machine which completely processes the blood of the donor into cellular elements and plasma fractions. The fundamental operation of the machine is *centrifugation*; i.e., the plasma fractions, after the cells have been removed, are separated much in the same way as cream is separated from milk when the latter is placed into a tube and spun at high speeds. At the last report, the machine has yielded about 70 fractions. The fractionation of blood is just another example of how the chemist has increased our span of life.

Tissue Fluid and Lymph. Tissue fluid is a protein-low filtrate of blood plasma, produced by blood pressure forcing fluid through the capillary wall. This fluid forms the environment of the body's cells. Thus, all the essentials of life must pass through tissue fluid before permeating the cell's membrane. In addition, tissue fluid acts as a fluid reservoir in maintaining blood volume.

Lymph is the term applied to the excess tissue fluid which is removed from the intercellular area by so-called *lymphatic vessels*. Lymph may be considered a protein-low plasma, containing about one-half the amount of blood plasma protein. Lymph gathered from the *lacteals* during digestion, of course, contains fat. The small lymphatics empty their contents into the *thoracic duct* and *right lymphatic duct*. These are large valved vessels which connect with the subclavian veins, thereby permitting the lymph to aid in maintaining blood volume. Located along the lymphatics are *lymph nodes* which act as bacterial filters.

RESPIRATORY SYSTEM

Respiration includes the mechanism for inhaling and exhaling air, transport of CO_2 and O_2 by the blood, and the utilization of O_2 by the cells. The principal chemical events involved are presented below.

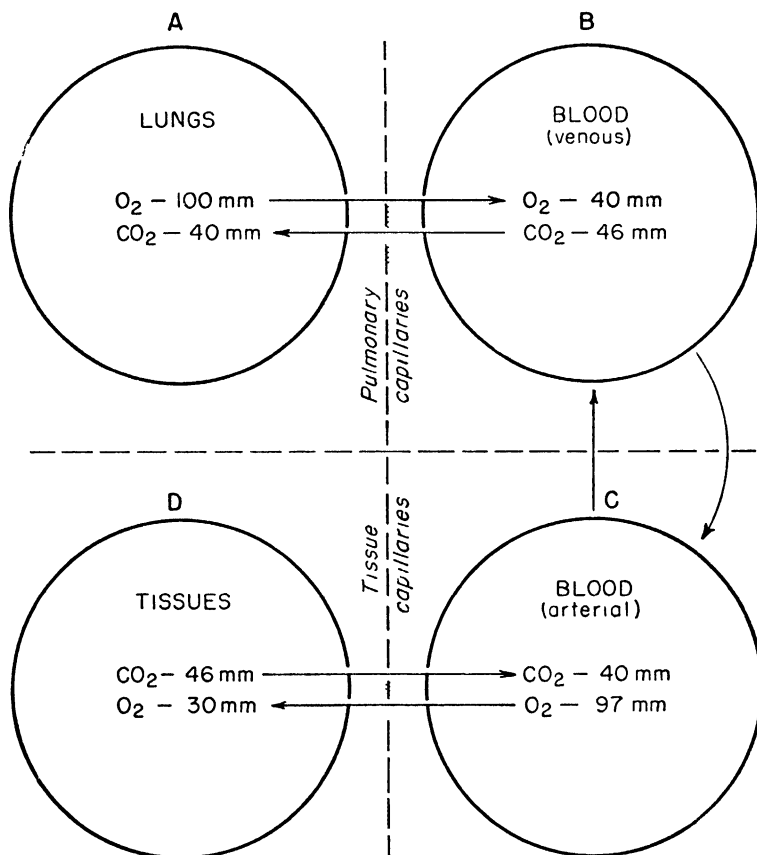
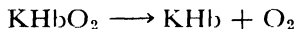


Fig. 62. The exchange of CO_2 and O_2 .

The Transport of O_2 and CO_2 by the Blood. When the blood passes through the lungs, CO_2 is given off and O_2 is absorbed; when blood passes through the capillaries of the tissues, the reverse occurs. It is important to appreciate that the chief force bringing about the exchange of O_2 and CO_2 is the *difference in pressures*. The pressure relationships are presented in Figure 62. The actual *transport* of O_2

and CO_2 is via chemical mechanisms.* The events are best understood by an analysis of the various reactions in the *lungs* and *tissues*.

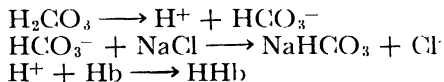
TISSUES. When arterial blood passes through the capillaries, O_2 is released from an unstable compound called *potassium oxyhemoglobin* (KHbO_2):



At the same time, CO_2 diffuses into the red cells where most of it reacts with H_2O —in the presence of an enzyme called *carbonic anhydrase*—to form carbonic acid:



The carbonic acid then ionizes to H^+ ions and HCO_3^- ions. Now, *most* of these HCO_3^- ions diffuse into the plasma where they react with NaCl to form NaHCO_3 and Cl^- . The H^+ ions, which are left behind, react with hemoglobin (Hb) to produce HHb (reduced Hb). These reactions may be represented thus:

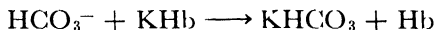


The Cl^- formed in the plasma diffuses into the red cell—*balancing the loss of HCO_3^-* —and reacts with KHb :

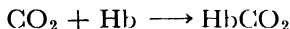


Actually, it is this shift of Cl^- ions (referred to as the *chloride shift*) which permits the plasma to carry CO_2 as NaHCO_3 .

All of the HCO_3^- ions do not leave the cell. Some react with KHb to form KHCO_3 and Hb :



Of the original CO_2 which entered the red cells, some combines directly with hemoglobin, forming *carbaminohemoglobin* (HbCO_2):



A study of the above reactions will disclose that CO_2 is carried by the blood in three ways: as NaHCO_3 , HbCO_2 and KHCO_3 . Most (two thirds) of the total blood CO_2 is carried in the plasma as NaHCO_3 ; one third is carried in the red cells (of which two thirds is HbCO_2 and one third KHCO_3). The chemical events in the tissues are presented diagrammatically in Figure 63.

* Only a very small amount of either gas is physically dissolved.

LUNGS. The reactions in the pulmonary capillaries are the reverse of those in the tissue capillaries. These reactions are easily memorized

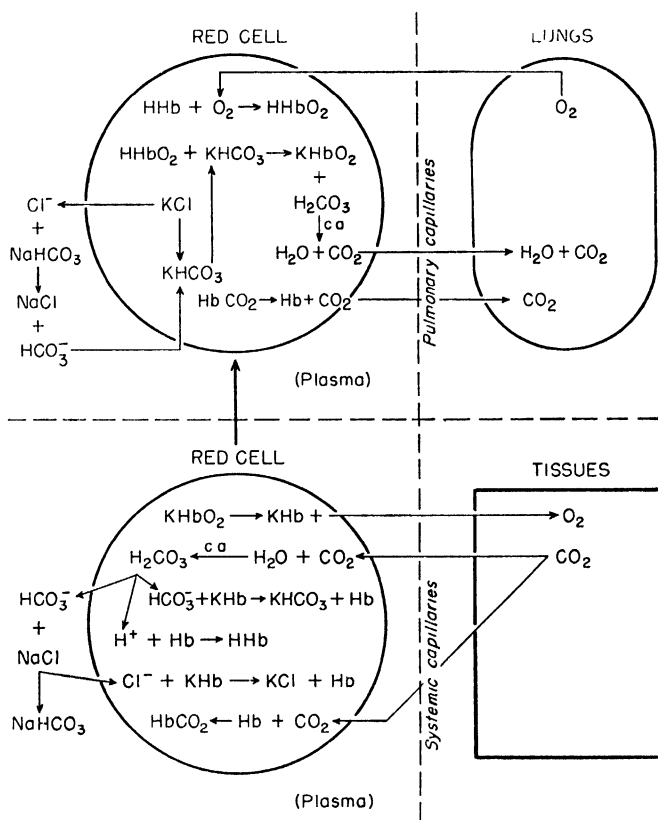
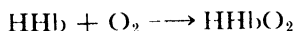


Fig. 63. The chief chemical events in the transport of CO₂ and O₂ via the blood. Start by reading from top to bottom the reactions between red cell and tissues, then read from top to bottom reactions between red cell and lungs.

if we start with the reaction between reduced hemoglobin (HHb) of venous blood and O₂ of the pulmonary air:



HHbO₂, or *oxyhemoglobin*, is an acid and reacts with KHCO₃ (also present in the red cell) to form *potassium oxyhemoglobin* (KHbO₂) and H₂CO₃:



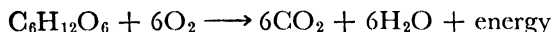
Carbonic acid then decomposes (in the presence of *carbonic anhydrase*) to CO_2 and H_2O , which are subsequently released from the red cell. This loss of KHCO_3 causes an imbalance in the equilibrium of HCO_3^- ; as a result, Cl^- diffuses out of the cell back to the plasma, where it reacts with NaHCO_3 to form NaCl and HCO_3^- (the reverse *chloride shift*). The HCO_3^- then diffuses back into the red cell where it is broken down to CO_2 and H_2O in the manner indicated above. The chloride shift continues until the blood's excess CO_2 is blown off. The entire sequence of respiratory reactions relative to O_2 and CO_2 transport is shown schematically in Figure 63.

It is interesting to note that the red cell is *permeable* to HCO_3^- and Cl^- ions, but *impermeable* to K^+ and Na^+ ions. If this were not so, all of the above reactions could not take place.

The air expired from the lungs is about 4 per cent CO_2 and 16 per cent O_2 , as compared to atmospheric air of 21 per cent O_2 and a negligible amount of CO_2 . *Alveolar air* contains 5.5 per cent CO_2 and 14 per cent O_2 .

Cellular Respiration. The energy that a cell needs to maintain itself and perform its specific function or functions is supplied by the intracellular *oxidation of food*. Just how this energy is transformed into work has proved to be a vastly complex problem. In most instances little is known, but considerable progress has been made in elucidating the mechanism of muscular contraction. For the present, however, we are just interested in the way in which amino acids, glucose, fats and oxygen yield energy.

In the early years of physiology, it was thought that *intracellular*, or *biologic*, *oxidation* was more or less like oxidation in the test tube. We now know that this kind of oxidation involves a myriad of extremely complex *enzymatic* reactions. The following equation, therefore, is merely a *summary* of a long series of catabolic chemical events in which glucose is oxidized to CO_2 , H_2O and *energy*.



The principal details of the intermediate steps are shown in Figure 64. It is most important to realize that each step shown (and the ones not shown) requires a *specific enzyme and coenzyme*. Moreover, we should take special note of the fact that each coenzyme contains a *vitamin* from the *B complex group*.

Let us briefly describe the events. *Glucose* and *glycogen* react with phosphoric acid to yield *hexose phosphate*. (In muscle tissue, glucose must be in the form of glycogen; in other tissues, glucose may be used directly.) Hexose phosphate then breaks down (passing through several

intermediates) to *pyruvic acid*. Up to this point no oxygen has been used—the so-called *anaerobic phase*.* During this phase a certain amount of energy has been released at several of the stages.

The next phase—the *aerobic phase*—involves the oxidation of pyruvic

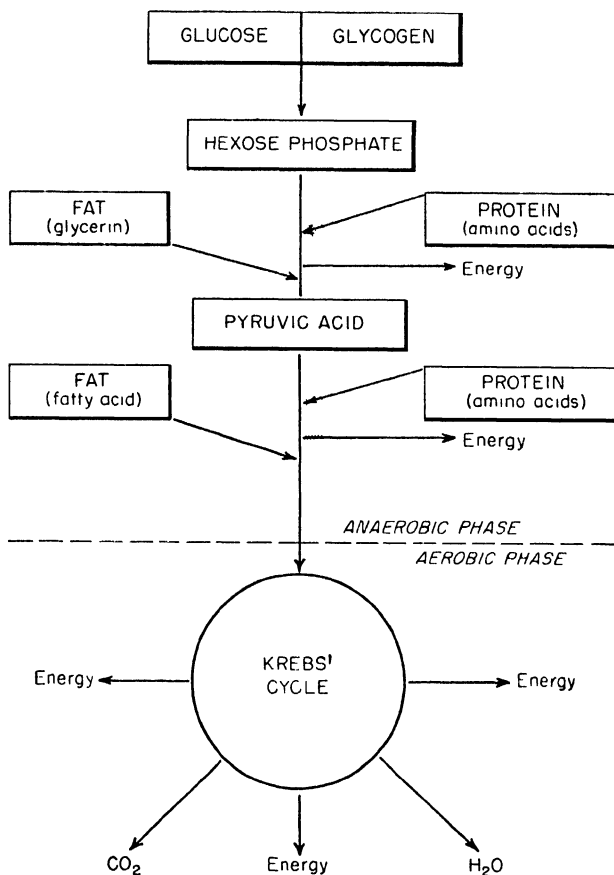


Fig. 64. The principal reactions in the process of intracellular oxidation.

acid to CO_2 , H_2O and *energy*. This part of the process proved to be the most difficult to understand. The specific chemical events remained a mystery until Krebs (and others) worked out the details. For the sake of simplicity, we shall ignore these details and accept the fact that pyruvic acid is “burned” in the so-called *Krebs' cycle* to yield *waste*

* Sometimes referred to as *glycolysis*.

products ($\text{CO}_2 + \text{H}_2\text{O}$) and *energy*. There are, then, two sources of energy: that derived from the *anaerobic phase*, and that derived from the *aerobic phase*.

What about the metabolism of fats and amino acids? The answer to this question demonstrates the amazing powers of the biochemist. It is now known for certain that glycerin, fatty acids and amino acids are burned in the same "furnace" which consumes glucose; i.e., they are broken down and converted into the same *intermediates* which pass through the anaerobic and aerobic phases of glucose catabolism. This is indicated in Figure 64.

BASAL METABOLIC RATE. The sum total of all the energies required by the body's cells to *maintain* themselves is referred to as the *basal metabolic rate*, or *B.M.R.* A subject's B.M.R. is determined by measuring the amount of heat* eliminated from the body, and expressing this amount as *Calories (large) per square meter (of body surface) per hour*. During this test the subject must remain at *complete rest* (no physiologic or mental activity) to insure that we are reading only *basal energy*. Once the B.M.R. has been calculated, it is compared to *standard values* (derived from a large number of readings taken on normal subjects) and expressed as a per cent above (+) or below (—) normal. The basal metabolic rate is not considered abnormal unless it varies more than 10 per cent from normal. The taking of the B.M.R. is a valuable diagnostic medical test. The status of the thyroid, for example, is ascertained via the B.M.R. (Hypothyroids have low B.M.R.'s; hyperthyroids have high B.M.R.'s.)

MUSCULAR SYSTEM

Energy for Contraction. Our chief chemical interest in muscle is concerned with the way in which muscle cells obtain their energy for contraction. Essentially this process is similar to that already presented under cellular respiration; it differs, however, in certain important aspects.

The contraction process requires a *sudden* jolt of energy. It has been appreciated for some time that energy of such a nature could not be supplied either from *glycolysis* (the breaking down of sugar or glycogen) or from the *oxidation of pyruvic acid*. This stimulated researchers in biochemistry to look for other plausible chemical mechanisms. As a result of these studies (especially those of Szent-Györgyi), the chemistry of muscle contraction is fairly well understood. The general idea of this complex picture may be described as follows.

* In practice this is done by measuring the amount of oxygen consumed over a definite period of time. This figure is then converted to Calories by consulting a chart.

The *immediate energy* for contraction has been demonstrated to be supplied by the hydrolysis of *adenosine triphosphate* (ATP) to *adenosine diphosphate* (ADP) and H_3PO_4 . The cell's supply of ATP, however, is small; ADP, therefore, must be reconverted into ATP. The energy for this reversion, or synthesis, is supplied by the hydrolysis of *phosphocreatine* (PC).^{*} But the supply of phosphocreatine is also limited and, like ATP, must be re-formed. Once again, this requires energy; this time the energy is yielded by the *hydrolysis* of *glycogen* to *lactic acid*. Up to this point no oxygen has been used; i.e., the muscle cell has been able to contract in the *absence* of oxygen (the *anaerobic*

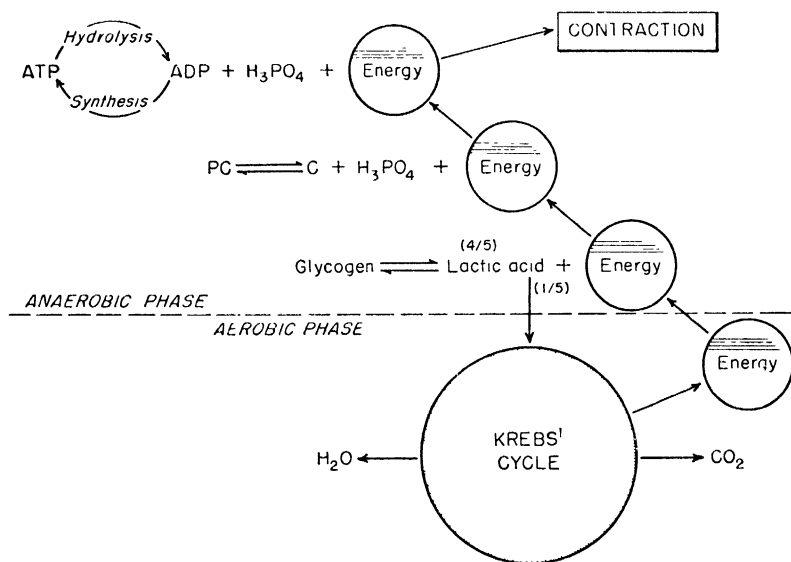


Fig. 65. Chemical events concerned in muscle contraction.

phase). Of the lactic acid which has been formed, approximately 20 per cent is burned in the Krebs' cycle, yielding CO_2 , H_2O and *energy*. This energy is then utilized to synthesize the remaining lactic acid (80 per cent) into glycogen. As can be easily perceived from the above steps, oxygen is the ultimate source of energy. The sequence of events is presented in Figure 65.

THE OXYGEN DEBT. Sustained muscle contraction piles up more lactic acid than the body can handle. Since this must be disposed of, we speak of the so-called "oxygen debt." This explains why the athlete

^{*} PC breaks down to form H_3PO_4 and creatine (C).

continues to pant after the completion of his exercise—*his body needs oxygen to burn up the excess lactic acid, and pay off its debt.*

MUSCLE FATIGUE. When excised muscle is electrically stimulated, the following happens: After the first few shocks the muscle seems to be more alert, and contracts with a greater force. Experimental evidence indicates that this is due to the accumulation of lactic acid, which in some manner sensitizes the muscle cells. Athletes take advantage of this chemical fact by mildly exercising—"warming up"—prior to the actual contest. Continuous and repeated shocking, however, places the muscle in a state of fatigue, a state in which the muscle is unable to respond to further stimuli. This results from a diminution of organic phosphates (ATP and phosphocreatine), and from the toxic effects of excess lactic acid on the muscle cells. Muscle fatigue in the body is probably due mainly to lactic acid formation, since the supply of organic phosphates is never completely exhausted.

TETANY. Muscle tissue, like other tissues, is extremely sensitive to a change in the *relative* concentrations of Na^+ , K^+ , Ca^{++} and Mg^{++} . In *tetany*, for example, we have a condition of extreme muscular contractibility due to a diminution of Ca^{++} ions. That this is true can be demonstrated by the fact that injections of calcium salts readily reverse the condition.

NERVOUS SYSTEM

The manner in which a nerve fiber carries an impulse has always intrigued researchers in physics, chemistry and physiology. There have been two schools of thought on this subject—the *electrical* and *chemical*. The electrical school holds that the passage of an impulse is analogous to the flow of current in a conductor; the chemical school likens the passage to a series of ultra-fast chemical reactions. It now appears, however, that the ability of nervous tissue to carry an impulse is best explained by a synthesis of both theories; namely, that a nerve fiber is somewhat like a *battery*. Thus, we may think of a nerve impulse as a flow of *electrical energy* which results from chemical activity within the fiber's protoplasm.

The chemical activity, or metabolism, within nervous tissue exceeds that of other tissues. The brain, for example, has been estimated to contribute 10 per cent of the body's total basal metabolism. Because of this high metabolism, nervous tissue must receive a continuous and generous supply of glucose and O_2 . This explains why a lack of either O_2 (*anoxia*) or glucose (*hypoglycemia*) easily damages certain vital centers in the brain.

Of considerable physiologic interest is the fact that the various types of nerve fibers have certain distinguishing chemical features. These

chemical features are referable to the way in which an impulse behaves at *synapses* and *myoneural junctions*. On such a basis, there are two types of nerves: *cholinergic* and *adrenergic* (see Fig. 66).

Cholinergic Nerves. Cholinergic nerves are nerve fibers which release *acetylcholine* at their endings. In this manner an impulse, after having arrived at the end of a nerve, is carried over to another nerve

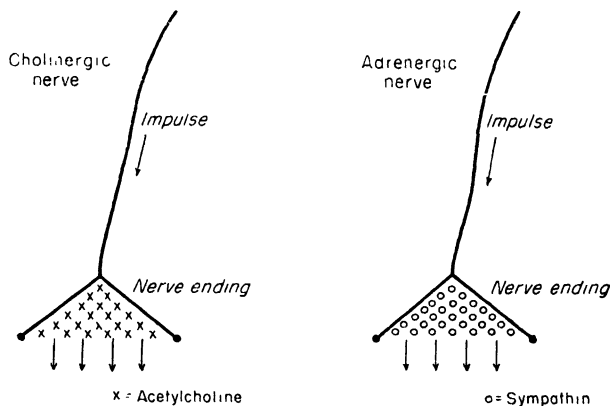
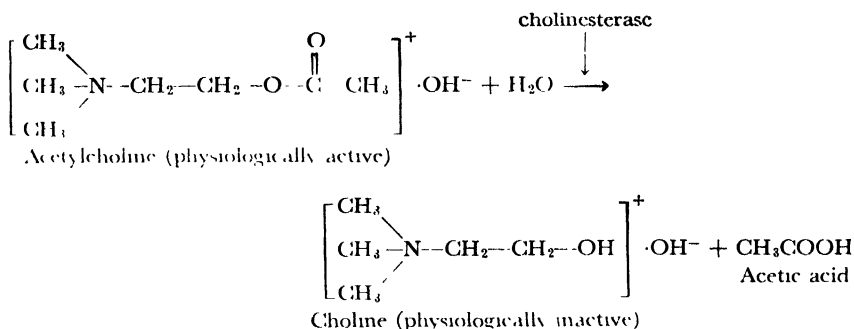


Fig. 66. The formation of acetylcholine and sympathin at nerve endings

(at a *synapse*) or passed on to muscle cells (at a *myoneural junction*). Thus, we may look upon acetylcholine as a “physiologic electrolyte.”

Once the impulse has passed over the “gap” it is “erased” by an enzyme called *cholinesterase*. Cholinesterase hydrolyzes acetylcholine to *choline* and *acetic acid* as follows:



Adrenergic Nerves. Adrenergic nerves are fibers which release an *epinephrine-like* substance called *sympathin* at their endings. Like acetylcholine, sympathin functions as a “physiologic electrolyte.” Sym-

pathin is hydrolyzed, or erased, by an enzyme located at the nerve ending.

Anatomy vs. Chemistry. For the sake of clarity, we should very briefly compare the anatomy of the nervous system with the chemistry presented above. Anatomically (and physiologically) there are two

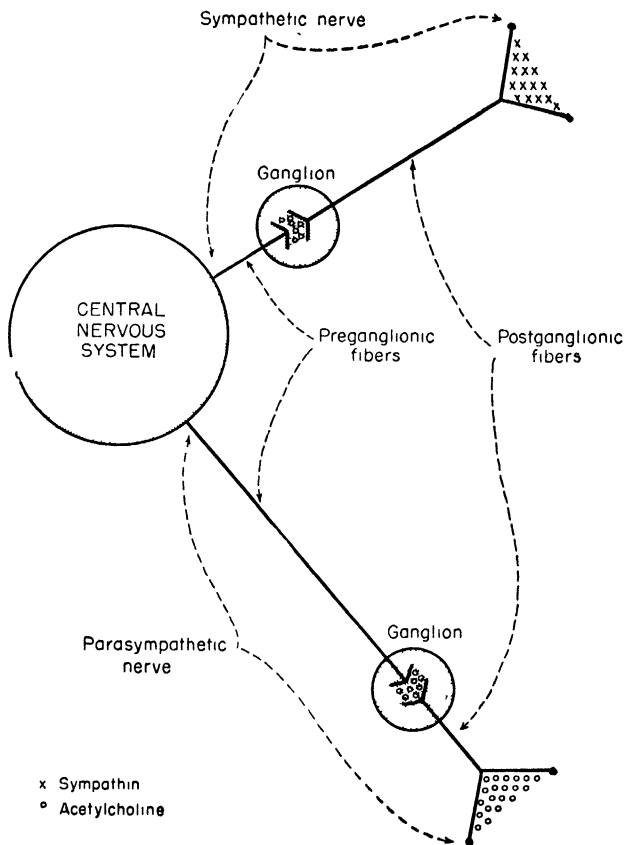


Fig. 67. A schematic representation of the anatomy and physiology of the autonomic nervous system.

types of nerves—*voluntary* and *involuntary*, or *autonomic*. The voluntary nerves activate *skeletal muscle*, and are under conscious control; involuntary, or autonomic, nerves activate *smooth muscle*, and are not under the control of our will. *All voluntary nerves liberate acetylcholine at synapses and myoneural junctions.*

Before we can make a similar statement for the autonomic nervous system, we must be familiar with the fact that an autonomic nerve has

two parts—a *preganglionic fiber* and a *postganglionic fiber*; furthermore, that there are two autonomic systems—the *sympathetic* and the *parasympathetic*. These two systems differ anatomically in respect to the *length* of their preganglionic fibers: Sympathetic nerves have *short* preganglionic fibers, whereas parasympathetic nerves have *long* ones (see Fig. 67). Chemically they differ in this respect: *Acetylcholine is formed at the ends of all preganglionic fibers and at the ends of postganglionic parasympathetic fibers, whereas sympathin is formed only at the ends of postganglionic sympathetic fibers*. Therefore, the following statement is true: All preganglionic fibers and all postganglionic parasympathetic fibers are *cholinergic*; all postganglionic sympathetic fibers are *adrenergic*. A study of Figure 67 will accurately disclose this relationship between chemistry and anatomy.

The above information has been extremely helpful to the physiologist and pharmacologist. For example, when acetylcholine is injected into the blood stream, it produces the same effects as those elicited by electrically stimulating the cholinergic nerves. Also, when *epinephrine* (Adrenalin) is injected, the results are referable to sympathetic stimulation. This, and a vast body of other facts, have made possible the development of a large number of useful drugs. There are four types of such drugs: (1) those that *mimic acetylcholine* (*parasympathomimetics*); (2) those that *inhibit acetylcholine* (*parasympatholytics*); (3) those that *mimic epinephrine or sympathin* (*sympathomimetics*); and (4) those that *inhibit epinephrine or sympathin* (*sympatholytics*). These drugs are employed in those conditions which are benefited by either stimulation or inhibition of nervous impulses. *Atropine*, for example, helps the patient with peptic ulcer by inhibiting the parasympathetic fibers which cause the release of hydrochloric acid in the stomach.

THE ENDOCRINE SYSTEM

At various locations in the body (Fig. 68) there are small glands (the *endocrines*) which manufacture potent chemical regulators called *hormones*. Anatomically, the endocrines are distinguished from the *exocrine* glands (e.g., the salivary glands) by the absence of a duct; for this reason, the exocrines and endocrines are commonly referred to as *duct* and *ductless glands*, respectively. The endocrine glands are stimulated (or inhibited) to secrete their hormone or hormones by the nervous system, or by the hormones of other glands, often by both. The hormones thus produced enter the blood directly, and by some chemical mechanism regulate (by stimulation or inhibition) the physiology of some other tissue or tissues.

The isolation and synthesis of hormones by the chemist have made it possible for the physiologist to clarify many of his concepts of life's

processes. In the field of medicine, hormones have enabled the physician to treat hopeless endocrine disturbances. The endocrines and their hormones are presented below. For the sake of time and space, only a brief physiologic description is given.

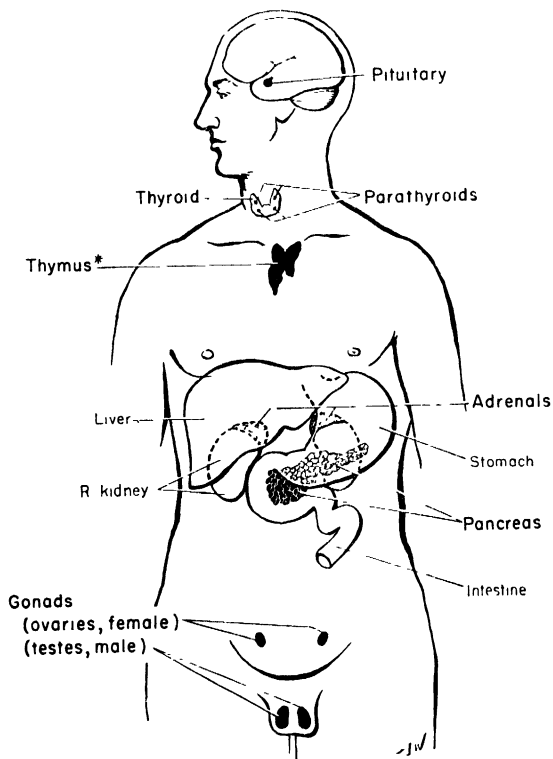
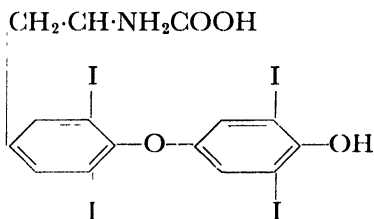


Fig. 68. Location of principal endocrine glands.

* Function unknown (present only up to puberty).

Thyroid Gland. The thyroid gland, located in the lower part of the neck, secretes an iodine-containing hormone called *thyroxin*. Thyroxin has the following chemical structure:



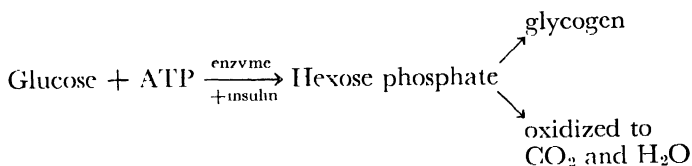
Thyroxin is a potent substance which controls the *rate of oxidative* processes in the tissues. *Hypothyroidism* (insufficient thyroxin) produces the clinical pictures of *cretinism* (in the child) and *myxedema* (in the adult). Both of the conditions are characterized by retarded growth of body and mind. The opposite condition, *hyperthyroidism*, is marked by nervousness, sleeplessness, loss of weight and muscular weakness. *Hyperthyroidism* (excessive thyroxin) results from the abnormal multiplication of thyroid cells (*hyperplasia*). This is evidenced by enlargement of the gland, producing a bulge in the neck. Such a condition is called a "toxic goiter." Toxic goiter should be distinguished from simple goiter. A simple goiter is caused by a lack of iodine in the diet, resulting in a decrease in the output of thyroxin. In order to compensate for this shortage, the gland enlarges. A simple goiter usually presents no problem other than the pressure caused by the enlargement.

Since thyroxin is concerned with the stimulation of intracellular oxidation, or *metabolism*, it is quite easy to understand that the *basal metabolic rate* (B.M.R.) is *decreased* in hypothyroidism and *increased* in hyperthyroidism. For this reason a B.M.R. test is a valuable diagnostic procedure.

Simple goiter may be *prevented* by the taking of extra iodine in the form of inorganic salts (Na, KI, etc.). Such regions in the United States as the basin of the Great Lakes and the Pacific Northwest are referred to as *goiter regions* because of the lack of iodine in the soil and water. Until iodine salts were given (in drinking water and in table salt), simple goiter was prevalent in these areas. Toxic goiter, if severe, necessitates removal of part of the gland. In milder cases the so-called antithyroid drugs (e.g., *propylthiouracil*) are effective. By some mechanism, they interfere with the synthesis of thyroxin. Cretinism and myxedema are dramatically controlled by the administration of thyroid extract, which contains the hormone.

Parathyroids. The parathyroids are four tiny glands embedded in the posterior aspect of the thyroid gland. These glands secrete a hormone called *parathyroid hormone*. Parathyroid hormone regulates the exchange of *calcium* between the bones and body fluids. *Hypoparathyroidism* (usually seen in those cases where the parathyroids were removed accidentally as a result of thyroidectomy) causes *tetany*. Since a *reduction* in the calcium ion (Ca^{++}) of the blood (and tissue fluid) is the cause of tetany, we may conclude that parathyroid hormone in some way stimulates the bone to *release* calcium to the blood. Excessive parathyroid activity, or *hyperparathyroidism*, brings about *decalcification*, a condition marked by soft and fragile bones. Parathyroid hormone is employed clinically in those conditions which are ameliorated by increasing blood calcium.

Pancreas. The pancreas is both a *duct* (secretes digestive juice) and *ductless* gland. The ductless portion, which is constituted by a specialized group of cells called the *islands of Langerhans*, manufactures one of the most important hormones in the body—*insulin*. Insulin is essential for the *metabolism of carbohydrates*: It promotes the *synthesis* of glycogen (*glycogenesis*), and accelerates the *oxidation* of glucose in the tissues.* These two facts have been known for many years. The mechanism of insulin's function, however, has only recently been understood. Most authorities now agree that insulin acts by *facilitating* the *first step* in the synthesis of glycogen and oxidation of glucose. This first step is the formation of *hexose phosphate* from *glucose* and *adenosine triphosphate* (ATP). The action of insulin may, therefore, be represented as follows:



DIABETES. Diabetes is an insidious and vicious disease which results from the inability of the islands of Langerhans to produce sufficient insulin for the body's needs. As a consequence, glucose accumulates in the blood (*hyperglycemia*). When hyperglycemic blood passes through the kidney, sugar appears in the urine—*glucosuria*. For this reason, urine serves as a valuable diagnostic aid in the detection of diabetes.†

The chief insult to the body arises from the abnormal metabolism of fat. Fats are burned because the body is unable to get its energy needs via the normal channel of glucose oxidation. In normal fat metabolism the liver converts fatty acids to simpler acids (e.g. *aceto-acetic acid*), which are then oxidized as an *alternate* source of energy. In diabetes, however, the liver is stimulated (by a *lack* of glycogen) to produce more aceto-acetic acid than the tissues can accommodate. As a result, aceto-acetic acid, together with its derivatives, *β-hydroxybutyric acid* and *acetone*, accumulate in the blood. (These acid substances are called *acetone*, or *ketone*, *bodies*.) If this continues, *acidosis* (referred to also as *ketosis*) results. It will be recalled from our earlier discussions that death results when the blood's *pH* drops below 7.2. The so-called *diabetic coma* is brought about by such a reduction in *pH*. Ketone

* One unit of insulin will metabolize about 1.5 gm. of glucose.

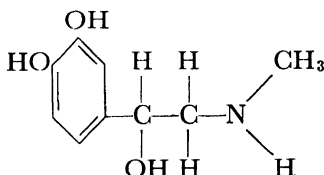
† As stated previously, Benedict's solution is used to detect the presence of glucose.

bodies in the blood “spill over” into urine. Their presence in the urine—along with glucose—is strongly suggestive of diabetes.

Diabetes is managed by limiting the carbohydrate in the diet, and by supplying insulin. In mild cases diet alone may remedy the condition; in severe diabetes, insulin is the only thing which will save the patient. The isolation of insulin by Banting and Best (1922) represents one of the most dramatic events in biochemistry.

Adrenals. The two adrenal glands are located on the top of each kidney. Each gland has an outer portion called the *cortex*, and an inner portion called the *medulla*. The cortex secretes several hormones, whereas the medulla elaborates one hormone—*epinephrine*.

EPINEPHRINE. Epinephrine (also known as *Adrenalin*) was one of the earliest discovered hormones. Takamine, a Japanese biochemist, synthesized epinephrine in 1900. It has the following chemical structure:



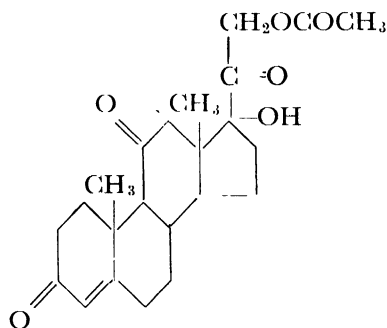
Epinephrine is the body's emergency hormone; i.e., all of its actions are designed to prepare the body for “fight or flight.” *It raises blood pressure, stimulates the heart, causes glycogen to yield glucose (glycogenolysis), and stimulates the sympathetic nervous system.*

Epinephrine is one of the most potent and important drugs in medicine. It is especially valuable in shock, where it is used to increase blood pressure.

CORTICAL HORMONES. The adrenal cortex secretes several hormones which exert a profound influence on the body's metabolic processes; unlike epinephrine, they are essential for life. The role that these various hormones play in the chemistry of the tissues has proved to be a vastly complex subject. It is certain, however, that the hormones so far isolated influence either the *distribution of sodium and potassium, the metabolism of carbohydrates, or sexual development*. Thus, it is easy to understand that any cortical abnormality causes severe and widespread repercussions. *Addison's disease*, for example, a *hypocortical condition*, displays an array of signs and symptoms—muscular weakness, reduced basal metabolism, reduced temperature, reduced blood volume and dehydration. A great many other pathologic disturbances are known to be caused by cortical malfunction.

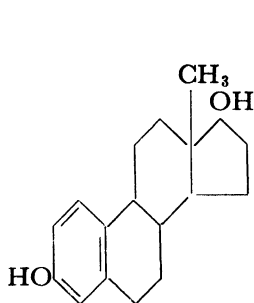
CORTISONE. Of the several cortical hormones, one, for our purpose, deserves special mention—*cortisone*. Cortisone, which was isolated from

cortical extracts by Kendall (1949), has the so-called *steroid* structure, characteristic also of the other hormones of the adrenal cortex. Cortisone has the following structure:

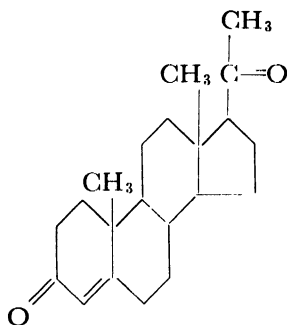


The advent of cortisone marks one of the great discoveries in the field of drug therapeutics. Once again the chemist has presented man with a magic cure via a magic formula. Although cortisone was originally introduced to relieve the extreme pain of *rheumatoid arthritis*, it has since been found to ameliorate 20 or 30 different clinical conditions. These diverse and miraculous effects can only be explained on a basis of its fundamental activity on the body's metabolic processes.

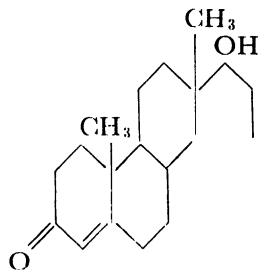
Sex Gland Hormones. The primary sex organs—*testes* in the male and *ovaries* in the female—secrete hormones which are necessary for the proper development of the accessory sex organs (male: prostate and other glands; female: mammary glands, uterus and vagina) and the so-called secondary sex characteristics such as voice, distribution of hair and shape of body. The testes secrete the hormone *testosterone*; the ovaries secrete principally *estradiol* and *progesterone*. These three hormones have the following *steroid* configurations:



Estradiol



Progesterone



Testosterone

Intestine. It was stated during our study of digestion that digestive juice from the pancreas and bile from the gallbladder are released into the intestine. Since this happens only during the time food is present, there must be some mechanism which *controls* the flow of these two juices. It is now generally held that the hydrochloric acid in the material

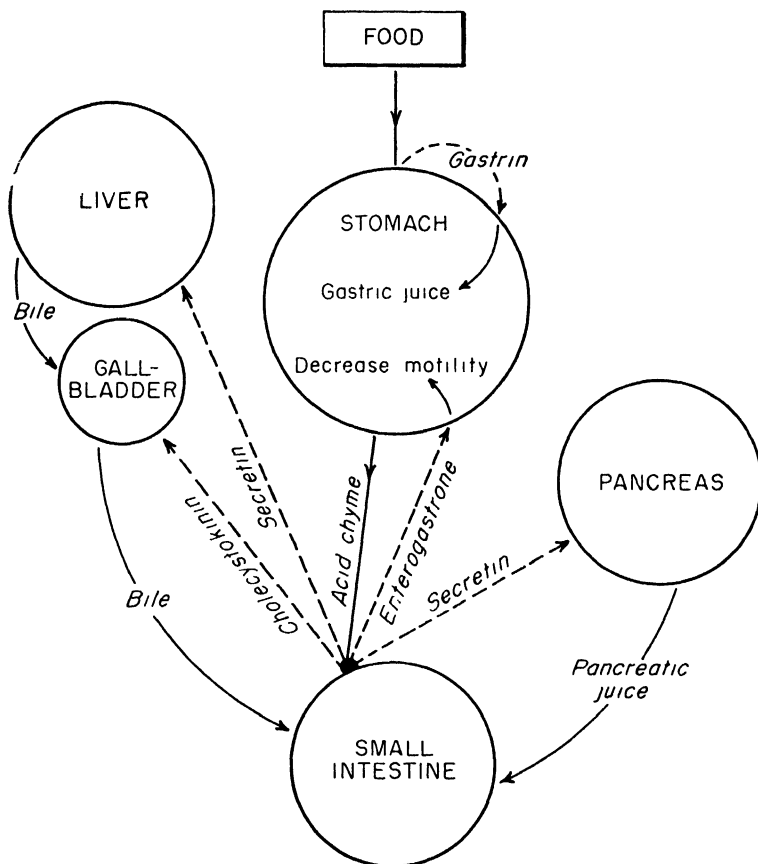


Fig. 69. Hormones (dotted lines) involved in the digestive process.

which leaves the stomach stimulates the intestinal mucosa to secrete two hormones—*secretin* and *cholecystokinin*. Secretin is absorbed by the blood and carried to the pancreas, where it then stimulates the flow of pancreatic juices;* *cholecystokinin* causes the gallbladder to empty its stored bile.

* Secretin also stimulates the liver and intestinal glands to secrete their secretions.

Other hormones concerned with digestion are *gastrin* and *enterogastrone*. Gastrin, released by the stomach wall in the presence of protein, brings about the flow of gastric juice. Enterogastrone, released by the duodenal wall when fat is present in the chyme ejected from the stomach, quiets the stomach, thereby allowing sufficient time for the intestine to cope with its digestion of fat before receiving a new charge. Figure 69 shows the relation of the above mentioned hormones to the digestive process.

Pituitary. The pituitary is a small gland located at the base of the brain. This gland is sometimes referred to—and quite accurately so—as the “master gland.” The pituitary not only affects the physiology of a variety of tissues, but also directs the activity of the other ductless glands. Close examination will disclose that the pituitary is composed of two distinct parts—the *anterior lobe* and *posterior lobe*. The anterior lobe synthesizes six or more hormones, and the posterior lobe, two. The principal hormones and their actions are presented in the table below.

Important Hormones of the Pituitary

<i>Hormone</i>	<i>Physiologic Effects</i>
Anterior Lobe:	
Adrenocorticotrophin	Stimulates adrenal cortex
Gonadotrophins	Stimulate ovaries in female and testes in male
Somatotrophin	Stimulates skeletal growth
Thyrotrophin	Stimulates thyroid activity
Diabetogenic factor	Inhibits insulin
Prolactin	Stimulates milk production
Posterior Lobe:	
Oxytocin (α -hypophamine)	Contracts uterine muscle
Vasopressin (β -hypophamine)	Raises blood pressure and decreases excretion of urine

EXCRETORY SYSTEM

The waste products from the cell are picked up by the blood as it circulates through the tissues. These wastes, in turn, are removed from the blood by the lungs (CO_2 , H_2O) and by the kidneys (solids). The principal solid wastes include urea ($(\text{NH}_2)_2\text{CO}$) and the salts (viz., Na, K, Ca, Mg, NH_4) of HCl, H_2SO_4 and H_3PO_4 . These substances (and a small quantity of other wastes) are dissolved in water and excreted as *urine*. Since a great many abnormal physiologic activities are reflected in the physical and chemical characteristics of urine, it serves

as a valuable diagnostic device in medicine. The presence of sugar, for example, together with acetone, is strongly suggestive of *diabetes*. The table below presents the characteristics and values for normal urine.

Human Urine

(24-hour sample)

Color—pale yellow	
Transparency—clear	
Odor—aromatic	
Acidity—about pH 6	
Specific gravity—1.015 to 1.030	
Analysis (ave. age):	
Water	1200–1500 cc.
Solids.	60 gm.
Nitrogen-containing constituents:	
Urea.	30.0 gm.
NH ₃	0.7 gm.
Uric acid	0.7 gm.
Creatinine	1.2 gm.
Indican.	0.01 gm.
Nitrogen-free constituents:	
Glucose.	0.7 gm.
Acetone bodies	0.01 gm.
Oxalates.	0.02 gm.
Inorganic salts:	
Chlorides	12 gm.
Phosphates.	3 gm.
Sulfates.	2 gm.

Abnormal Constituents of Urine. The following pathologic constituents are of diagnostic value.

GLUCOSE. There is normally a small amount of glucose in the urine, but not enough to give a positive test with Fehling's or Benedict's solution. When glucose is present in appreciable amounts (*glucosuria*, or *glycosuria*) it is indicative of *diabetes mellitus*. A temporary glucosuria is present following the ingestion of a high carbohydrate meal.

ALBUMIN. The presence of albumin in the urine (*albuminuria*) is indicative of impaired kidney function. Albumin may be detected by heating the upper layer of urine in a test tube. If a cloudiness appears, dilute acetic acid is then added to determine whether phosphates or albumin is present. Persistent cloudiness following the addition of acid (phosphates are soluble in acetic acid) is a positive test for albumin.

ACETONE BODIES. Acetone, or ketone, bodies include *acetone*, β -*hydroxybutyric acid* and *aceto-acetic acid*. Normal urine contains only traces of these substances. In diabetes, however, they are present in sufficient quantities to produce a positive test. The test is performed by adding a mixture of *sodium nitroprusside* and *ammonium sulfate* to

urine, and then overlaying with a small quantity of strong *ammonia water*. A positive test is indicated by the formation of a *pink to purple* color at the junction of the two liquids.

BLOOD. Blood in the urine is referred to as *hematuria* if red cells are present, and *hemoglobinuria* if hemoglobin is present. Hematuria indicates a hemorrhage in either the kidneys or along the urinary tract; hemoglobinuria (due to the hemolysis of red cells) occurs in diseases such as scurvy and purpura. Very small amounts of blood can be readily detected by adding a solution of *benzidine* and *hydrogen peroxide* (the so-called *benzidine test*) to some urine in a test tube. The formation of a *blue color* constitutes a positive test.

BILE. In jaundice the urine turns a *greenish-yellow* color, due to the presence of bile pigments. There are several tests which have been devised to detect these pigments. One test (the Smith test) is performed by overlaying urine with tincture of iodine. A positive test is shown by the formation of an *emerald-green* ring at the point of contact of the two liquids.

PUS. A large number of pus cells in the urine (*pyuria*) are indicative of an infection of the urinary tract or kidneys. Their presence is detected by microscopic examination.

CASTS. Casts are living cells which appear in the urine in diseases of the kidney. Like pus cells, they can be readily seen by microscopic examination.

SKELETAL SYSTEM

Our bones contribute substantially to the total weight of the body. The bulk of bone (and teeth) is constituted by the elements calcium and phosphorus in the form of calcium phosphate. Of the calcium in the body, about 99 per cent is found in bone; of the body's phosphorus, 75 per cent is located there. From this information we can easily appreciate that the diet must contain relatively large amounts of foods with a high content of calcium and phosphorus.

The "laying down," or deposition, of bone requires not only the elements calcium and phosphorus, but also vitamin D. Vitamin D acts by promoting the absorption of calcium and phosphorus from the intestine, and by assisting in the splitting off of *phosphate ions* (from complex molecules), which are then free to unite with calcium ions.

As pointed out in our brief study of the parathyroids, the *parathyroid hormone* promotes decalcification of bone. It is by this mechanism that the body calls upon the calcium in the bone to supply (in time of need) the calcium ions for its various tissues. Muscle, it will be recalled, requires a definite concentration of the calcium ion. Parathyroid hormone and vitamin D, therefore, are physiologically

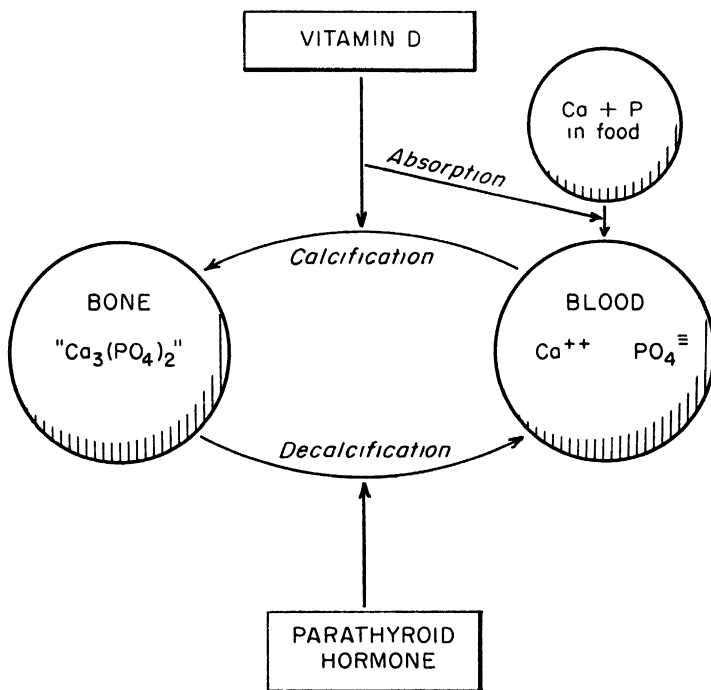


Fig. 70. Calcification and decalcification of bone.

antagonistic. A brief summary of bone chemistry is presented in Figure 70.

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

A.

Column I

- _____ protoplasm
- _____ organic catalyst
- _____ vitamin C
- _____ regulate certain physiologic processes
- _____ tissue fluid
- _____ intracellular
- _____ necessary for proper distribution of water

Column II

1. carbohydrates
2. folic acid
3. vitamins
4. water-soluble
5. approximately 70 per cent of the body's water
6. type of enzyme
7. enzyme

Column I

- _____ carbohydrase
- _____ supply energy
- _____ B complex vitamin

B.

- _____ glycerin
- _____ ptyalin
- _____ mucus
- _____ chyme
- _____ feces
- _____ pepsinogen
- _____ peptone
- _____ erepsin
- _____ lymph
- _____ maltase
- _____ pH 8
- _____ pH 1
- _____ adipose tissue and energy
- _____ a nitrogenous waste product
- _____ amino acids

C.

- _____ serum
- _____ plasma
- _____ NaHCO_3
- _____ carbonic anhydrase
- _____ oxyhemoglobin
- _____ thromboplastin
- _____ inhibits thrombin
- _____ a blood fraction
- _____ hemolysis
- _____ Na_2HPO_4

Column II

- 8. part of the extracellular water
- 9. "stuff of life"
- 10. salts and proteins
- 1. protoplasm
- 2. starch to dextrins
- 3. sugar
- 4. acts on a disaccharide
- 5. urea
- 6. an intermediate product
- 7. inactive
- 8. intestine
- 9. acts on peptides
- 10. reacts with certain acids to form fat
- 11. lubrication
- 12. cellulose and bacteria
- 13. contains fat
- 14. stomach
- 15. semiliquid consistency
- 1. gamma globulin
- 2. chief carrier of CO_2
- 3. difference in pressure
- 4. buffers
- 5. heparin
- 6. 0.9 per cent NaCl
- 7. forms fibrin
- 8. release of hemoglobin
- 9. oncotic pressure
- 10. plasma minus fibrinogen

Column I

- ___ fibrinogen
- ___ responsible for exchange of gases
- ___ constant pH
- ___ isotonic
- ___ plasma albumin

D.

- ___ exchange of gases in lungs
- ___ internal respiration
- ___ anaerobic phase
- ___ oxidation of pyruvic acid
- ___ B.M.R.
- ___ adenosine triphosphate
- ___ glucose plus H_2PO_4
- ___ energy to rebuild ATP
- ___ "oxygen debt"
- ___ glycogen to lactic acid
- ___ B complex vitamins
- ___ enzymes
- ___ waste products
- ___ tetany
- ___ +30

E.

- ___ release acetylcholine
- ___ release sympathin
- ___ parasympathetic nerves
- ___ cholinesterase
- ___ sympathetic nerves
- ___ pH 6
- ___ chief constituent of urine
- ___ glucosuria

Column II

- 11. released by tissue cells when injured
- 12. liquid portion of blood
- 13. needed for the synthesis of H_2CO_3
- 14. has acid properties
- 15. buffers acids
- 1. hexose phosphate
- 2. coenzymes
- 3. glycolysis
- 4. lack of Ca^{++}
- 5. immediate source of energy
- 6. hyperthyroidism
- 7. Krebs' cycle
- 8. energy to synthesize phosphocreatine
- 9. CO_2 and H_2O
- 10. required for all respiratory reactions
- 11. external respiration
- 12. decomposition of phosphocreatine
- 13. minimal expenditure of energy
- 14. exchange of CO_2 and O_2 in tissues
- 15. accumulation of lactic acid
- 1. chemical messenger
- 2. urea
- 3. diabetes
- 4. absorption of Ca and P
- 5. cholinergic nerves
- 6. insulin
- 7. postganglionic fibers are adrenergic
- 8. pituitary

Column I

- _____ benzidine
- _____ epinephrine
- _____ parathyroid hormone
- _____ vitamin D
- _____ hormone
- _____ metabolism of sugar
- _____ regulates other endocrines

Column II

- 9. urine
- 10. adrenergic nerves
- 11. hydrolysis of acetylcholine
- 12. pre- and postganglionic fibers are cholinergic
- 13. releases Ca^{++} from bone
- 14. test for blood
- 15. adrenal medulla

1. By means of a diagram, outline the chemical functions of the blood.
2. By means of a diagram, outline all the chemical steps of the digestive process.
3. Outline the reactions involved in the transport of CO_2 and O_2 by the blood.
4. Discuss the release of energy within the cell (internal respiration).
5. Describe the sequence of events involved in the contraction of muscle.
6. Briefly describe the endocrine system.
7. What is the composition of urine? Name 3 abnormal constituents.
8. Discuss the meaning and use of the B.M.R.
9. Discuss the chemical events concerned with the transmission of nerve impulses.
10. What is the function of vitamin D?

CHAPTER 12

NUCLEAR CHEMISTRY

The discovery of x-rays by Röntgen in 1895 was the beginning of a new phase of man's life on earth—the “atomic age.” It is the purpose of this chapter to present briefly the basic ideas of atomic chemistry and its applications to our society. In contrast to our earlier studies, we are now interested in the chemistry of the atom's nucleus.

RADIOACTIVITY

The discovery of x-rays (Fig. 71) stimulated scientists to look for other sources of similar penetrating rays. The French scientist, Becquerel, found that *uranium compounds* possessed this power. In 1903

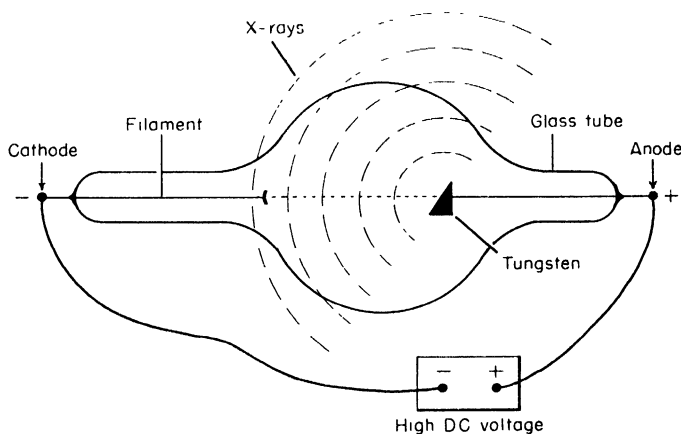


Fig. 71. X-rays are produced when high velocity electrons (dotted line) from the filament hit the tungsten anode.

Madame and Pierre Curie received the Nobel Prize for the isolation of a new element called *radium*—an element two million times more potent than uranium. At this time a new word appeared upon the horizon—*radioactivity*. *Radioactivity is the term applied to all chemical substances which emit energy rays.* It was Rutherford and his associates

who explained the nature of these mysterious radiations. By the use of photographic plates and a powerful magnetic field (Fig. 72), they were able to demonstrate that all radioactive elements give off three types of rays. These rays were named *alpha*, *beta* and *gamma*. Alpha rays consist of *helium nuclei*; i.e., they are positively charged particles containing 2 protons and 2 neutrons; beta rays are streams of electrons derived from the disintegration of neutrons; gamma rays are similar

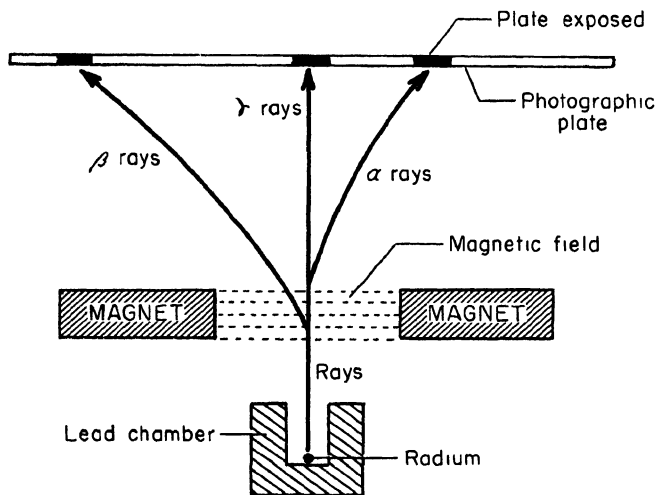


Fig. 72. A diagram of the apparatus used to demonstrate that radium emits three types of rays.

to x-rays,* but more penetrating. Of the three types, the gamma rays are the most powerful.

What is the explanation of radioactivity? The answer to this question is best supplied by stating that radioactive elements possess *unstable* nuclei. In contrast to ordinary elements, the nuclei of radioactive elements are evidently unhappy about their *number of protons and neutrons*; i.e., they prefer some other combination than the one they have. In order to obtain the desired combination, the nuclei release alpha, beta and gamma rays. The radiation continues until the nuclei have attained their desired number.

Half-life. The disintegration of radioactive nuclei is spontaneous and not changed by outside forces. Each radioactive element, therefore,

* Gamma and x-rays are *electromagnetic waves of energy*; alpha and beta rays are referred to as *particulate rays*.

has a characteristic *rate* of disintegration called its “half-life.” A radioactive element’s half-life is defined as the time required for a given amount of the element to lose half of its mass. It would take 1590 years, for example, for 1 gm. of radium to reduce to 0.5 gm. Uranium has a half-life of several billion years. On the other hand, there are some radioactive elements which have a half-life of only a few minutes.

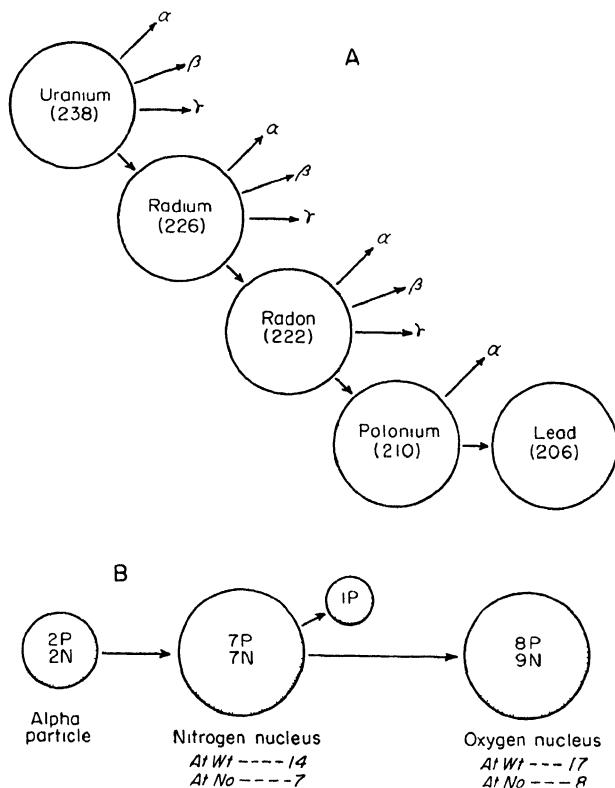


Fig. 73. Natural (A) and artificial (B) transmutation. (See text for details.)

When working with radioactive materials it is essential to know an element's half-life value.

Transmutation. As stated above, alpha and beta particles are shot out from the nucleus during the process of radiation. Since each element is composed of atoms whose nuclei contain a *characteristic number of protons and neutrons*, it follows that a radioactive element *ceases* to remain the same element. This means that a radioactive element can

pass through several other elements before it reaches a stable form. The earth's *lead*, for example, resulted from the disintegration of *radium* which, in turn, resulted from the disintegration of *uranium*. This phenomenon of one element changing into another element is called *transmutation*.*

The concept of transmutation served as the most powerful stimulus to the minds of the early atomic scientists. The implication was this: If natural transmutation (uranium to lead) is possible, why would it be impossible to bring about *artificial transmutation*? The great mind of Rutherford demonstrated to the world that artificial transmutation was possible. Rutherford succeeded in bringing about the transmutation of nitrogen to oxygen by knocking protons out of nitrogen nuclei, using

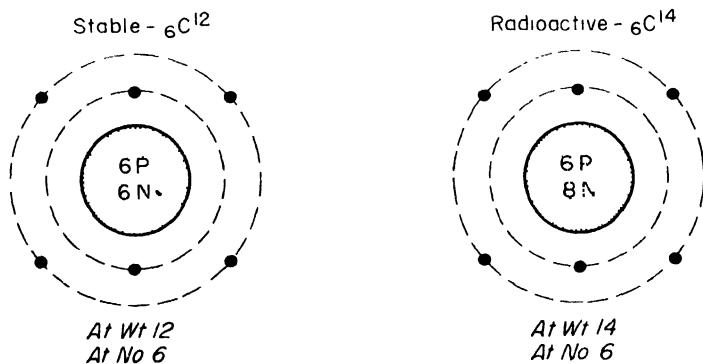


Fig. 74. Isotopes of carbon.

alpha particles (supplied from radium) as "atomic bullets." Since this time (1919) a large number of other transmutations have been achieved, yielding new elements and *radioactive isotopes*. Figure 73 illustrates natural and artificial transmutation.

Radioactive Isotopes. As previously defined, isotopes are atoms which have the *same atomic number*, but *different atomic weights*. Chemically, therefore, they are the *same*. It has been discovered, however, that an element's isotopes may vary in another respect—radioactivity. Researchers have disclosed that many elements which heretofore were considered stable contain *traces* of radioactive isotopes. Various complicated physical and chemical techniques have been

* Since the earth's uranium is slowly but surely disappearing in a *horologic* manner, man is now able to accurately determine the earth's age by comparing the *ratio* of uranium to lead in uranium ore.

developed to isolate the radioactive isotope from the stable variety. It has been shown, for example, that ordinary carbon contains traces of a radioactive isotope with an atomic weight of 14 (written as ${}^6\text{C}^{14}$); the stable isotope of carbon has an atomic weight of 12 (${}^6\text{C}^{12}$).^{*} These two varieties of carbon are illustrated in Figure 74.

The Detection of Radioactivity. As time goes on, more and more people are working with radioactive substances. It is essential, therefore, that we have suitable devices for the detection of invisible radiations. The simplest method is the use of *photographic plates*. Plates are exposed even when encased in metal shields. Other devices include the *electroscope*, *Wilson cloud chamber* and *Geiger-Müller counter*. At the present time the Geiger-Müller counter is used routinely in all establishments which employ radioactive elements and isotopes. The counter not only detects radiation, but also is able to furnish the *degree* of radiation.

ATOMIC MACHINES

The atomic scientist was not content with his knowledge of radioactivity and transmutation—he wanted to probe still deeper into the atom's nucleus. How was it possible to learn more about the nucleus? Rutherford's work appeared to offer the greatest possibilities, i.e., the use of "atomic bullets." It was reasoned that once the nucleus was split, the resulting fragments would offer a wealth of atomic information. Rutherford's bullets—*alpha particles*—were not of sufficient velocity, however, to do the job; atomic bullets with unbelievable velocities were needed. The answer came in 1929 when E. O. Lawrence invented the first "atom smasher"—the *cyclotron*. By the use of huge electric currents and magnetic fields, the cyclotron imparted protons with an energy of 1.2 million electron volts. Since this time more powerful machines have been developed, such as the *betatron* and *synchrotron*. The latest atom smasher is reported to hurl subatomic particles at energies in the neighborhood of 6 billion electron volts.

The various atom smashers have enabled the physicist and chemist to study the nucleus in detail. When one reads of the advancements in this field it is difficult to believe that man possesses such fundamental knowledge. It is not true to assume, however, that matter has yielded its final secrets; indeed, the picture sometimes seems more complex. For

^{*} In the same manner that he is able to determine the earth's age accurately (i.e., by comparing the amounts of uranium and lead in a given deposit of ore), the chemist can now accurately date any carbonaceous substance by comparing the relative amounts of ${}^6\text{C}^{14}$ and ${}^6\text{C}^{12}$ in a given sample. Thus, the age of a piece of wood from the interior of a pyramid can be determined with an insignificant error.

example, it is now known that the proton and neutron are not the only inhabitants of the nucleus; scores of other particles (e.g., the *positron*, *meson*, *neutrino*, etc.) are present. So far, it remains to be seen just where all these subatomic particles fit into the architecture of the atom. In addition to the splitting of nuclei for the purpose of yielding basic information, the chemist and physicist have utilized their atomic machines to produce *artificial radioactive isotopes* and *new*

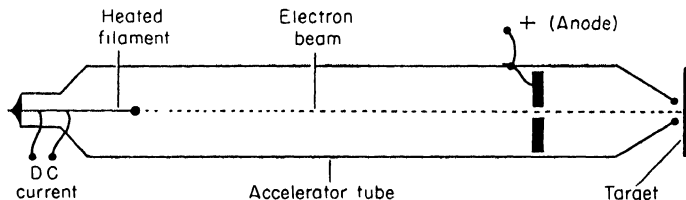


Fig. 75. Simple type "atom smasher." In the various types of atomic machines, or "atom smashers," subatomic particles are hurled at tremendous velocities at a "target" for the purpose of transmuting or splitting the target's nuclei. In the atom smasher above, electrons (negative particles) are accelerated by placing a high positive charge on the anode (unlike charges attract). A hole in the anode permits the high velocity electrons to strike the target.

elements. At the present time there are 101 elements—9 of which are *artificial*.* Figure 75 illustrates the basic concept of the atom smasher.

NUCLEAR FISSION

In the early part of our study, we said that chemical reactions usually release energy—sometimes in small amounts as in the rusting of iron, and sometimes in huge amounts as in the blast of TNT. Regardless of the magnitude, however, the energy is released by the same mechanism—the *loss or gain of electrons*. In 1939 it was demonstrated that atoms are able (under certain conditions) to yield terrific amounts of energy by another mechanism—*nuclear fission*. Nuclear fission is the term applied to the splitting of an atom's nucleus. Long before this experimental proof, it was realized that unbelievable amounts of energy were locked in the nuclei of atoms. This theory was supported by the fact that if this tremendous energy were not present the nucleus would fly apart, since the protons of the nucleus, being of the same charge, would repel one another. It was further realized that if the nucleus could be split, this energy would be *released*. Until 1939, however, no

* These include all the elements heavier than uranium: neptunium (${}_{237}\text{Np}^{93}$), plutonium (${}_{242}\text{Pu}^{94}$), americium (${}_{243}\text{Am}^{95}$), curium (${}_{246}\text{Cm}^{96}$), berkelium (${}_{248}\text{Bk}^{97}$), californium (${}_{250}\text{Cf}^{98}$), einsteinium (${}_{251}\text{Es}^{99}$), fermium (${}_{254}\text{Fm}^{100}$), and mendelevium (${}_{256}\text{Mv}^{101}$).

one had been able to split atoms (in the atom smashers) in sufficient number to produce any significant amount of energy. Moreover, more energy was required to operate these giant machines than was released by fission.

The fission reaction of 1939 was concerned with an isotope of uranium— U^{235} (ordinary uranium is U^{238}). It was demonstrated that slow-moving neutrons penetrate the U^{235} nuclei, forming U^{236} . Being unstable, U^{236} immediately splits into smaller nuclei and two or more *additional neutrons*. These neutrons touch off other U^{235} nuclei, so that the fission is not only sustained but *intensified*. This unique type of fission is referred to as a *chain reaction*. The implication of this phenomenon was this: A pound or so of U^{235} could yield energy with a force billions of times that possessed by an equivalent amount of TNT.

We can perhaps better appreciate how the infinitely small nucleus is capable of releasing such energy if we consider Einstein's formula— $E = mc^2$ (energy equals mass times the speed of light squared). When the uranium nucleus splits, the sum of the nuclei which are produced weighs *less* than the original nucleus; matter, therefore, has been *converted into energy* in accordance with $E = mc^2$. What is important to appreciate is this: Even though the matter (mass) which disappears is unbelievably minute, it is being *multiplied* by the speed of light squared (186,000 miles per second). Moreover, this figure is further multiplied by the astronomic number of atoms present in a small amount of the material. The reason why a volcanic explosion did not take place in 1939 was because the reaction was *controlled*; that is, the bulk of the neutrons which were released by the fission of U^{235} were absorbed by inert material. See Figure 76 for a pictorial presentation of nuclear fission and the chain reaction.

The Atomic Bomb. As we all know, the *atomic bomb* came as an inevitable sequel to the chain reaction. The development of the bomb was the most complex and expensive project that man had ever undertaken. The chief obstacle resulted from the tremendous task of separating the infinitesimal quantities of U^{235} from uranium ore— U^{235} *constitutes less than 1 per cent of a given quantity of the element*. A huge chemical plant was built at Oak Ridge, Tennessee, exclusively for the production of U^{235} .

Soon after atomic scientists had started their work on U^{235} , it was discovered that another element possessed fissionable powers—*plutonium*. Since plutonium could be produced from the relatively abundant U^{238} in a device called an *atomic pile*, there was no longer any question about the success of the bomb. For the production and isolation of plutonium from uranium, another giant chemical plant was constructed at Hanford, Washington.

The bomb itself (Fig. 77) consists of two charges—a small mass of U^{235} separated from a larger mass of plutonium. As long as these two fissionable masses are kept apart, no explosion occurs. This is because a good share of the neutrons which are being released by the fission of their nuclei are escaping into the air. When brought together, however, so as to exceed the so-called “critical mass,” the neutrons are present in sufficient quantity to set off a chain reaction which is com-

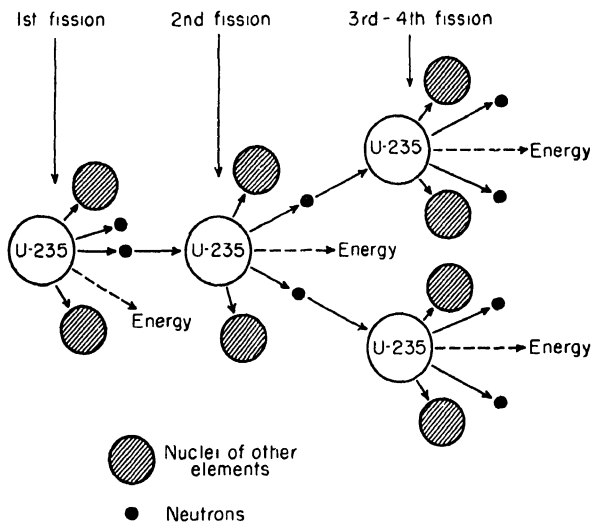


Fig. 76. A diagram to illustrate the fission of uranium-235 atoms. Since the first fission “sets off” other U^{235} nuclei, we have a so-called “chain reaction.”

plete in about a millionth of a second. The two bombs used in World War II unleashed an energy equivalent to about 20,000 tons of TNT.

The Hydrogen Bomb. Already the atomic bomb has been made obsolete and tame in comparison to the hydrogen bomb.* In contrast to the atomic bomb, the hydrogen bomb explodes by a *fusion* of its nuclei instead of fission. The principle, however, is the same—mass is converted into energy. The hydrogen bomb is reported to contain a charge of *tritium*—an isotope of hydrogen (${}^3\text{H}$). When the tritium nuclei are detonated by a “small atomic bomb,” they *fuse* to form larger nuclei (viz., helium). A loss of mass results (the large nuclei weigh less than the sum of the smaller nuclei from which they were formed) and energy is released. Unlike the atomic bomb, there is no

* Also referred to as a *thermonuclear* bomb.

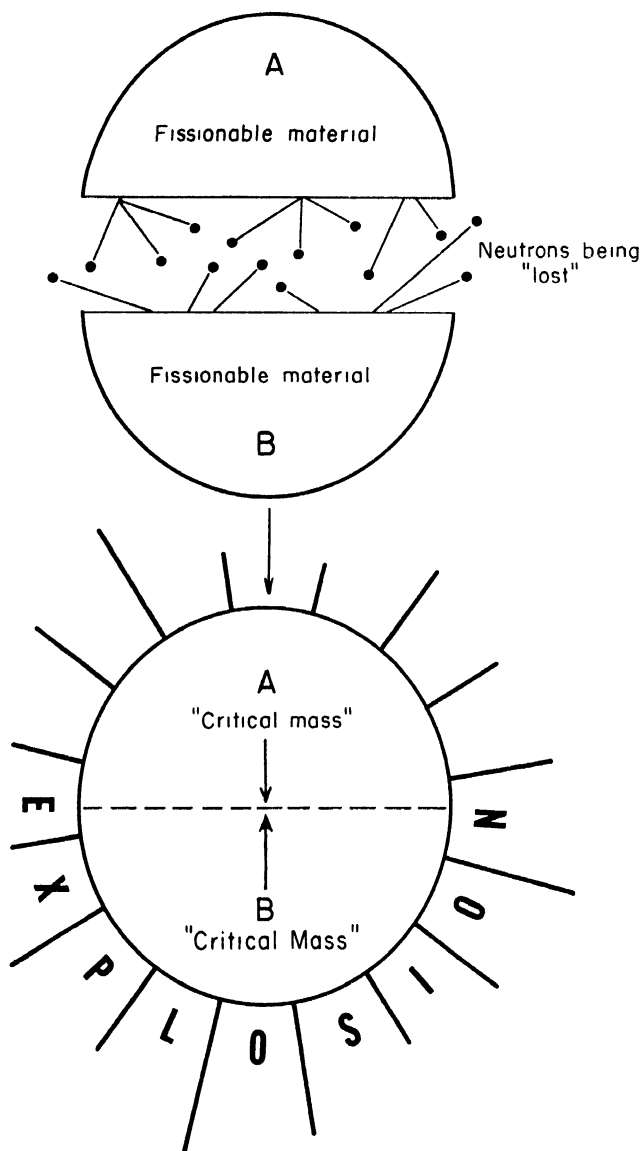


Fig. 77. It is now known that atomic bombs are detonated by bringing together two masses of fissionable material to form a "critical mass." When kept apart these two masses (subcritical) lose sufficient neutrons to the air to prevent a "fast" chain reaction.

critical mass involved, which means that a hydrogen bomb may be made as *large as desired*. Since the sun derives its energy by the same mechanism, i.e., the conversion of hydrogen isotopes into helium, the chemist and physicist have duplicated one of the most fundamental reactions of the universe.

Effects of Radiation. When an atomic device explodes, the blast represents only one of our fears—the other is the radiation which is deadly to all living things within several square miles surrounding the blast. In addition, polluted air and water may be carried far into the interior of a region. The radiations accompanying an atomic blast are due principally to *gamma rays and neutrons*. Gamma rays are more penetrating and dangerous than x-rays. Unlike alpha and beta rays, which are stopped by thin sheets of metal, gamma rays are capable of passing through *several inches* of lead. Neutrons are dangerous to life in that they transmute certain of the body's elements (e.g., sodium and phosphorus) into radioactive isotopes. Although radiation sickness presents a concert of pathologic changes, the early effects are referable to the blood, where there is usually a reduction of both red cells (*anemia*) and white cells (*leukopenia*). Animal studies and human studies (of those people who survived the atomic explosions in Japan) demonstrate that radiation can also bring about adverse inheritable changes. At present, however, this area of investigation is quite speculative. In spite of the terrible implications of radiation studies, there is a good side: What we learn about protecting ourselves can be applied to all those who handle radioactive materials for peaceful purposes.

ATOMIC ENERGY AND SOCIETY

Atomic energy is a term which has evolved to include all phases of nuclear chemistry—*radioactivity, transmutation, fission, fusion*, and so on. When the time comes when man respects his fellow men, this energy will serve to enable society to construct a world far beyond our most vivid imaginations. Even though the threat of war has demanded that the scientists of the free world direct the bulk of their energies to the process of survival via nuclear weapons, there has still been a significant gain in peaceful pursuits. There seems to be no limit to the usefulness of atomic energy. Every area of science, medicine and industry has already enjoyed the fruits of atomic research. The following topics present the avenues through which the atom can serve all of us.

Atomic Power. Atomic power is already a giant reality. The year 1954 will be remembered as the year of the first form of atomic locomotion (the submarine *Nautilus*) and the first atomic electric plant (located at Shippingport, Pennsylvania). Unlike conventional sources of

power—viz., coal, oil, water—atomic power is without limit, and could be available to all people. If atomic power projects are permitted to flourish, every society will enhance its standard of living. There is no reason not to believe that atomic power will some day supplant all forms of conventional power.

The theory of atomic power is not difficult to understand. A small amount of fissionable material is placed into a special device, or holder, called a *reactor*. Since the fission is *controlled*, no explosion occurs; instead, great amounts of heat are released. The heat can then be used to heat water for steam, and the steam used to generate electricity. In practice, a reactor plant^{*} is not this simple; great problems had to be solved, such as finding a material which could withstand the heat of the reactor, and the disposal of radioactive wastes.

Radioactive Isotopes. So far, radioactive isotopes have been employed in innumerable ways in just about every branch of science. Their usefulness arises from the fact (already discussed) that they emit rays of energy. The following brief statements will illustrate the manner in which they are handled.

THE TRACER TECHNIQUE. In the biologic sciences, radioactive isotopes are used to “tag” compounds in order to follow—via the *Geiger-Müller counter*—their disposition within plant and animal tissues. A tagged compound is prepared by replacing an element’s stable isotope with a radioactive isotope. Carbon dioxide, for example—prepared from ${}^{14}_6\text{C}$ instead of ${}^{12}_6\text{C}$ —has enabled the botanist to learn a great deal more about the process of photosynthesis. In general, this so-called *tracer technique* has brought forth information which otherwise could never have been elicited by conventional methods.

MEDICINE. The rays emitted by radium and radioactive isotopes have a profound influence on protoplasm. It is thought that the effects of radiation are due to the ability of the rays to *ionize* atoms and molecules, and in this manner alter the cell’s chemistry. X-rays and radium have been used for years in the treatment of cancer. The availability of artificial radioactive isotopes, however, has enabled the physician to treat the patient in a more efficacious and economical way. Moreover, certain isotopes offer special advantages. For example, radioactive iodine has proven to be highly effective in the management of cancerous thyroid. Radioactive iodine—like the stable isotope—accumulates in the thyroid tissue, and delivers a powerful dose of radiation at *exactly* the spot where it is needed. At the present time, several artificial isotopes are employed in medicine. The most frequently used include: carbon-14 (${}^{14}_6\text{C}$), sodium-24 (${}^{24}_{11}\text{Na}$), phosphorus-32 (${}^{32}_{15}\text{P}$), cobalt-60 (${}^{60}_{27}\text{Co}$) and iodine-131 (${}^{131}_{53}\text{I}$).

QUESTIONS

Matching: Write the number of the word or expression found in Column II in front of each word or expression in Column I which shows the *most* relation.

Column I

- . . isotope
- . neutrons plus protons
- . . . gamma rays
- . beta rays
- . transmutation
- . . alpha rays
- . . fission
- . . fusion
- . atom smasher
- . a "tagged" compound
- . like gamma rays
- . photographic plates
- . ionization
- . $E = mc^2$
- . ^{14}C decreases; ^{12}C increases

Column II

- 1. detect the presence of invisible rays
- 2. reaction by which the sun produces energy
- 3. helium nuclei
- 4. x-rays
- 5. atomic weight
- 6. the splitting of nuclei
- 7. $^{23}_{11}\text{Na}$ replaced with $^{24}_{11}\text{Na}$
- 8. radium to lead
- 9. differs from another element in relation to its atomic weight
- 10. subatomic particles accelerated
- 11. high velocity electrons
- 12. more penetrating than x-rays
- 13. explains the tremendous power of an atomic blast
- 14. happens in a piece of wood
- 15. mechanism by which radiation "denatures" protoplasm

APPENDIX

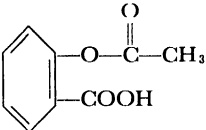
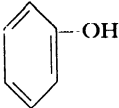
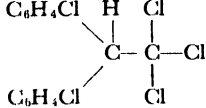
TABLE OF ELEMENTS
International Atomic Weights

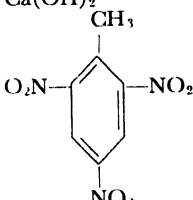
<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Actinium	Ac	89	227
Aluminum	Al	13	26 9
Americium	Am	95	241
Antimony	Sb	51	121 7
Argon	A	18	39 9
Arsenic	As	33	74 9
Astatine	At	85	211
Barium	Ba	56	137 4
Berkelium	Bk	97	243
Beryllium	Be	4	9 0
Bismuth	Bi	83	209 0
Boron	B	5	10 8
Bromine	Br	35	79 9
Cadmium	Cd	48	112 4
Calcium	Ca	20	40 0
Californium	Cf	98	244
Carbon	C	6	12 0
Cerium	Ce	58	140 1
Cesium	Cs	55	132 9
Chlorine	Cl	17	35 5
Chromium	Cr	24	52 0
Cobalt	Co	27	58 9
Copper	Cu	29	63 5
Curium	Cm	96	242
Dysprosium	Dy	66	162 5
Einsteinium	E	99	247
Erbium	Er	68	167 2
Europium	Eu	63	152 0
Fermium	Fm	100	254
Fluorine	F	9	19 0
Francium	Fr	87	223
Gadolinium	Gd	64	156 9
Gallium	Ga	31	69 7
Germanium	Ge	32	72 6
Gold	Au	79	197 2
Hafnium	Hf	72	178 6
Helium	He	2	4 0

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Holmium	Ho	67	164.9
Hydrogen	H	1	1.0
Indium	In	49	114.8
Iodine	I	53	126.9
Iridium	Ir	77	193.1
Iron	Fe	26	55.9
Krypton	Kr	36	83.8
Lanthanum	La	57	138.9
Lead	Pb	82	207.2
Lithium	Li	3	6.9
Lutetium	Lu	71	174.9
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mendelevium	Mv	101	256
Mercury	Hg	80	200.6
Molybdenum	Mo	42	95.9
Neodymium	Nd	60	144.3
Neon	Ne	10	20.2
Neptunium	Np	93	239
Nickel	Ni	28	58.7
Niobium	Nb	41	92.9
Nitrogen	N	7	14.0
Osmium	Os	76	190.2
Oxygen	O	8	16.0
Palladium	Pd	46	106.7
Phosphorus	P	15	30.9
Platinum	Pt	78	195.2
Plutonium	Pu	94	238
Polonium	Po	84	210
Potassium	K	19	39.1
Praseodymium	Pr	59	140.9
Promethium	Pm	61	147
Protactinium	Pa	91	231
Radium	Ra	88	226.0
Radon	Rn	86	222.0
Rhenium	Re	75	186.3
Rhodium	Rh	45	102.9
Rubidium	Rb	37	85.5
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.4
Scandium	Sc	21	44.9
Selenium	Se	34	78.9
Silicon	Si	14	28.1
Silver	Ag	47	107.9
Sodium	Na	11	22.9
Strontium	Sr	38	87.6

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Sulfur	S	16	32.1
Tantalum	Ta	73	180.8
Technetium	Tc	43	99.0
Tellurium	Te	52	127.6
Terbium	Tb	65	159.0
Thallium	Tl	81	204.4
Thorium	Th	90	232.1
Thulium	Tm	69	169.4
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.9
Uranium	U	92	238.1
Vanadium	V	23	50.9
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.0
Yttrium	Y	39	88.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

COMMON NAMES OF SOME IMPORTANT CHEMICALS

<i>Common Name</i>	<i>Chemical Name</i>	<i>Formula</i>
Acetone	dimethyl ketone	$(\text{CH}_3)_2\text{CO}$
Alcohol	ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$
Alum (common)	potassium aluminum sulfate	$\text{KAl}(\text{SO}_4) \cdot 12\text{H}_2\text{O}$
Ammonia	ammonium hydroxide	NH_4OH
Ammonia water	ammonium hydroxide	NH_4OH
Arsenic	arsenic trioxide	As_2O_3
Aspirin	acetylsalicylic acid	
Baking soda	sodium bicarbonate	NaHCO_3
Benzene	benzol	
Bicarbonate of soda	sodium bicarbonate	NaHCO_3
Bichloride of mercury	mercuric chloride	HgCl_2
Bleaching powder	calcium hypochloride	CaOCl_2
Blue vitriol	cupric sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Borax	sodium tetraborate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Boric acid	boracic acid	H_3BO_3
Calomel	mercurous chloride	Hg_2Cl_2
Cane sugar	sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Carbolic acid	phenol	
Carbon tetrachloride	tetrachloromethane	CCl_4
Caustic potash	potassium hydroxide	KOH
Caustic soda	sodium hydroxide	NaOH
Chile saltpeter	sodium nitrate	NaNO_3
Choke damp	methane	CH_4
Chloride of lime	calcium hypochloride	CaOCl_2
Chloroform	trichloromethane	CHCl_3
Copperas	ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Corrosive sublimate	mercuric chloride	HgCl_2
Dakin's solution	0.5% solution of sodium hypochlorite	NaClO
Dextrose	glucose	$\text{C}_6\text{H}_{12}\text{O}_6$
DDT	dichlorodiphenyltrichloroethane	

<i>Common Name</i>	<i>Chemical Name</i>	<i>Formula</i>
Epsom salt(s)	magnesium sulfate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Ether	diethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$
Ethyl ether	diethyl ether	$(\text{C}_2\text{H}_5)_2\text{O}$
Fire damp	methane	CH_4
Formalin	a 37% solution of formaldehyde	HCHO
Glauber's salt	sodium sulfate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Glycerin(e)	glycerol	$\text{C}_3\text{H}_5(\text{OH})_3$
Grain alcohol	ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$
Grape sugar	glucose	$\text{C}_6\text{H}_{12}\text{O}_6$
Green vitriol	ferrous sulfate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Household ammonia	ammonium hydroxide	NH_4OH
Iodoform	triiodomethane	CHI_3
Laughing gas	nitrous oxide	N_2O
Levulose	fructose	$\text{C}_6\text{H}_{12}\text{O}_6$
Limestone	calcium carbonate	CaCO_3
Limewater	a saturated solution of calcium hydroxide	$\text{Ca}(\text{OH})_2$
Lunar caustic	silver nitrate	AgNO_3
Lye	sodium hydroxide	NaOH
Malt sugar	maltose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Marsh gas	methane	CH_4
Milk of magnesia	magnesium hydroxide	$\text{Mg}(\text{OH})_2$
Milk sugar	lactose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$
Muriatic acid	hydrochloric acid	HCl
Nitroglycerin(e)	glyceryl trinitrate	$\text{C}_3\text{H}_5(\text{NO}_3)_3$
Normal saline	a 0.9% solution of sodium chloride	NaCl
Oil of vitriol	sulfuric acid	H_2SO_4
Plaster of Paris	calcium sulfate	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$
Precipitated chalk	calcium carbonate	CaCO_3
Quicklime	calcium oxide	CaO
Quicksilver	mercury	Hg
Salt (common)	sodium chloride	NaCl
Saltpeter	potassium nitrate	KNO_3
Simple sugar	glucose	$\text{C}_6\text{H}_{12}\text{O}_6$
Slaked lime	calcium hydroxide	$\text{Ca}(\text{OH})_2$
TNT	trinitrotoluene	CH_3  O_2N NO_2
Washing soda	sodium carbonate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
White vitriol	zinc sulfate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Wood alcohol	methyl alcohol	CH_3OH

GENERAL RULES OF SOLUBILITY*

Ammonium salts	all common salts <i>soluble</i> .
Bromides	all <i>soluble</i> except those of lead, silver and mercury.
Chlorides	all <i>soluble</i> except lead, silver and mercurous chlorides.
Carbonates	all the common carbonates are <i>insoluble</i> except those of sodium, potassium and ammonium.
Hydroxides	sodium, potassium and ammonium are <i>soluble</i> ; those of calcium, barium and strontium are only <i>moderately soluble</i> ; all other hydroxides are <i>insoluble</i> .
Nitrates	all <i>soluble</i> .
Oxides	sodium, potassium, calcium, barium and strontium react with water to form <i>hydroxides</i> . Oxides of other common elements are <i>insoluble</i> .
Phosphates	all are <i>insoluble</i> except those of sodium, potassium and ammonium.
Potassium salts	all common salts <i>soluble</i> .
Sodium salts	all common salts <i>soluble</i> .
Sulfates	barium, calcium, lead and strontium are <i>insoluble</i> , all others are <i>soluble</i> .

Organic Compounds

Alkali and ammonium salts of organic acids (e.g., sodium acetate) are *extremely soluble* in water. Alcohols, ketones, low molecular weight acids and sugars are, in general, *fairly soluble in water*. In general, all other organic compounds are *sparingly soluble or insoluble in water*, but *soluble in organic solvents* such as alcohol, chloroform and acetone.

* In water.

GLOSSARY

ABSORPTION. To be taken into the "inside" of a substance.

ABSOLUTE TEMPERATURE. A scale for measuring temperature which is obtained by adding algebraically 273° and degrees Centigrade. For example, 273° Absolute (A.) is equal to 0° Centigrade (C.).

ACETONE BODIES. Refers to organic ketone compounds (such as acetone) which accumulate in the blood during certain diseases (viz., diabetes).

ACETYLENE SERIES. A series of hydrocarbons whose members contain a triple bond.

ACID. A compound which, in solution, furnishes hydrogen ions.

ACID ANHYDRIDE. A nonmetallic oxide which reacts with water to form an acid.

ACIDOSIS. A condition in which the blood's buffer system is "overtaxed" either without a change in pH (compensated acidosis), or with a lowering of the pH (uncompensated).

ADDISON'S DISEASE. A disease which is caused by insufficient production of the adrenals' cortical hormones.

ADDITION. The reaction between an unsaturated organic compound and another element, whereby the element's atoms "add" on to the unsaturated molecule.

ADRENAL CORTEX. The outer portion of the adrenal gland.

ADRENAL MEDULLA. The inner portion of the adrenal gland.

ADRENALS. The two endocrine glands which are located on the top of each kidney.

ADSORPTION. To collect on a substance's surface.

AEROBIC. Oxygen present (or needed).

AEROSOL. An extremely fine spray where the droplets of liquid are of colloidal size.

ALBUMINURIA. The presence of albumin in the urine.

ALCOHOL. An organic compound which contains a hydroxyl (OH) group.

ALDEHYDE. An organic compound which contains the so-called aldehyde group—CHO.

ALICYCLIC. Saturated compounds whose molecules are constituted by carbon atoms arranged in rings.

ALIPHATIC. Compounds whose molecules contain carbon atoms arranged in chains.

ALKALI. A term usually applied to strong soluble bases, e.g., sodium hydroxide, NaOH.

ALKALOID. A complex nitrogenous organic compound of plant origin which possesses physiologic activity in extremely small amounts. Alkaloids are optically active, with the levorotatory isomer usually being the most active.

- ALLOTROPISM.** A condition in which an element is capable of existing in more than one form, e.g., red and white phosphorus.
- ALPHA RAYS.** One of the three types of rays emitted by radioactive substances. They are composed of helium nuclei.
- ALVEOLUS.** The smallest respiratory unit of the lung.
- AMINO ACID.** An organic acid which contains an amino group.
- AMINO GROUP.** NH_2 .
- AMPHOTERIC.** Applies to a compound which exhibits both acidic and basic properties. Applied to elements, it refers to one which has both metallic and nonmetallic properties.
- ANABOLISM.** Refers to all constructive, or synthetic, chemical processes in the body.
- ANAEROBIC.** Oxygen absent (or not needed).
- ANALYSIS.** A process which breaks up the constituent atoms of a molecule.
- ANEMIA.** A condition in which the red cells and/or hemoglobin of the blood are reduced below normal.
- ANESTHETIC.** A substance which brings about loss of sensation, either of the whole body, or a certain part.
- ANHYDROUS SALT (ANHYDRATE).** A salt whose water of crystallization has been removed.
- ANION.** A negatively charged ion.
- ANODE.** The positive electrical pole.
- ANTIBIOTIC.** A drug derived from mold or bacterial cultures which inhibits the growth of other microorganisms.
- ANTISEPTIC.** A chemical substance which inhibits microbial growth.
- ANTISPASMODIC.** A drug which inhibits muscular spasms.
- AROMATIC COMPOUNDS.** A term applied to all derivatives of the benzene series.
- ARTERIAL BLOOD.** That blood which has been oxygenated.
- ATOM.** The smallest "unit" of an element.
- ATOM SMASHER.** A complex electrical device which splits nuclei of atoms by hurling, at tremendous speeds, subatomic particles.
- ATOMIC NUMBER.** Refers to the number of electrons about the nucleus of an atom. It is also numerically equal to the number of protons in the nucleus.
- ATOMIC PILE.** A device for carrying out controlled chain reactions.
- ATOMIC WEIGHT.** A number which is derived by adding the number of protons and neutrons present in the nucleus of an atom.
- AUTONOMIC NERVOUS SYSTEM.** Refers to all those nerves which involuntarily govern the body's smooth muscle.
- AVOGADRO'S LAW.** This law states that equal volumes of gases, measured under the same conditions of temperature and pressure, contain the same number of molecules.
- ATOMIC THEORY.** This theory states that all elements are composed of atoms, and that chemical activity between elements is really the combining of their atoms.

BACTERIA. Microscopic plants.

BASAL METABOLIC RATE (B.M.R.). The minimum amount of energy (expressed as Calories per square meter per hour) which is required to sustain life in a body at complete physical and mental rest.

BASE. A compound which in solution furnishes hydroxyl ions.

BASIC ANHYDRIDE. A metallic oxide which reacts with water to form a base.

BENEDICT'S SOLUTION. A solution used to test for the presence of reducing sugars.

BETA RAYS. One of the three types of rays emitted by radioactive substances; they are constituted by high velocity electrons.

BENZIDINE TEST. A test for hemoglobin employing benzidine (dissolved in glacial acetic acid) and hydrogen peroxide. A positive test is indicated by a blue color.

BILE. A secretion manufactured in the liver (and stored in the gallbladder) which aids in the digestion of fats.

BIOCHEMISTRY. The chemistry of living processes.

BIURET TEST. A test for proteins employing copper sulfate and sodium hydroxide. When these two substances are heated with a protein, a pink to violet color is produced.

BOND. A line (used in structural formulas) which represents a pair of shared electrons.

BOYLE'S LAW. This law states that the volume of a gas is inversely proportional to the pressure, provided there is no change in the temperature.

BRÖNSTED THEORY. A theory—more comprehensive than the conventional theory of acids and bases—which defines an acid as a proton donor, and a base as a proton acceptor.

BROWNIAN MOVEMENT. Refers to the rapid zigzag motion of colloidal particles as observed under the microscope.

CALCIFICATION. Deposition of bone.

CALORIE. A small calorie (cal.) is the amount of heat required to raise the temperature of 1 gram of water 1° Centigrade; a large calorie (Cal.) is 1000 times a small calorie.

CALORIMETER. A device used to measure calories.

CAPILLARIES. Microscopic vessels, one cell thick, which lie between the arteries and veins.

CARBOCYCLIC COMPOUND. An organic compound whose molecules are constituted by rings containing only carbon.

CARBOHYDRATES. A class of organic compounds whose members contain only carbon, hydrogen and oxygen, with the hydrogen in ratio to the oxygen of 2:1.

CARBONATES. Compounds which contain the CO_3 group.

CARBON CYCLE. The exchange of carbon dioxide, carbohydrates and oxygen between plants and animals.

CARBONYL GROUP. The CO group present in aldehydes and ketone.

CARBOXYL GROUP. The COOH group—characteristic of organic acids.

CATABOLISM. The breaking down of chemical substances within living tissues—"destructive metabolism."

CATALYTIC AGENT. An agent which in extremely small quantities enhances or retards a chemical reaction.

CATAPHORESIS. The migration of colloidal particles to an electric pole of opposite sign; similar to electrolysis of true solutions (also called electrophoresis).

CATHODE. The negative pole or electrode.

CATION. A positively charged ion.

CENTIGRADE. A scale for measuring temperature (used in scientific work) at which water freezes at 0° and boils at 100° . It is derived from the Fahrenheit reading by the following formula: $C. = \frac{5}{9}(F. - 32)$.

CENTRAL NERVOUS SYSTEM. Refers to the brain and spinal cord.

CHAIN STRUCTURE. Organic molecules whose atoms are arranged in chains; i.e., they have open ends.

CHARLES' LAW. The volume of a gas is directly proportional to the absolute temperature, provided there is no change in pressure.

CHEMICAL CHANGE. A change which involves a rearrangement of a substance's atoms.

CHEMISTRY The study of matter.

CHEMOTHERAPY. The treatment of disease (usually infectious) using specific chemical substances.

CHLORIDES. Salts of hydrochloric acid.

CHYME. The semifluid material which leaves the stomach.

COAGULATION. The process of becoming viscous or jelly-like.

COAL TAR. The black, sticky, viscous material derived from the destructive distillation of bituminous coal.

COENZYME. A chemical agent which enhances the action of an enzyme.

COMBUSTION. Rapid oxidation—with heat and light.

COMPOUND. A substance whose molecules are constituted by two or more elements in a definite ratio by weight.

CONCENTRATED SOLUTION. A solution which contains a relatively large amount of solute.

CONDENSATION. Changing from a vapor to a liquid as, for example, steam changing to water.

COLLOID. Technically speaking, refers to a "system" where one state (gas, liquid or solid) is dispersed in another state (gas, liquid or solid).

COVALENCE. The sharing of electrons.

CRACKING. An industrial process which produces low molecular weight hydrocarbons, viz., gasoline, by subjecting higher molecular weight hydrocarbons to high pressure and heat.

CRETINISM. A condition of hypothyroidism in infants.

CRITICAL MASS. That amount of fissionable material (e.g., uranium-235) which, if exceeded, produces an atomic explosion.

CRYSTALLIDS. Substances which dissolve to form true solutions.

CUBIC CENTIMETER. A common unit of volume employed in chemistry. It is equivalent to approximately $\frac{1}{30}$ of an ounce.

CYCLIC COMPOUNDS. Organic compounds whose molecules are constituted by atoms arranged in rings.

CYCLOTRON. The first successful large scale atom smasher.

DECALCIFICATION. The breaking down (chemical) of bone.

DEHYDRATING AGENT. A substance which removes water.

DELIQUESCENT. The process whereby certain substances remove sufficient water from the air to dissolve themselves.

DENSITY. Mass divided by volume.

DERMATITIS. Inflammation of the skin.

DESTRUCTIVE DISTILLATION. The heating of a substance out of contact with air

DETERGENT. An agent which cleans by virtue of its ability to greatly lower surface tension.

DEXTROROTATORY. An optically active isomer which turns the plane of polarized light to the right (abbreviated, *d*-).

DIABETES MELLITUS. A disease caused by an insufficient secretion of insulin by the pancreas.

DIALYSIS. The separation of a crystalloid and a colloid using a parchment or cellophane membrane.

DIGESTION. The process of breaking down proteins to amino acids; carbohydrates to glucose, fructose and galactose; fats to glycerin and fatty acids.

DILUTE SOLUTION. A solution which contains relatively little solute.

DIRECT CURRENT. Current which flows in one direction only and has polarity, i.e., a positive and a negative pole.

DISACCHARIDES. Sugars having the formula $C_{12}H_{22}O_{11}$.

DISINFECTANT. An agent which kills pathogenic microorganisms.

DISPERSED PHASE. That part of a colloidal system which is suspended in another phase; also called internal phase

DISPERSION MEDIUM. The phase (gas, liquid or solid) of a colloidal system which holds the dispersed phase; also called external phase.

DISSOCIATION. The formation of ions in solution.

DISTILLATION. A process of heating a liquid and condensing its vapors. Employed for separation and purification of liquids.

DYNAMIC EQUILIBRIUM. Applied to reversible reactions where the speed to the right is equal to the speed to the left.

EDEMA. A pathologic state where water accumulates in the tissues.

EFFERVESCENCE. The giving off of a gas.

EFFLORESCENCE. The spontaneous loss of water by a compound.

ELECTROLYSIS. The decomposition of a compound by means of an electric current.

ELECTROLYTE BALANCE. Refers to the constant concentration of metallic ions in the body's fluids.

ELECTROLYTES. Compounds (acids, bases and salts) which carry an electric current when placed in solution.

ELECTROPHORESIS. The migration of colloidal particles to an electric pole; also known as cataphoresis.

ELECTRON THEORY. The theory which states that atoms are constituted by protons, neutrons and electrons, where the protons and neutrons are located in a dense core called the nucleus, with the electrons revolving around this nucleus in definite orbits.

ELECTRON VOLT. A measure of energy.

ELECTROVALENCE. The loss or gain of electrons.

ELEMENT. A substance composed of like atoms. There are 92 natural elements and 9 artificial.

EMPIRICAL FORMULA. A formula which states the kind and number of atoms which constitute the molecules of a compound, without reference to how they are arranged.

EMULSIFYING AGENT. An agent which enhances the formation of an emulsion by reducing surface tension.

EMULSION. A colloidal system of one liquid dispersed in another liquid.

EMULSOID. A colloidal system of a solid in a liquid, where the solid has an affinity for the liquid; gels are emulsoids.

ENDOCRINE GLANDS. Glands which deliver their secretions directly to the blood; also called ductless glands.

ENERGY. The ability to do work.

ENZYME. A proteinaceous catalyst found in living tissues, commonly referred to as an organic catalyst.

EQUATION. A balanced chemical expression which states the reactants and products of a reaction.

EQUIVALENT WEIGHT. The equivalent weight of an element is equal to its atomic weight divided by its valence. The equivalent weight of a compound is equal to its molecular weight divided by the highest valence present in the compound; e.g., the equivalent weight of CaCl_2 is equal to 111 (its molecular weight) divided by 2 (the valence of calcium), or 55.5. The equivalent weight is expressed in grams.

ESTERIFICATION. The reaction between an alcohol and an acid to form an ester.

ESTERS. Organic salts formed by reacting alcohols with acids.

ETHERS. Organic oxides.

ETHYLENE SERIES. A series of hydrocarbons whose members contain a double bond.

EXOCRINE GLANDS. Glands which deliver their secretions through a duct, e.g., the salivary glands.

EXTERNAL PHASE. See *Dispersion medium*.

EXTRACELLULAR COMPARTMENT. Refers to the fluids (viz., blood and tissue fluid) outside the body's cells.

FAHRENHEIT. A scale for measuring temperature where water freezes at 32° and boils at 212° . It is derived from the Centigrade scale by the following formula: $F. = {}^\circ\text{C.} + 32^\circ$.

- FAT.** An ester formed from glycerin and a fatty acid.
- FECES.** That material which is not digested and is excreted via the rectum.
- FEHLING'S SOLUTION.** A solution used to test for the presence of reducing sugars.
- FISSION.** The splitting of atomic nuclei.
- FLUX.** A material used to remove impurities, e.g., the use of limestone in the blast furnace.
- FOAM.** A colloidal system of a gas dispersed in a liquid.
- FOG.** A colloidal system of a liquid dispersed in a gas.
- FRACTIONAL DISTILLATION.** Separation of liquids by virtue of their different boiling points.
- FUSION.** The synthesis of larger nuclei from smaller nuclei. Also used synonymously with the term "melting."
- GALLBLADDER.** A muscular sac contiguous to the liver which stores and concentrates bile.
- GAMMA RAYS.** One of the three types of rays emitted by radioactive substances. They are electromagnetic and more penetrating than x-rays.
- GANGLION.** A group of nerve cells located outside the central nervous system.
- GAY-LUSSAC'S LAW.** When gases react, the volumes of these gases and the volumes of the products, if gaseous, are in a ratio to each other that may be expressed by small whole numbers.
- GEIGER-MÜLLER COUNTER.** An electric device used to detect radioactive rays.
- GEL.** A semisolid colloid.
- GLUCONEOGENESIS.** The formation of glucose from proteins.
- GLUCOSURIA.** See *Glycosuria*.
- GLYCOGENESIS.** The building up in the liver of glycogen from glucose.
- GLYCOGENOLYSIS.** The breaking down in the liver of glycogen to glucose.
- GLYCOSIDE.** A physiologically active principle of plant origin whose molecules contain a monosaccharide.
- GLYCOSURIA.** The presence of sugar in the urine, also referred to as glucosuria.
- GONADS.** A general term for the sex glands, i.e., the ovaries and testes.
- GRAM.** The unit of weight in the Metric System. One avoirdupois ounce is equal to 28.4 grams.
- GRAM MOLECULAR VOLUME.** This is equal to 22.4 liters; i.e., at 0° Centigrade and 760 mm. Hg, 1 mole of a gas occupies 22.4 liters.
- HALF-LIFE.** The time required for a given amount of a radioactive element to lose half of its mass.
- HALOGENS.** Fluorine, chlorine, bromine and iodine.
- HARD WATER.** Water which contains salts of (principally) calcium and magnesium. These salts react with soap to form a precipitate, thereby reducing the efficacy of the soap.

HEAT OF FUSION. The latent heat required to change a solid (at its melting point) to a liquid. It is expressed as calories per gram.

HEAT OF VAPORIZATION. The latent heat required to convert a liquid (at its boiling point) to a gas. It is expressed as calories per gram.

HEMATURIA. The presence of blood in the urine.

HEMOGLOBIN. The red pigment located in the red cell of the blood. It is a protein containing iron.

HEMOGLOBINURIA. The presence of hemoglobin in the urine.

HEMOLYSIS. The rupturing of the blood's red cells with the subsequent loss of hemoglobin.

HENRY'S LAW. The solubility of a gas in a liquid is directly proportional to the pressure.

HETEROCYCLIC COMPOUNDS. Organic compounds whose molecules are constituted by rings which contain carbon and some other atom or atoms.

HEXOSE. A monosaccharide sugar having the formula $C_6H_{12}O_6$.

HORMONE. A complex chemical substance secreted by an endocrine gland which regulates the physiology of one or more of the body's tissues.

HYDROCARBONS. Organic compounds which contain hydrogen and carbon only.

HYDROGENATION. A process whereby vegetable oils (containing unsaturated molecules) are reacted with hydrogen, in the presence of a catalyst, to produce a solid fat.

HYDROLYSIS. Any reaction involving water.

HYDRONIUM. H_3O^+ .

HYPERACIDITY. Excess acid in the stomach.

HYPERTHYROIDISM. A condition in which the thyroid gland secretes an excess amount of thyroxin.

HYPERTONIC SOLUTION. A solution which has a greater osmotic pressure than some other solution.

HYPOTHYROIDISM. A condition in which the thyroid gland secretes an insufficient amount of thyroxin.

HYPOTONIC SOLUTION. A solution which has a lower osmotic pressure than some other solution.

IMMISCIBLE LIQUIDS. Liquids which do not mix, (e.g., oil and water).

INDICATOR. A dye which changes color in an acidic or basic medium.

INORGANIC CHEMISTRY. The study of all the elements and their compounds, except carbon.

INTERNAL PHASE. See *Dispersed phase*.

INTRACELLULAR COMPARTMENT. Refers to the total amount of water within the body's cells.

ION. An electrically charged particle in solution.

IONIZATION THEORY. States that acids, bases and salts form ions (ionize in solution).

ISLANDS OF LANGERHANS. Specialized cells throughout the pancreas which manufacture insulin.

ISOMERS. Compounds which have the same empirical formula but different properties.

ISOTONIC SOLUTION. A solution which has the same osmotic pressure as another solution; e.g., normal saline (which contains 0.9 per cent sodium chloride) is isotonic with blood.

KERATINIZATION. A disease of the skin characterized by abnormal amounts of keratin, a nonliving hard substance present on the skin's surface.

KETONE BODIES. Ketone compounds (viz., acetone) which accumulate in the blood in certain pathologic conditions (viz., diabetes).

KETONES. Organic compounds which contain the carbonyl group (CO).

LACUNAE. Minute lymph vessels within the villi of the intestine which absorb fat during digestion.

LAW OF CONSERVATION OF ENERGY. Energy—under ordinary conditions—is neither created nor destroyed.

LAW OF CONSERVATION OF MATTER. Matter—under ordinary conditions—is neither created nor destroyed.

LAW OF DEFINITE PROPORTIONS. When elements react to form a compound, they always combine in a definite proportion by weight; thus, a compound always has the same formula.

LAW OF MASS ACTION. The speed of a chemical reaction is directly proportional to the concentration of the reacting substances.

LEUKOPENIA. A decrease in the number of white cells in the blood.

LEVOROTATORY. An optically active isomer which rotates the plane of polarized light to the left (abbreviated, *l*-).

LIPID. A fat or oil.

LITER. The unit of volume in the metric system. It is equal to 1000 milliliters (ml.) or 1000 cc.

LOCAL ANESTHETIC. A drug applied locally to obtund pain.

LYMPH. A water-like liquid which circulates through the lymph system, i.e., lymph nodes and lymphatic vessels.

LYOPHILIC. Having an affinity for the solvent.

LYOPHOBIC. Not having an affinity for the solvent.

MATTER. Anything that occupies space or has weight.

METABOLISM. The sum total of chemical processes taking place in the body.

METAL. Physically, an element which is a conductor of electricity and heat; also it is hard and has luster. Chemically, an element whose atoms form positive ions.

METER. The unit of length in the metric system; it is equal to 39.37 inches.

METHANE SERIES. A series of saturated hydrocarbons which has the general formula C_nH_{2n+2} ; also known as the paraffin series.

MICRON. A microscopic unit of measure which is equal to 0.001 mm., or 1/25,000 of an inch.

MILLIEQUIVALENT WEIGHT. This is equal to the equivalent weight divided by 1000.

MILLIMETERS OF MERCURY. A scientific way of expressing pressure. At sea level atmospheric pressure is equal to 760 mm. Hg.

MILLIMICRON. $\frac{1}{1000}$ of a micron.

MIOTIC. A drug which constricts the iris of the eye, thereby making the pupil smaller.

MISCIBLE LIQUIDS. Liquids which mix in all proportions.

MIXTURE. An indefinite combination of substances.

MOLAR SOLUTION. A solution which contains 1 mole of a compound per liter.

MOLE. The molecular weight expressed in grams.

MOLECULAR WEIGHT. The sum of the atomic weights in a molecule.

MOLECULE. The smallest particle of a compound.

MONOSACCHARIDES. Sugars which have the formula $C_nH_{2n}O_n$.

MUCOUS MEMBRANE. A thin membrane which lines all open cavities.

MYDRIATIC. A drug which relaxes the iris, thereby enlarging the pupil.

MYONEURAL JUNCTION. Refers to the zone where the nerve endings are in proximity to the muscle.

MYXEDEMA. A condition of hypothyroidism in the adult.

NASCENT. Refers to the monatomic state of a diatomic gas; e.g., the nascent form of O₂ is O.

NEUTRALIZATION. The reaction between an acid and a base, forming salt and water.

NEUTRON. A neutral particle located in an atom's nucleus.

NITRATES. Salts of nitric acid (NO_3^-).

NITRITES. Salts of nitrous acid (NO_2^-).

NITROGEN BALANCE. The normal condition in which the body is receiving sufficient nitrogen, via proteins, to offset nitrogen losses. The balance is offset in malnutrition and certain other pathologic states.

NITROGEN CYCLE. The exchange of nitrogen between the inorganic and organic worlds through the agency of microorganisms.

NITROGEN-FIXING BACTERIA. Bacteria which are capable of incorporating the free nitrogen of the air into plant proteins or protoplasm.

NONELECTROLYTES. Compounds which, in solution, do not conduct an electric current.

NONMETAL. Physically, an element which is light, soft and a nonconductor of heat and electricity. Chemically, an element which forms negative ions.

NONPOLAR COMPOUND. A compound which does not furnish ions in solution.

NORMAL SALINE. A 0.9 per cent aqueous solution of sodium chloride.

NORMAL SOLUTION. A solution which contains the equivalent weight (in grams) of an element per liter of solution. Equivalent weight is equal to the atomic weight divided by the valence.

NUTRIENT. A substance essential for life.

OIL. Strictly speaking, an oil is a fat which is liquid at room temperature. The term is often applied to certain viscous liquids which chemically are not fats.

OLEFINS. Members of the ethylene series.

OPTICAL ACTIVITY. The ability of a compound in solution to rotate the plane of polarized light.

ORGANIC CHEMISTRY. The study of carbon compounds.

OVARY. The female sex gland.

OXIDATION. The union of oxygen with some other element; also, the loss of electrons.

OXIDE. A compound of oxygen and some other element.

PANCREAS. A long slender gland located beneath the stomach which manufactures a digestive juice and insulin.

PARAFFINS. Members of the methane series.

PARASYMPATHETIC NERVOUS SYSTEM. That portion of the autonomic nervous system whose fibers originate in the lower part of the brain and sacral portion of the spinal cord.

PARATHYROIDS. Tiny glands which are located on the posterior surface of the thyroid.

PELLAGRA. A disease caused by lack of niacin, or nicotinic acid.

PERIODIC TABLE. A table which arranges the elements according to their atomic numbers in such a way that similar elements fall into the same group.

PEPTIDE. A simple protein, i.e., one composed of only a few amino acids. Usually applied to certain intermediate products of protein digestion.

PERMANENT HARD WATER. Hard water which can be "softened" only by the use of chemical agents.

PETROLEUM. A dark, viscous, odoriferous liquid which was formed by the degradation—over millions of years—of plant and animal life.

pH. A mathematical expression of a solution's hydrogen ion concentration.

A pH of 7 is neutral. Any pH from 0 to 7 is acid; a pH of 7 to 14 is basic.

PHENOLS. Aromatic compounds constituted by molecules which contain hydroxyl groups attached directly to rings.

PHOSPHATES. Salts of phosphoric acid (PO_4^{3-}).

PHOTOSYNTHESIS. The synthesis of sugar by green plants from carbon dioxide and water, in the presence of sunlight and chlorophyll.

PHYSICAL CHANGE. Any change which does not alter a substance's atomic or molecular configuration. Usually, it is merely a change of state.

PHYSICS. The study of energy.

PITUITARY. An endocrine gland located at the base of the brain whose hormones regulate other endocrine glands.

PLASMA. The liquid portion of the blood.

PLASMOLYSIS. The shrinking of cells when placed in a hypertonic solution.

POLAR COMPOUNDS. Compounds which furnish ions in solution.

POLARIMETER. An instrument used for measuring optical rotation.

POLYMERIZATION. The building up of large molecules from smaller molecules.

POLYPEPTIDE. Used synonymously with peptide.

POLYSACCHARIDES. Polymers of monosaccharides having the formula $(C_6H_{10}O_5)_x$.

PRECIPITATE. An insoluble substance which falls from solution as a result of a chemical reaction.

PROTEINS. High molecular weight polymers of amino acids.

PROTON. A positively charged particle located in an atom's nucleus.

PROTOPLASM. The "stuff" from which living cells are made.

QUINONES. Aromatic ketones whose molecules contain oxygen attached directly to the ring.

RADICAL. A group of two or more elements which acts as a unit.

RADIOACTIVITY. The spontaneous emission of alpha, beta and gamma rays by a substance.

REACTOR. A device in which the heat evolved from a controlled chain reaction is used to furnish power; usually the heat is used to convert water into steam.

REAGENT. A chemical used to detect the presence of some other element or compound; e.g., silver nitrate is the reagent used in testing for chlorine. It reacts to form silver chloride, a white precipitate.

REDUCTION. The removal of oxygen from a compound; also, the gaining of electrons.

RESPIRATION. The exchange of oxygen, carbon dioxide and water vapor in the lungs and tissues.

RICKETS. Malformation of bone due to a lack of vitamin D.

RING STRUCTURE. Applied to organic compounds whose molecules are constituted by atoms arranged in rings.

RUBEFACIENT. A drug which is applied locally to cause reddening of the skin.

SAPONIFICATION. The reaction between a fat and a base, forming a soap.

SATURATED COMPOUND. An organic compound which does not contain double bonds.

SATURATED SOLUTION. A solution which is not able to dissolve any more solute at a given temperature.

SCURVY. The disease caused by a lack of vitamin C.

SEMIPERMEABLE MEMBRANE. A membrane which allows only water to pass. When it separates two solutions of different concentrations, an osmotic pressure develops.

SERUM. Plasma minus fibrinogen.

SOAP. A metallic salt of a fatty acid.

SOL. A colloidal system of a solid dispersed in a liquid.

SOLUTE. That which is dissolved in the solvent.

SOLUTION. A homogeneous mixture of two or more substances.

- SOLVENT.** Usually applied to the liquid in which a solid is dissolved. In the case of miscible liquids, the liquid which is in greater volume is usually considered the solvent.
- SPECIFIC GRAVITY.** The ratio of a given weight of a substance to the weight of an equal volume of water.
- SPONTANEOUS COMBUSTION.** The self-ignition of a substance as a result of the accumulation of heat formed by the slow oxidation of some component of the substance.
- STARCH.** A polysaccharide which forms a purple color with iodine.
- STERIODS.** Derivatives of cyclopentanoperhydrophenanthrene.
- STEROLS.** Alcohols derived from cyclopentanoperhydrophenanthrene; steroid alcohols.
- STRUCTURAL FORMULA.** A formula which shows how atoms are arranged in the molecule.
- SUBLIMATION.** The process of passing from a solid to a gas, and from the gas back to the solid without passing through the liquid state.
- SUBSTITUTION.** The replacement of an organic compound's hydrogen by some other element.
- SUGAR.** A white, crystalline, sweet, water-soluble carbohydrate.
- SULFITES.** Salts of sulfurous acid (SO_3^-).
- SURFACE ACTIVE AGENT.** An agent which reduces surface tension.
- SUSPENSION.** A mixture of a solid and a liquid in which the solid particles settle out upon standing.
- SUSPENSOID.** A colloidal sol of a metal or metallic compound dispersed in a liquid.
- SYMBOL.** The letter(s) used to designate an element.
- SYMPATHETIC NERVOUS SYSTEM.** That portion of the autonomic nervous system whose fibers originate in the thoracic and lumbar portions of the spinal cord.
- SYNAPSE.** The junction between the terminal endings of one neuron and the dendrites of another.
- SYNTHESIS.** The process of "building up" a compound by the union of elements or simpler compounds.
- TAUTOMERISM.** The vacillation of a hydrogen atom between an oxygen atom and some adjacent atom. Compounds in which this occurs are composed of half the enol form (when the hydrogen is attached to the oxygen) and half the keto form (when the hydrogen is not attached to the oxygen).
- TEMPORARY HARD WATER.** Hard water which is softened by boiling.
- TESTES.** The male sex glands.
- THYMUS.** An endocrine gland present (in the upper chest) in the infant, but absent in the adult.
- THYROID.** The endocrine gland located in the neck.
- TRANSMUTATION.** The act of one element changing into another.
- TYNDALL EFFECT.** Where the path of a beam of light is evidenced when it passes through a colloidal substance.

UNSATURATED COMPOUNDS. Compounds which have double or triple bonds.

URINE. A solution excreted by the kidneys which contains waste solids dissolved in water.

VALENCE. The combining power of an element.

VENOUS BLOOD. Blood which has lost its oxygen to the tissues.

VILLUS. A microscopic finger-like projection of the intestinal wall.

VITAMIN. An essential chemical substance which regulates one or more physiologic processes.

VOLUNTARY NERVOUS SYSTEM. That portion of our nervous system which is under voluntary control. The nerves of this system innervate skeletal muscles.

WATER BALANCE. The proper distribution of water between the body's intracellular and extracellular compartments.

WATER OF CRYSTALLIZATION. That water present in a molecule of a hydrous salt.

WAX. A fatty acid ester of a high molecular weight alcohol.

XANTHOPROTEIC TEST. A test for protein using concentrated nitric acid. A positive test is indicated by a yellow color.

X-RAYS. Electromagnetic radiations of great penetrating power.

YEAST. Microscopic, unicellular fungi which thrive in sugar solutions, bringing about alcoholic fermentation.

ZYMASE. An enzyme produced by yeast cells which converts glucose to alcohol.

ZYMOGEN. An inactive enzyme.

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