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ORGANIC CHEMISTRY SIMPLIFIED

Based Completely on the Electron Theory

by

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SECOND REVISED AND ENLARGED EDITION

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FROM THE PREFACE TO THE FIRST EDITION

I

This book was written for students taking a course in organic chemistry who find that most textbooks jump into the subject with the suddenness and alacriy (though not always with the grace) of a professional diver going headfirst into a swimming pool. These students will find this book of assistance in clarifying the approach to organic chemistry.

II

This book was also written for those engaged in work of a chemical nature who are not able to take a classroom course in organic chemistry and would like a book for home study.

Many practical organic chemists at the present time cannot follow certain parts of the current chemical literature because of lack of knowledge of such terms as dipole moments, covalent compounds, and resonance. The first part of this book is therefore devoted to an elementary study of atomic structure so that older readers who have not followed recent developments of chemistry may become familiar with the modern attitude toward the structure of organic compounds.

III

The author is indebted to Dr. E. Emmet Reid for his critical reading of the first draft of the manuscript; to Dr. Wendell M. Latimer for his criticisms and suggestions with respect to the pages on valence theories; and to Dr. C. A. Rouiller for his advice on the galley proofs.

PREFACE TO THE SECOND EDITION

The original novel outline has been followed in the preparation this new edition, but the text has been extensively rewritten considerably enlarged by addition of new material.

The author is grateful to Dr. S. Glasstone for reviewing chapt 13, and to Dr. R. S. Mulliken for advice on the pictorial represent tion in figure 17.3b. The author also acknowledges indebtedness Dr. C. S. Fuller, Dr. F. W. Hoffmann, Dr. H. Mueller, Dr. T. Schoch, and Dr. W. H. Summerson, and expresses his appreciatio to those who pointed out errors in the first edition, particularly M. T. Bogert. The author alone is responsible for errors that remain, and would be glad to receive letters from readers who mistakes in the book or wish to comment on the subject matter

Acknowledgment is made for the following material: to Professor E. A. Hauser for the original of figure 8.2; to Mr. G. V. Caesar and Dr. M. L. Cushing for the original of figure 46.4; to *Industrial and Engineering Chemistry* for use of the poem "Nomenclature" in section 10.12, and of the material in figure 13.8; to the *Journal of Physical Chemistry* for permission to reproduce figure 46.4; to the *Journal of Chemical Education* for permission to reproduce figure 8.2, and to use material in figures 6.2, 22.22, and 22.23; to the University of Chicago Press for permission to use material in figure 13.3; to John Wiley and Sons, Inc., for permission to use figure 17.6; to Interscience Publishers for use of table 43.2; to both Cambridge University Press and Elsevier Publishing Company for use of material in figure 13.5; and to the *Proceedings of the National Academy of Sciences* for permission to reproduce figures 46.6 and 46.7.

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o the Reader:

The plan of this book is different from that of the standard textbooks of organic chemistry. It is advisable to find out what this plan is by reading pages 1, 65, 271, and 444, which introduce the four parts into which the book is divided, and then study the paragraph in italics on page 282.

Cross-references are numerous in order to facilitate use of the book without formal instruction. The topics in each chapter have section numbers, and for quick reference these are shown at the top of each page on the inside margin.

The quotation on the reverse of this page is from the Frankland Memorial Lecture, *Chemistry and Industry*, **53**, 459 (1934).

The element carbon stands out as the central luminary in the great mystery of life.

— H. E. ARMSTRONG

PART 1

The Unique Position of the Carbon Atom in Chemistry

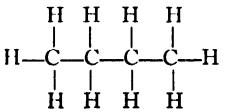
The elements are listed in the table on the inside front cover of this book.

Chemistry is a study of the properties of these elements and of the combinations which can be made from them.

Most elements, when they enter into combination, form comparatively simple compounds, such as sodium chloride, NaCl, or potassium dichromate, $K_2Cr_2O_7$.

One quite exceptional element has the unique property of forming highly complex compounds, many of which are found in living things. This element is carbon.

Carbon tends to combine with itself to build up molecules with an apparently endless variety of chain and ring structures such as these:*



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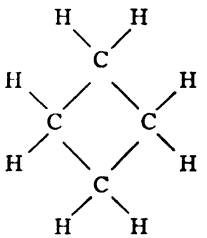


In combination with hydrogen, oxygen, and very few other elements, the carbon atom forms more than half the compounds known to science.

In Part 1 of this book we shall try to make clear why it is that carbon is so different from the other elements. This explanation requires an elementary study of the structures of atoms and molecules.

*See tables 10.2 and 11.1 for the names of these two compounds.

1. THE NATURE OF ORGANIC CHEMISTRY

1. 1. Origin of Atoms and Molecules. Every schoolboy knows that two famous revolutions occurred in the later years of the eighteenth century. These are the American Revolution and the French Revolution.

In this same period of history, however, when Thomas Jefferson was writing the Declaration of Independence in Philadelphia, and Marie Antoinette was losing her head in Paris, an equally important revolution was taking place in the scientific world. Chemists had finally begun to stage a revolution against methods which classed their work simply as the *art of alchemy,* and had begun to replace those methods by others that made it the *science of chemistry.*

The chemists discovered that the best way to determine the relationship of various materials to one another is to know their composition. They began to study substances on this basis as well as from their superficial nature.

Thus we find that Lavoisier, a French chemist, was devising methods of breaking down a uniform chemical substance into its constituent parts at the very same time Washington, in America, was struggling to build a uniform nation from an aggregation of states. Lavoisier was a leader of a revolutionary school of chemists who taught that we cannot truly understand the chemical behavior of substances until we know their composition.

Lavoisier, for example, found out how to measure the composition of sugar and showed that it is composed of the three distinct substances, carbon, hydrogen, and oxygen, united in a definite ratio by

weight. In our modern system of formula writing, this ratio is indicated by the expression $C_{12}H_{22}O_{11}$.

The quantitative method of examining substances led John Dalton, an English schoolmaster, to the first attempt to picture the elementary particles of matter (known since ancient times as atoms) combined in definite ratios. This was in 1803.

Dalton's conception of the atom was that of a hard nucleus, which he represented on paper by a circle with certain signs indicating the nature of the atom, thus:

Hydrogen Oxygen Nitrogen Carbon

In this system the exact composition of a compound substance was easily pictured by placing the component atoms side by side. For example, the following picture shows the way Dalton wrote the formulas of the oxides of carbon:

Carbon monoxide CO

Carbon dioxide CO_2

The Dalton formulas The modern formulas

By means of these symbols Dalton was able to indicate how atoms unite not only in one definite ratio, but also in more than one ratio.

The symbols of atoms and formulas of molecules which we use in our modern chemistry seem so clear that we often lose sight of the fact that they have been in use for little more than 100 years, and that they are the result of many centuries of shrewd thinking of the most brilliant men.

1. 2. The Birth of Organic Chemistry. In the old days men classified chemical compounds according to their origin; that is, they were either animal, vegetable, or mineral. Formic acid (from the distillation of red ants) and urea (from animal excretions) were called animal substances. Alcohol (from the fermentation of grain) was labeled a vegetable substance. Ordinary salt, of course, was placed in the mineral kingdom.

However, when chemists invented methods for prying into the composition of familiar substances, they discovered a most astonishing rule which is well illustrated by the data in table 1.1. This table is a brief list of some substances commonly known about the year 1800. They are grouped according to the kingdom of nature in which they occur and with modern formulas.

TABLE 1.1. CLASSIFICATION OF COMPOUNDS ACCORDING TO ORIGIN

Mineral Compounds		*Compounds from Vegetable Life*		*Compounds from Animal Life*	
Sodium chloride	$NaCl$	Sugar	$C_{12}H_{22}O_{11}$	Formic acid	CH_2O_2
Magnesium sulphate	$MgSO_4$	Alcohol	C_2H_6O	Glycerin	$C_3H_8O_3$
Calcium carbonate	$CaCO_3$	Prussic acid	HCN	Urea	CH_4N_2O
Iron sulphide	FeS_2	Citric acid	$C_6H_8O_7$	Lactic acid	$C_3H_6O_3$
Magnesium carbonate	$MgCO_3$	Tartaric acid	$C_4H_6O_6$		
		Lactic acid	$C_3H_6O_3$		
		Glycerin	$C_3H_8O_3$		

These new adventures into the interior of molecules brought to light the remarkable fact that *carbon* atoms occur in all *living* things. The carbon atom and life go hand in hand. (See motto page of this book.)

The carbon atom is seldom a constituent of compounds obtained from the mineral kingdom; the carbonates listed in the table are exceptions to the general rule. Carbon compounds are not common in inanimate nature.

In the early 1800's it became evident that the science of chemistry could be divided into two branches: first, inorganic compounds, the substances from inanimate nature, and, second, organic compounds, the substances which always contain carbon atoms and are obtained from life. By 1850, it was further recognized that this definition of organic chemistry was not entirely accurate, because certain carbon compounds isolated from living things can also be made in the laboratory. In fact, most of the carbon compounds recorded in our literature do not even occur in nature, but have been made by synthetic processes.

Today we define organic chemistry as the *chemistry of carbon compounds.*

Since we can prepare carbon compounds from inanimate materials, as well as from living matter, it is possible to classify organic substances in two divisions:

1. Carbon compounds present in living nature.
2. Carbon compounds made in the laboratory.

This distinction, however, is seldom employed, except in that the study of carbon compounds present in nature is often called *biochemistry*.

The current literature on the chemistry of carbon contains data on about 700,000 carbon compounds, and about 30,000 new compounds are being made every year. With the exception of hydrogen (section 45.1), the carbon atom is the most prolific in the society of the elements. This information on carbon compounds is collected in one library and called organic chemistry. The study of the compounds of all other elements constitutes inorganic chemistry.

2. THE ORGANIC CHEMIST LOOKS AT A MOLECULE

2. 1. The Inorganic Point of View. In this book we are assuming that the reader has an understanding of the general principles of inorganic chemistry. This means that he has certain definite ideas as to the nature of atoms and molecules which were taught to him by *inorganic* chemists.

To illustrate the difference between the inorganic and organic ways of looking at things we shall take as an example the simple compound, carbonic acid, H_2CO_3. This is an appropriate molecule to start with, because it is not new to anyone who has studied inorganic chemistry, and, since it contains a carbon atom, it may be classed as an organic as well as an inorganic compound.

Let us imagine that we are inorganic chemists and that we are describing in the usual chemical shorthand one of the chemical properties of carbonic acid, such as its reaction with an alkali:

$$\underset{\text{Carbonic acid}}{H_2CO_3} + \underset{\text{Sodium hydroxide}}{2\ NaOH} \longrightarrow \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Water}}{2H_2O}$$

Although we do not generally write out our thoughts completely, we say to ourselves when we write this reaction,

"Carbonic acid is really ionized in solution, thus

$$H_2CO_3 \rightleftarrows 2\ H^+ + CO_3^=$$

and sodium hydroxide also ionizes, thus

$$NaOH \rightleftarrows Na^+ + OH^-$$

and if we evaporate the solution to dryness, the positive and negative particles change partners and we get sodium carbonate as a solid residue."

In general, inorganic chemistry deals with reactions like this one, between compounds which divide in water solution into two or more ions. These ions are electrically charged atoms or groups of atoms. (At a later point in this book, in section 31.5, it will be shown that the ionization of acids is not so simple as pictured here for H_2CO_3.)

2. 2. The Organic Point of View. Before considering the problems of organic chemistry in detail, we must first become acquainted with the way in which the *organic* chemist looks at a molecule.

Inorganic chemists are principally concerned with the simple existence of family groups of ions, and do not bother, as a rule, about the way in which they are constructed. An organic chemist, however, would hardly feel at ease writing H_2CO_3 for carbonic acid, just to show it is composed of H^+ and $CO_3^=$. Nine times out of ten he would fix his attention on the molecule as a whole and write out its complete structure like this, $\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH}$, because from experience he finds it is a much more useful plan to do so.

The organic chemist, therefore, looks at the reaction between carbonic acid and sodium hydroxide in this way:

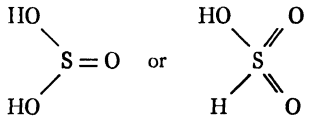
$$\begin{matrix} Na\,|\,\overline{OH} + H\,| \\ Na\,|\,\underline{OH} + H\,| \end{matrix} \quad \begin{matrix} O \\ C=O \\ O \end{matrix} \longrightarrow \begin{matrix} NaO \\ C=O \\ NaO \end{matrix} + 2H_2O$$

It would not be wise to give now all the reasons for this procedure of the organic chemist. One of the several reasons, however, may appropriately be considered at this point in our gradual approach to an understanding of organic chemistry.

The reactions of organic compounds do not usually take place between ions, for the simple reason that most organic compounds are not soluble in water, and they ionize slightly, if at all, in those solvents in which they do dissolve. When organic compounds are in solution they generally behave as if they existed in their originally

complete molecular form, and consequently the *organic chemist fixes his attention on the molecule as a whole rather than on any one part.*

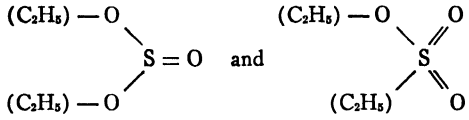
Only if we have a clear picture of the detailed structure of most organic compounds can we understand how they go through their chemical changes. For example, the simple inorganic substance known as sulphurous acid is H_2SO_3 to an inorganic chemist, but is



to an organic chemist.

The organic chemist thinks of this compound structurally, because he has found that the two hydrogen atoms in H_2SO_3 are not always equivalent.

One of the hydrogen atoms sometimes acts as if it were linked to the sulphur atom; thus, by replacing each H atom with the organic group (C_2H_5) we can prepare two quite different compounds of the same formula, $(C_2H_5)_2SO_3$, and after considering their properties, the experts have assigned the following structures to them:



It is, therefore, apparent that if we picture the structure of sulphurous acid graphically we can understand its chemistry much better than by writing it H_2SO_3, even though we are not certain whether the acid itself exists entirely in one form or as a mixture of both. Such examples of dual structure are seldom found in inorganic chemistry, but are very common in organic chemistry.

As a matter of fact, it was only when chemists began to look at a molecule from the standpoint of its structure (as explained below) that the real science of organic chemistry had its beginning.

2. 3. The Vital Force Theory. When a chemist looked at a molecule in the early days of organic chemistry, he could not possibly see it as plainly as we do today. It was not due to poor eyesight, nor to lack

of intelligence; it was because he was a pioneer in new territory and had to feel his way slowly.

Even with his limited vision, however, the early chemist was able to see that an inorganic compound is simplicity itself compared with the organic type. He was able to classify inorganic compounds into sulphates, nitrates, carbonates, and so on, but was completely lost when he tried to classify organic compounds:

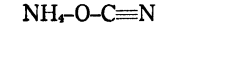
Inorganic		*Organic*	
Magnesium sulphate	$MgSO_4$	Alcohol	C_2H_6O
Sodium sulphate	Na_2SO_4		
		Acetic acid	$C_2H_4O_2$
Magnesium carbonate	$MgCO_3$		
Sodium carbonate	Na_2CO_3	Glycerin	$C_3H_8O_3$
Magnesium chloride	$MgCl_2$	Urea	CH_4N_2O
Sodium chloride	NaCl		
		Sugar	$C_{12}H_{22}O_{11}$
etc.		etc	

There did not seem to be any rhyme or reason to the way these elements (C, H, O and a few others) were able to combine in so many different ways *when present in organic compounds*. It is easy to see how much of a puzzle it must have been to those who first tried to develop order out of this apparent chaos.

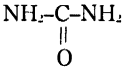
In those days, chemistry had only recently emerged from alchemy, and there was still a tendency toward ascribing unusual things to the agency of supernatural powers. For this reason, it was a common belief that when elements combine to form compounds in living nature they obey entirely different laws from those prevailing in inanimate nature. It was generally supposed that the Creator had instilled a "Vital Force" into the original seeds and eggs of living things which enabled elements to form combinations in a different way than when found in the mineral kingdom.

As recently as the 1840's, leaders in chemical theory stated that although man could break down a complex organic substance like uric acid (section 43.5) into urea, he would never be able to perform the building up (regeneration) process. It is now believed that the first experimental evidence to show that a "Vital Force" is not required for the synthesis of organic compounds was published by Kolbe in 1845. He synthesized acetic acid from carbon by a series of reactions which will be found outlined in section 31.9.

When the chemist no longer had the feeling that he was dealing with the supernatural and felt free to attempt the preparation of other organic compounds in the laboratory, science began an amazing expansion. Most of the organic compounds that we know today do not occur in nature. Eliminating the "Vital Force" theory, however, was not nearly so important as the fact that the attention of chemists was necessarily directed to the structure of the molecule. For example, in the study of urea, it was found that a salt called ammonium cyanate has exactly the same composition as urea. A difficulty like this could not be explained without an attempt at writing *structural* formulas. The organic chemist found he had to take a closer look at the molecules of the two compounds and, in modern style, he wrote their formulas as follows:



Ammonium cyanate



Urea

This, in brief, typifies the attitude we must adopt in trying to unravel the mysteries of organic chemistry. The structure of the molecule is all-important. We must consider the molecule as a piece of architecture, built up brick by brick. And just as model houses conform with a few, well-known, simple designs, so we shall find that organic compounds are constructed along plans which are beautifully simple.

SUGGESTED READING

McKie, D., "Wohler's 'Synthetic Urea' and the Rejection of Vitalism: a Chemical Legend," *Nature,* **153**, 608 (1944).

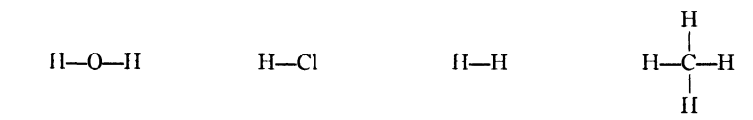
3. VALENCE

3. 1. The Meaning of Valence. In the preceding chapter we found that an organic chemist is really an architect who uses atoms to build up molecules. He is not content with a knowledge of how many atoms there are in a molecule, but also wants to know how they are put together. In other words, an organic chemist takes an extraordinary interest in the phenomenon of valence, which, the reader will recall from inorganic chemistry, is the word used to describe the attractive force between atoms.

The trouble with valence is that up to a few years ago even the learned pedagogs who told us all about it had no definite picture as to what the term actually signified. Our teachers even now are not certain they know it all, so they often represent the union between two atoms by a straight line and let it go at that. For example, the molecule of salt is written Na—Cl, a straight line being used to show there is a chemical union between the atoms.

The straight line used in written formulas to indicate which atoms are held together is called a valence bond. For most purposes, this is all an organic chemist needs even today to express his thoughts on paper, or to show the structures of molecules.

The average student likes to read his chemistry from a background of definitions; therefore, before continuing on this topic we shall give the customary definition of valence as *the combining power of elements when they unite to form molecules.* The simplest of the elements is hydrogen, and here are some examples of hydrogen compounds:



Water Hydrogen chloride Hydrogen molecule Methane

In all hydrogen compounds it has been found that only one valence bond is ever necessary to show the linkage of a hydrogen atom to other atoms.

Since the valence of hydrogen can be expressed by the number *one* it has been adopted as the standard, or unit, for assigning valence powers to other elements. For this reason, valence is also defined as *the number of H atoms with which an element can combine.*

From the preceding examples, it will be seen that oxygen has a valence of two in the water molecule, and carbon has a valence of four in the molecule of methane. The formula of hydrocyanic acid, H–C≡N, indicates that carbon as usual has a valence of four and that nitrogen has a valence of three.

3. 2. Objections to the Old-fashioned Ideas on Valence. The scheme of using straight lines for valence bonds is very useful for representing the structures of compounds, and, as we have already stated, has been extensively employed by organic chemists. An example of this was given in the preceding chapter when writing the picture formula of sulphurous acid, H_2SO_3.

The objections to this conception of valence are:

1. It leaves in the mind of the student the impression that an atom is an object in space with a number of grappling hooks attached to it, by means of which it can hook on to other atoms.
2. It does not tell us why atoms have different valences, such as one for hydrogen, two for oxygen, four for carbon, and so on.
3. (Most important) it does not explain why the union between some elements is different from that between others.

This last factor is the principal complaint against the use of a straight line as a valence bond, and the importance of this criticism is apparent from the following illustration. The salt molecule and the chlorine molecule are given similar structures when using straight lines for valence bonds,

Sodium chloride Chlorine

and there is nothing in these formulas to indicate that there is any difference between the way chlorine is united to sodium, and the way the two chlorine atoms are united with each other. In each case, the valence (bonding power) is represented simply by a line.

However, we do know from inorganic chemistry that these two molecules differ a great deal in properties. When sodium chloride dissolves in water it breaks apart (ionizes) into Na^+ and Cl^- ions. Chlorine, however, dissolves only slightly in water and the dissolved molecules do not tend to separate in the same manner as do the sodium chloride molecules. Consequently, we think there must be something unusual about the valence bond, not expressed in our customary formulas, which permits two atoms to break apart so easily in one case yet holds them so tightly together in the other case.

Organic chemistry, more than any other branch of chemistry, is concerned with the process of building up larger molecules from simpler ones. We must have a clearer understanding of the nature of these valence bonds (or grappling hooks, if you wish) if we expect to use them intelligently in the construction of molecules.

Suppose we return now to the remark made at the opening of the chapter concerning the learned pedagogs who have told us about valence without having a clear picture as to what it all means. Our teachers have not been to blame. For over a hundred years, physicists and chemists have been searching for a simple explanation of what holds atoms together. The chemists, naturally, could not wait for this mystery to be unraveled. While the search by physicists was going on, chemists decided they might as well invent a symbol for themselves. In short, they decided to write the two atoms on paper and connect them with a straight line, this line being a symbol for the valence force, no matter whether that force may actually be like an ice tongs, a grappling hook, or an electromagnet.

Such symbols are common in science. When the average man is unable to set up a physical symbol for an idea, then the idea itself loses much of its meaning. For example, a meter is approximately a ten millionth of the earth's quadrant, but no one has ever seen the earth's quadrant, so we commonly think of a meter as the length of our favorite meter-stick. The meter-stick is a physical symbol which we can see and feel, and without it, the word meter would be quite vague to most of us.

In a similar way, the invention of a straight line as a symbol to represent all the unknown factors which prevail in the bond between two atoms was a wise and useful one.

3. 3. What a Valence Theory Should Explain. Fortunately, the physicists have made a good beginning in their quest for the secret of atomic structure. On the basis of this new information, the chemists have developed a simple theory to explain the troublesome questions which we have just listed in connection with the problem of valence, namely,

1. How atoms combine to form molecules.
2. Why there are different kinds of valence bonds.
3. Why each atom has a characteristic valence, or combining power.

The most fortunate thing about all this is that it does not upset any of the pet notions of the organic chemist. We still write our formulas with straight lines for valence bonds, but now all these lines mean much more than grappling hooks.

In the chapters which follow, we shall describe briefly the structure of the atom, not from the standpoint of the physicist, but from that of the chemist who has waited so patiently for an explanation of valence. A lazy reader could skip the next few chapters completely and pick up the story of organic chemistry again in chapter 9. This proves that modern theories concerning the atom have not changed the fundamental nature of organic chemistry. This omission would leave the lazy reader, however, without a basic understanding of *modern* organic chemistry.

4. NEW IDEAS ON VALENCE

4. 1. The Nature of the Atom. We have just observed that the properties of sodium chloride, Na–Cl, are quite different from the properties of chlorine, Cl–Cl, and that the difference between the two compounds is presumably due to the difference in the way the atoms are bound together.

If the atoms in these two compounds are linked differently, then there must be at least two kinds of valence.

Reasoning from what has been said about these two molecules, one might be led to suppose that a large variety of valence bonds is possible, depending on the particular atoms which are united in the compound, but this is not the case. We find it convenient to differentiate between two extremes in types of bonds, and we have selected Na–Cl and Cl–Cl as representative molecules because they are excellent examples of compounds in which these two general kinds of bonds are found. In these preliminary chapters we shall find that although the valence bond in Na–Cl is a type which occurs frequently in the architecture of certain inorganic compounds, the type of bond in Cl–Cl is more universal and is especially useful in explaining the structures of organic chemistry.

We know so much more about valence today because we know so much more about the structure of the atom. Since the reader may not be familiar with modern theories of the structure of the atom, a chapter on this topic will follow (chapter 6). At that time we shall describe the atom as it appears to the chemist.

The atom is so complex that it is best to introduce it slowly. In the next few pages we shall consider the general nature and composition of an atom and the general nature of valence, before taking up the detailed study planned for a future chapter.

The evidence of modern science has led chemists to picture the atom as having the general appearance shown in figure 4.1. The

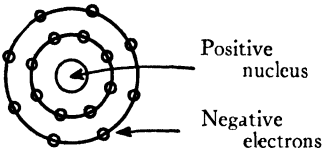


FIGURE 4.1. The atom.

atom is a structure built up principally of positively charged particles called *protons,* negatively charged particles called *electrons,* and neutral particles which are known as *neutrons.*

At the center of the atom is a nucleus which contains a certain number of neutrons and free protons. At various distances from the center of the atom, a certain number of electrons are situated. The electrons are supposed to bear the same relation to the nucleus as the planets bear to the sun at the center of our solar system. In a normal atom there are an equal number of protons and electrons; this produces an electrical balance. When thus balanced electrically, the atom is said to be neutral.

The chemist is not particularly interested in the protons and neutrons at the center of the atom, but takes considerable interest in the activity of the external electrons. We have good reason to believe that the chemistry of the atom is associated with the behavior of these electrons.

Since we employ the Na–Cl and Cl–Cl *molecules* so frequently in the explanation of valence, let us examine the sodium and chlorine *atoms* on this basis of atomic structure. Without any preliminary explanation we shall draw the pictures of these atoms with a certain

number of electrons arranged in circles or shells around the nucleus, as in figure 4.2.

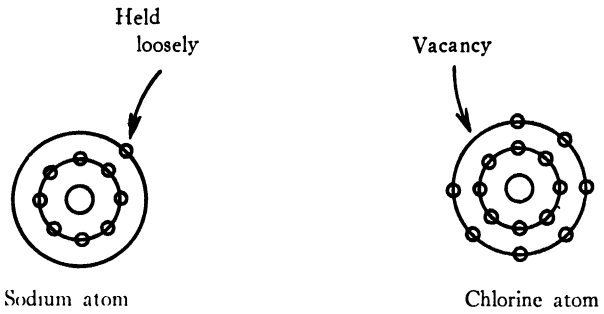


FIGURE 4.2. Atoms of sodium and chlorine.

The reader will observe that we have constructed these shells with no more than eight electrons in each. This magic number eight is of great importance in the structure of the atom, as will be made plain in a later chapter when atoms are considered in greater detail. We do not yet need to know the reason for it in order to obtain a working knowledge of the nature of the valence bond.

4. 2. Electrovalent (Ionic) Molecules. The sodium atom contains one electron which seems to be attracted to a lesser extent by the positive nucleus than are all the other electrons. We have pictured this electron by itself at the edge of the atom. We know that this electron is held with only a slight attractive force and under certain conditions will completely depart from its parent, leaving one unbalanced proton in the nucleus.

The chlorine atom contains a nucleus which acts as if it were not completely satisfied by the number of electrons in the outer portion of the atom. If a loosely held electron comes within its radius of attraction, the nucleus of the chlorine atom will at once pull the stranger into its own territory to fill up its outer shell of eight.

This is what probably happens when sodium and chlorine unite to create sodium chloride, NaCl. When a molecule of sodium chloride is formed, the loosely held electron is drawn from the sodium atom by the greater attractive force of the chlorine atom and becomes

a member of the chlorine family. The state of affairs in the resulting molecule may be pictured as shown in figure 4.3.

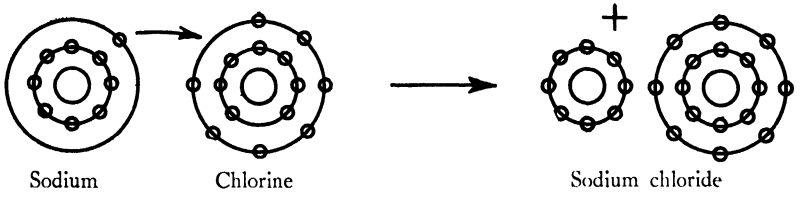


FIGURE 4.3 Formation of an electrovalence bond.
The molecule consists of ions, oppositely charged, electrically attracted.

Since the sodium atom has lost one electron in this process, one of the protons in its nucleus is left unbalanced. The resulting atom is therefore said to have a positive charge of one, and is a positive ion.

The chlorine atom, which has pulled away the loosely held electron from the sodium atom, now has one more negative particle than can be electrically balanced by its nucleus. The resulting atom is said to have a negative charge of one, and is a negative ion.

The sodium and chlorine atoms, as a result of this simple migration of an electron, thus become oppositely charged ions, and hold on to each other by electrical attraction. Such a union between atoms is called *electrovalence,* or *ionic* valence. This is the first of the two kinds of valence which we started to discuss at the beginning of the chapter (a more exact picture of the NaCl molecule will be found in figure 8.1).

4. 3. Covalent Molecules. Now let us examine the molecule of chlorine. When two atoms of chlorine combine to form the Cl–Cl molecule the arrangement is much different from that in Na–Cl. As we just mentioned, the chlorine atom shows a marked tendency to pull an additional electron into its system. Two chlorine atoms can, therefore, help each other out by forming a close partnership as indicated in figure 4.4.

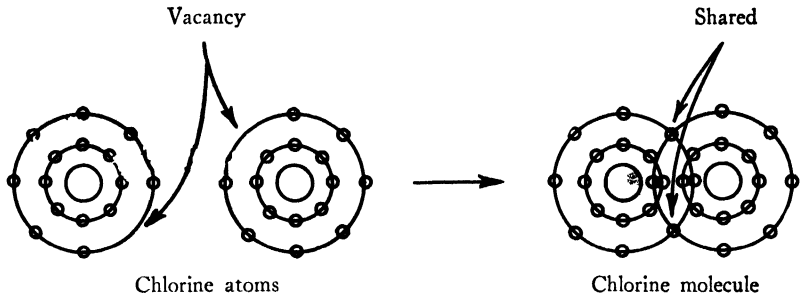


FIGURE 4 4. Formation of a covalence bond.
The molecule consists of atoms, sharing electrons.

In the chlorine molecule, each atom contains one more electron than it did before and thus its inherent tendency to add an additional electron is satisfied. The important fact, however, is that in the formation of the chlorine molecule no passage of an electron takes place from one atom to the other. It is a case of a mutual sharing of electrons. The new molecule is a complete unit in itself, and does not consist of two oppositely charged parts.

To indicate the intimacy of this type of union between atoms and its spirit of partnership, we call it *covalence*. This is the second of the two kinds of valence.

The student should constantly bear in mind that a *flow* of electric charge from one atom to another takes place in an electrovalence bond, whereas a mutual *sharing* of electric charge occurs in a covalence bond.

4. 4. Precursors of the New Valence Ideas. It is interesting to compare these two kinds of valence with the conception of valence as it developed from its earliest forms. The doctrine that compounds are composed of certain combinations of atoms was first stated in 1803 by Dalton (see chapter 1). A few years later, Davy and Berzelius developed the first theory of a valence force between atoms, in which it was assumed that the atoms or parts of a molecule are held together by an electrostatic attraction. This, the reader will observe, is exactly in accord with our modern idea of the electrovalence bond in $Na^+ Cl^-$, for which we now have a good mechanical picture.

The difference between the old theory and the modern one is that in the first, it was believed that certain elements were always positive and others always negative and they combined for that reason. Now it is believed they become positive or negative during the act of combining.

The electrical valence theory of Berzelius was satisfactory because most of the compounds for which the chemists of 1810 to 1830 had any detailed information were inorganic compounds, similar to sodium chloride in structure. They did not know enough about the composition of chlorine to get worried. If they had known, as we do now, that the chlorine molecule simply contains two atoms of chlorine (Cl–Cl), Berzelius would have been at a loss to explain how the two atoms are held together. He could not assume that one atom is positive and the other negative, since all atoms of chlorine are supposedly alike.

Later, when the composition of the chlorine molecule did become known, chemists realized that the electrical attraction theory of valence did not explain the structure of all compounds, and this became more evident after the period 1840 to 1850, when organic chemistry began its rapid expansion. It was found that most organic compounds (like the inorganic substance, chlorine) do not consist of oppositely charged atoms or groups; therefore, it was concluded that there must be some other kind of valence bond in addition to the simple attraction bond first announced by Berzelius. This second kind of valence is that which has just been described as covalence.

It is apparent, then, that our electrovalence bond is an old theory in modern dress; because of our knowledge of atomic structure, the actual mechanical process by which the atoms are linked together has become clearer. The covalence bond is of entirely modern origin; its presence in molecular structures is so universal that it has been called *the chemical bond.*

At this point, we must admit quite frankly that we are still content with a straight-line bond between atoms to indicate chemical combinations of all types. The straight-line bond was first used successfully in 1858 as a means of showing the positions of the various atoms in the molecule, as well as the combining powers of the atoms, and it is still a serviceable tool for the chemist.

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5. THE UNIQUE POSITION OF CARBON AMONG THE ELEMENTS

5. 1. The Periodic System of the Elements. In the preceding chapter we described how the chlorine molecule is built because we believe most organic compounds are covalent, like chlorine. But, the reader will observe, the chlorine molecule itself does not belong to organic chemistry. Organic chemistry, we learned in the very first chapter, is the chemistry of the carbon atom.

Let us see, then, how carbon fits into the world of atoms and molecules.

We shall consider the relationship of carbon to the other elements, and then we shall be in a better position to explain why it is that carbon compounds are almost always *covalent* like the Cl–Cl molecule rather than *ionic* like the $Na^+ Cl^-$ molecule.

Inside the back cover of this book there is a table of the periodic system of the elements. The periodic table was the result of the efforts of certain chemists to make their information easier to remember. They found that if the elements are arranged in the order of their atomic weights, thus,

	Hydrogen	Helium	Lithium	Beryllium	Boron	Carbon	etc.,
weight =	1	4	7	9	11	12	

then every eighth element will be found to have similar properties. The complete list of known elements was accordingly placed in a tabular form, in groups of eight.

To illustrate the usefulness of the table, notice the elements in the column labeled group O. These elements are called the noble gases, and all have a similar characteristic in that they never com-

bine with anything to form molecules. They are chemically inert, exert no valence force, and thus have a valence of zero.

In the next column, group 1, we find the closely related elements: lithium, sodium, and potassium. These have very similar chemical properties. For example, if we can prepare a compound like lithium nitrate, $LiNO_3$, then we know that there must also exist a potassium nitrate, KNO_3, with similar properties.

In group 2, we find other families of related elements. At the bottom of the group, the reader will notice the element radium. Now there are not many chemists who have handled either radium or its compounds, but any chemist with a working knowledge of the periodic system can give a fairly good account of its chemistry, simply from its similarity to the other elements in the family. Thus, the solubility of the sulphates in this family is in the following order:

$MgSO_4$ $CaSO_4$ $SrSO_4$ $BaSO_4$ $RaSO_4$
most soluble ← → least soluble

Therefore, we know automatically that radium sulphate is the least soluble of all.

Uniform variations in properties, such as we have just described for the elements in group 2, are also the rule for other columns of elements in the table.

5. 2. Ionization Potential. The periodicity of the properties of the elements is strikingly shown by their ionization potentials. This property is the energy required to remove an electron from the outer shell of an atom, converting it to an ion as shown by the reaction $Na \rightarrow Na^+ + e^-$. This ionization is illustrated in figure 4.3.

The relative ionization potentials of the elements are shown schematically in figure 5.1, in which the vertical axis indicates the volts required to remove one electron from the outer shell. When we arrange the elements horizontally in the order of increasing atomic number, we periodically get back to elements which have similar ionization potentials and, in general, have similar properties. It will be seen that it is most difficult to ionize the inert gases in group 0 of the periodic table, whereas the elements in group 1 of the table, which we commonly call the alkali metals, are most easily ionized.

The relatively easy ionizability of metals like sodium is readily understood by referring once more to figure 4.3. The positive charge

in the nucleus pervades the entire atom, but this charge is so effectively screened by the inner shell of electrons that the effective positive charge at the surface of the atom is rather small, and the lone outer electron is easily lost.

Now let us look ahead a little, and refer to figure 6.1. Read across the row of elements from sodium to chlorine and note that the positive charge in the nucleus grows larger. The increase in positive

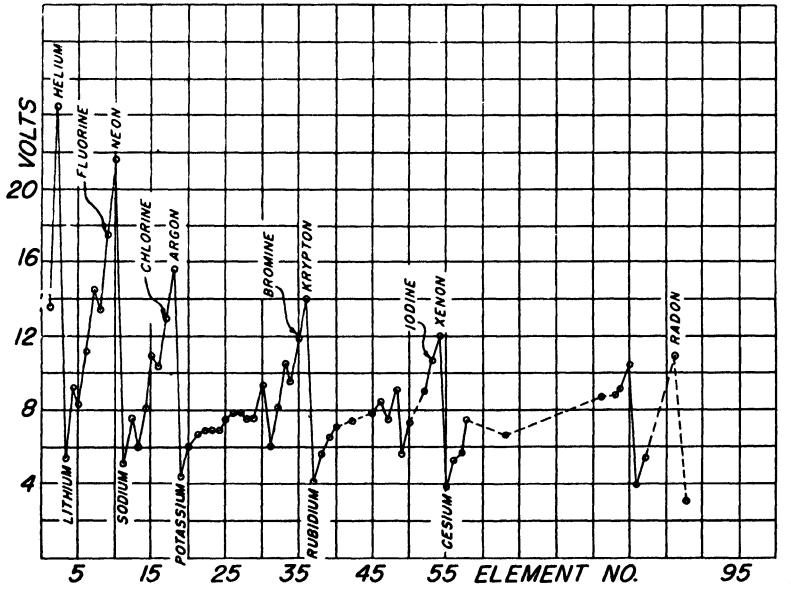


FIGURE 5.1. Ionization potentials of the elements.

charge will tend to pull in the shell of electrons and make the atom smaller, as illustrated in figure 6.2. Since the positive charge of the chlorine nucleus is so much greater than that of the sodium nucleus, it will, even though screened by more electrons, exert a greater effect, so that there is a more positive charge on the surface of the chlorine atom. That is why we found in figure 4.3 that the chlorine atom so readily attracts a negative electron, according to the reaction $Cl + e^- \rightarrow Cl^-$, to produce a chloride ion.

The reader should observe in figure 6.2 the increased size of the chloride ion over that of the chlorine atom, that is, the expansion in the effective electron orbits when some of the positive charge due to the nucleus is offset by the one added electron.

The reasoning which we applied to the sodium atom applies to the other elements in its group in the periodic table; they all have somewhat similar ionization potentials, as shown in figure 5.1. In the same way, we can explain the similarity in behavior of the halogen family in group 7 of the table. This will be commented on in greater detail in the next chapter.

5. 3. Position of Carbon in the Periodic System. Now that we have reviewed the meaning of the periodic arrangement of the elements,

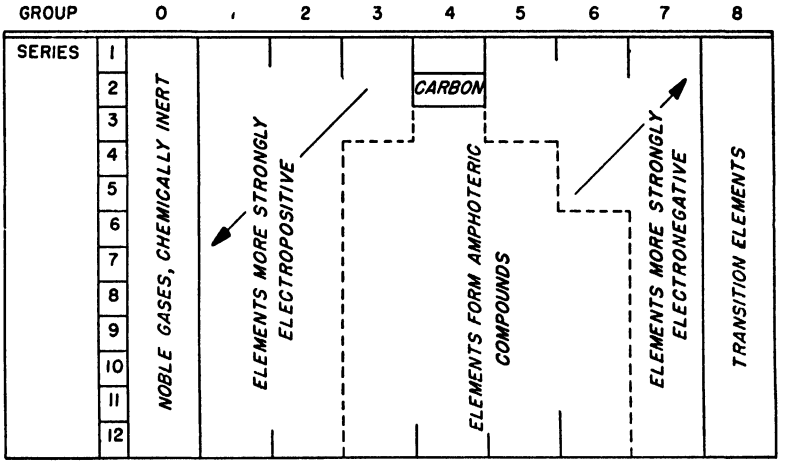


FIGURE 5.2. The periodic system outlined

and its usefulness in systematizing our knowledge, let us consider the position of the carbon atom in the table. To make the relationships of the elements more apparent we have constructed a skeleton outline of the periodic system as shown in figure 5.2.

This brief outline indicates that, with the exception of the inert gases in group O, the elements to the left of carbon are the electro-

positive elements. By this, we mean that when they appear in molecules they tend to lose electrons to form the positive end of the molecule as explained in the case of sodium chloride in the preceding chapter. It was shown that in sodium chloride the sodium atom loses an electron easily and then has an excess of positive electricity:

Na^+ — Positive end

Cl^- — Negative end

The more easily an element allows an electron to be taken from it by the opposing element in the molecule, the more electropositive it is said to be. The left-hand arrow in the outline of figure 5.2 indicates that the elements to the left of carbon become progressively more electropositive in character. These elements are said to be base-forming, as illustrated by sodium hydroxide, NaOH.

The other arrow in the outline indicates the variation in degree of electronegativity of the elements. The chlorine atom, we explained, has a positive charge on its surface, but we usually call it an electronegative element because it exerts a strong attractive force when pulling another electron into its atomic radius. Of course, it does not actually become negative until it has acquired the electron, as shown in the formation of the molecule of sodium chloride. Just as the elements to the left of carbon in the periodic system of the elements are electropositive in character, the elements to the right of carbon are electronegative. The electronegative elements are also called acid-forming as illustrated by the molecule of hydrochloric acid, HCl.

The elements below carbon in the periodic table may be termed the weak-minded members of the family. Sometimes they have base-forming tendencies and enter into combination in the positive end of a molecule. At other times, under other conditions, they have acidic tendencies and appear in the negative portion of molecules. This is illustrated by aluminum, the oxide of which is *amphoteric* in that it reacts with either acids or bases:

$$Al_2O_3 + 6\,HCl \rightarrow 3H_2O + 2\,AlCl_3$$

Aluminum chloride

$$Al_2O_3 + 6\,NaOH \rightarrow 3\,H_2O + 2\,Na_3AlO_3$$

Sodium aluminate

The carbon atom cannot be definitely placed in any of the categories which we have just described. It is not inert like the noble gases; it is considered neither electropositive nor electronegative, and its compounds rarely show amphoteric behavior (however, most readers can profitably refer to section 9.6 for a pertinent discussion of amphoterism). Carbon occupies a sort of key position among the elements. It is a transition substance, situated at the border line between the other recognized types. It has a set of distinctive properties, all its own.

The outstanding tendency of the carbon atom is to *share* electrons with other atoms (covalence) in the formation of molecules. This will become more evident in the chapters which follow, especially when we apply our knowledge of covalence and electrovalence to the study of the polarity of molecules in sections 8.5 to 8.10.

6. THE :Ö:C:T:E:T: IN CHEMISTRY

6. 1. Historical Introduction. We have just seen how necessary it is to consider the elements as a big family in order to understand the position of the carbon atom among them. In the process of studying the big family which we call the periodic system of the elements, we find that it is built up of a number of smaller family groups. These smaller families are set apart by a periodic arrangement in groups of eight.

A fancy word for a group of eight is *octet,* so naturally some people would much rather use it than the prosaic term *group of eight.* We have also made the word octet in our chapter heading look a little fancier by means of an octet of dots around each letter, for reasons which will not be entirely clear until this chapter and the next one will have been read.

The periodic arrangement of elements in octets shown on the back cover of this book was first suggested about 1860. It has proved to be helpful for systematizing the knowledge and facts of chemistry as we have just indicated in the preceding chapter. It has also served as a basis for theorizing about the structure of the atom, as we shall explain in this chapter.

In 1897 the electron was discovered and it was shown to be a constituent of all atoms. It was then suggested that the differences between the elements are due simply to variations in:

1. the number of electrons in each atom, and
2. the positions of the electrons in each atom.

Everything seemed bright and clear then to the scientific philosophers, because all they would have to do was to develop methods for determining how many electrons there were in each atom, and how they were arranged in the atom. An elementary exposition of their speculations will be found in the diagrams of the first eighteen elements shown in figure 6.1.

Everything seemed clear, as we have just stated, except for one important detail. It was not evident how these electrons, or negative particles of electricity, are held together in the atom.

The answer to this last question was supplied in 1911 by Lord Rutherford. He proposed the theory that the atom is like the solar system, in that it contains a positive nucleus corresponding to the sun and electrons which correspond to the planets. According to the modern version of this theory, the nucleus consists of protons and neutrons together with certain other entities that are being daily discovered and which act as a binding agent to condense the protons into a comparatively tiny space. The nucleus occupies only a very small space at the center of the atom, but serves to hold the electrons in their proper places.

This is the type of structure already introduced to the reader in chapter 4, when we explained the new ideas on valence. In figure 4.3, the models for the sodium and chlorine atoms were shown with positive nuclei, enveloped by shells of negative electrons. We shall now consider this type of atom in detail.

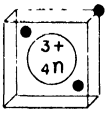
6. 2. The Cubic Atom. Determining the exact number of electrons in the atom of each element did not offer a very difficult problem. It was found that this quantity could be measured in several different ways. Finding out how the electrons are arranged in each element, however, proved to be much more difficult.

When the theoretical physicists and chemists got together to figure out what these arrangements are like, it was quite natural for them to choose the periodic table of the elements as their guiding star. In short, they decided that if every eighth element has similar properties then some outstanding principle may be discovered by arranging the electrons in the atom in such a way that a group of eight electrons, or an octet, is a common factor.

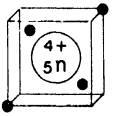
A cube contains eight points symmetrically spaced. As far back as 1902, this figure suggested itself to Professor G. N. Lewis as a suit-

Hydrogen
Atomic wt 1
Atomic no 1

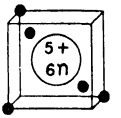
Helium
Atomic wt 4
Atomic no. 2



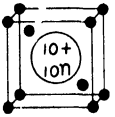
Lithium
Atomic wt 6 9
Atomic no 3



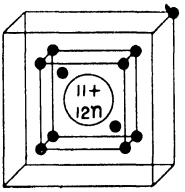
Beryllium
Atomic wt 9
Atomic no 4



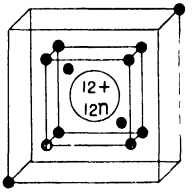
Boron
Atomic wt. 10 8
Atomic no. 5



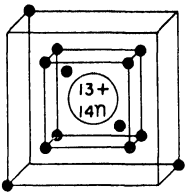
Neon
Atomic wt. 20 2
Atomic no. 10



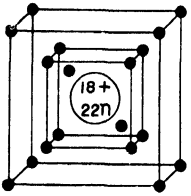
Sodium
Atomic wt 23
Atomic no. 11



Magnesium
Atomic wt 24 3
Atomic no 12



Aluminum
Atomic wt. 27
Atomic no 13



Argon
Atomic wt. 39.9
Atomic no. 18

able hatrack on which to hang the electrons in "groups of eight," and, consequently, we have the cubic pictures of the first eighteen elements of the periodic system as shown in figure 6.1.

Physicists, of course, are amused by the free and easy way with which the chemist takes a complex substance like an atom and indi-

cates the complete skeleton of the atom on a printed page. The chemist, however, does not mind being laughed at, as long as these diagrams or pictures can be used to explain chemical reactivity.

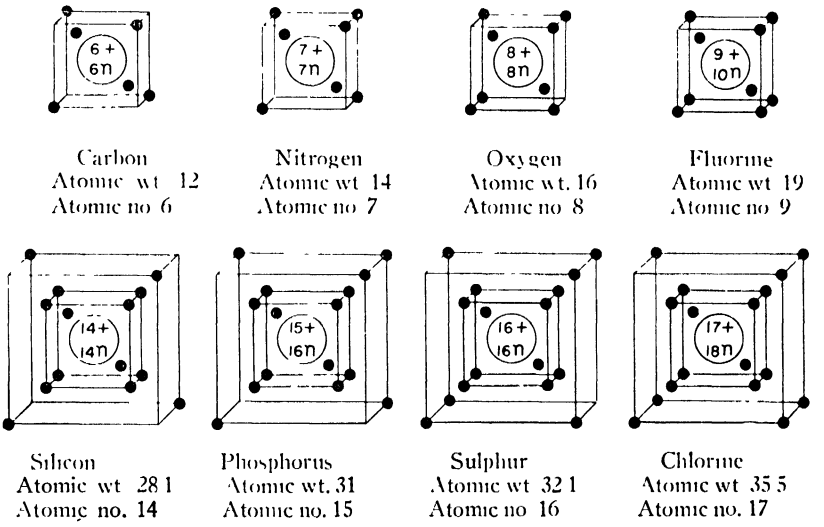


FIGURE 6 1. Cubic models of the first eighteen elements.

Note the relation between the atomic weight of an element and the number of protons and neutrons in the nucleus

The significance of the term atomic number will be discussed in detail in chapter 45 It is apparent, however, that the atomic number is the number of electrons outside the nucleus, or the number of protons inside the nucleus.

Chemists have found from long experience that it is profitable to place their thoughts on paper in the form of pictures. The diagrams of the elements in figure 6.1, showing the cubic arrangement of the electrons, should, therefore, be consulted constantly when reading the following pages for the first time.

The proton is indicated by a + sign. The electron is generally indicated by a — sign, but in these diagrams the electrons are more conveniently represented by black dots. The neutron is represented by the letter *n*, and is a neutral particle whose weight is very close to that of the proton. The proton is nearly 2,000 times as heavy as

an electron, so that the weight of an atom depends almost entirely on the number of protons and neutrons which it contains.

The simplest atom is that of hydrogen; it is nothing more than one proton with one electron whirling around it.

Hydrogen is the lightest of the elements, and in the tables of the elements it is assigned an atomic weight of 1. This tells us that the weight of the proton is one unit, since that is the only thing in the hydrogen atom which has appreciable weight.

The second element, helium, is four times as heavy as hydrogen. Therefore, we know it must contain four protons, either free or combined in the form of neutrons.

The protons and neutrons of the helium atom, as shown in the diagram, are massed at the center; this portion of the atom is called the nucleus. The nucleus of the helium atom contains two free protons, which leaves two positive charges to be balanced by electrons outside the nucleus. These external electrons are called planetary electrons, because they (on paper at least) resemble the planets in motion around the sun.

Although hydrogen is the simplest of the elements, helium is the most stable. We shall refer to this again.

The third element, lithium, we find is seven times as heavy as hydrogen and contains three protons in the nucleus, which are balanced by external electrons. It appears that only two electrons can fit into the space immediately around the nucleus, so the third electron takes up a position slightly removed from the inner two. This third electron we have indicated in the diagram as placed at the corner of a cube, in accordance with our scheme of using a cube to represent the fundamental importance of the number eight.

Referring once more to the diagrams, we find that all the elements in the first horizontal series are constructed by drawing the outline of the *helium atom,* and placing electrons at the corners of *the cube drawn around it.* For compactness, the cubes are drawn around a helium structure rotated 45° from the position shown in the diagram of the helium atom itself. As we proceed from one element to the next, the nucleus constantly grows heavier, and there is a one-by-one increase in the number of electrons at the corners of the cube.

When the eight corners of the cube have been filled, that particular shell around the nucleus has its full quota. It will be observed that

such a condition occurs when we reach the element neon, which is just below helium in the illustrations and is the first element of the second horizontal series.

The next element in the second series is sodium, which we talked about so much in preceding chapters. It contains one more electron than neon, but since there is no room for a ninth electron in the neon structure, this additional electron is found as the first member of still another cubic shell around the nucleus. The sodium atom con-

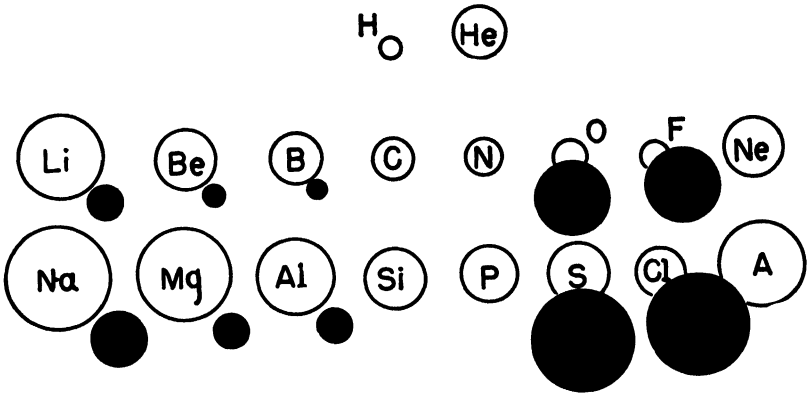


FIGURE 6 2. Relative sizes of atoms and ions The ion is in black, below and to the right of the corresponding atom. [Adapted from a chart by J. A. Campbell, *J. Chemical Education*, **23**, 525 (1946) which shows most of the elements in the periodic system].

tains three electronic shells — two electrons in the first, eight in the second, and one in the third.

The eighteenth element in the table is argon. This element is just below neon in the illustrations and is the first member of the next horizontal series. It has three filled shells.

This is as far as we need to go in the diagrams of the elements in order to obtain enough information for our purpose. Here, also, the author pauses to remark that the pictures of some of the succeeding elements present difficulties and exceptions beyond the scope of this book.

6. 3. The Periodic System. The men who first devised the periodic arrangement of the elements in octets knew nothing about electrons

and nuclei, but they had observed that starting from any one element, every eighth element has similar properties.

Using the cubic atom, as we have done in this chapter, we get a much better idea of the fundamental meaning of the periodic system. We see that, beginning with helium, the appearance of an additional shell occurs with rhythmic frequency at every eighth element. This is a periodic phenomenon, the periods in this case being octets.

Also, if we inspect the vertical columns in the table we find that the external shells are similar and contain the same number of electrons. For example, lithium and sodium probably have similar chemical properties because they contain only one electron in the outermost shell. And the similar properties of fluorine and chlorine are due to the fact they contain seven electrons in the outer shell. The number of electrons in the outer shell is the same as the group number in the periodic system of the elements.

6. 4. The Noble Gases. We come now to the interesting group of elements, helium, neon, and argon, in the first vertical column of the diagrams in figure 6.1. These are very symmetrical elements, and very inactive. They are so inert, in fact, that they do not combine with themselves to form molecules like O_2, H_2, and Cl_2, but prefer to exist singly in the atomic state in the form of He, Ne, and A, which are gases.

Because these elements are chemically inactive they have been called noble. This term was also applied to certain metals by ancient alchemists. For example, gold was called a noble metal because it does not tarnish (combine with oxygen) when heated in the air. Tin and copper tarnish readily and were called base metals. A modern psychologist probably would not have applied the term noble to the helium group. They might more appropriately have been labeled bachelor elements due to their reluctance to go mating with other elements.

Let us refer once more to the periodic table on the back cover. There we find the noble gases all listed in the first vertical column with the heading group 0, and assigned a zero valence because of their lack of chemical reactivity. In figure 5.1, we found the noble gases are the most difficult to ionize. If we glance again at the pictures of these elements in figure 6.1, we can draw the inference (which is supported by many facts) that the inactivity must be due to their

full quota of electrons. So far as electrons are concerned, these elements are completely satisfied.

6. 5. The Octet Theory. These observations lead to the fundamental theory that an atom becomes completely inactive when its external shell contains a full quota of electrons (an octet), and when the atom contains an equal number of protons and electrons. This is known as the octet theory, or the rule of eight.

We have indicated this theory in our chapter heading by the label :O:C:T:E:T: Each dot stands for an electron, and each letter in the word is encased in a shell of eight electrons — the ideal state for an atom.

In the next chapter we shall find that atoms apparently go through chemical reactions with each other just for the sake of reaching that ideal state of the complete octet. It will also be seen that the process depends on a *pair* of electrons acting as a unit.

In the next chapter, therefore, in addition to the rule of eight, our attention will also be directed to the rule of two, or the :D:U:E:T:.

7. THE :D:U:E:T: IN CHEMISTRY

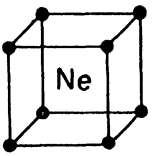
7. 1. Nucleus, Kernel, and Valence Shell. In the last chapter we emphasized the importance of the octet, or the rule of eight, in the chemistry of the atom, and the diagrams of the atoms in figure 6.1 were given the shape of a cube in order to indicate a symmetrical arrangement of an octet of electrons in a valence shell. In this chapter we proceed to what is perhaps even more fundamental, namely, the duet of electrons, or the rule of two. It will be found that *the pair of electrons* is a unit which is referred to more frequently by the chemist, and *represents the modern idea of a chemical valence bond.*

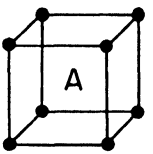
As explained in the last chapter, the *nucleus* is the positively charged mass at the center of the atom, where practically all the weight of the atom is situated. In explaining the mechanism of chemical reactions, however, the chemist is less concerned with the nucleus than he is with the electrons around it. A moment's reflection will make it clear that the outermost electrons in an atom are probably those which are most intimately tied up with its chemistry. It is quite reasonable to suppose that when two atoms are brought into intimate contact their external electrons will be affected first.

Indeed, the modern theory of valence was originally based on the belief that the chemistry of an atom depends on the number and arrangement of the electrons in the shell farthest removed from the nucleus. For this reason, the external electron shell of an atom is called the *valence shell,* and the rest of the atom beneath it is called the *kernel.* Electrons in the valence shell are called the valence electrons; for example, there are three valence electrons in the atom

of aluminum shown in figure 6.1. Electrons of the inner shells may also sometimes engage in chemical combinations, but that need not concern us in this elementary study.

7. 2. Valence Electrons as Dots. Since the chemist is primarily interested in the valence shell of the atom, let us examine first the valence shells of the noble gases. The noble elements which we have mentioned in this book are helium, neon, and argon, for which the cubic pictures may be written as follows, with special emphasis on the valence shell:

He 



In these pictures, the eight electrons in the valence shell are placed at the corners of a cube. The rest of the atom inside the valence shell, that is, the nucleus and inner shells of electrons, which we call the kernel, is represented by the chemical symbol of the element, such as Ne for neon and A for argon. The helium atom is remarkably inert (the two electrons shown in figure 6.1 being nonreactive), so that we regard helium as having no valence shell at all. It is, therefore, simply indicated as a kernel by the symbol He. If the pictures which we have drawn here are compared with those in figure 6.1, it will be observed that the neon kernel looks exactly like the helium atom.

Although the electrons actually occupy planetary orbits, we have found it convenient to place them at the corners of a cube because in that way we correlate the electron theory with the periodic system (see chapter 6). When atoms engage in chemical reactions, however, the electrons act in pairs, or groups of two, so that we find it even more convenient to place pairs of electrons at the corners of another symmetrical figure, the tetrahedron, as illustrated by the models in figures 8.4 to 8.7. We can, however, indicate the electronic nature of the valence shell of an atom without giving the atom a definite shape at all. In short, the three noble elements which we just discussed can be represented in this simple manner:

He	·Ne:	:A:
Helium	Neon	Argon

The dots represent the electrons in the valence shell, and everything inside the valence shell is indicated by the chemical symbol.

If the first nineteen elements are written according to this scheme they appear as follows:

	H.						
He	Li·	Be:	·B:	·C:	·N:	:O:	:F:
:Ne:	Na·	Mg:	·Al:	·Si:	·P:	:S:	:Cl:
:A:	K·						

In these symbols the pairs of dots represent the electrons which are "coupled" in certain subshells of the valence shell, a phenomenon which will be explained later in section 7.7.

7. 3. Tendency of Elements to Acquire Nobility. In the last chapter we stressed the fact that the noble gases have a *complete octet* of electrons in the valence shell. They are the only elements blessed with such a condition. If we should assume that all the elements try to acquire an outer coat similar to that of the noble gases, we then have a very simple way of explaining chemical combination. Stated more pointedly, we explain union between atoms on the basis that each atom does its best to join the aristocracy of noble gases.

Let us see what this means. If the atom of chlorine gained one electron, it would have a complete octet and would look like argon. It would look like argon and in that way put up the appearance of a noble gas, but of course it would still be only a chlorine atom with an extra electron, which is not balanced electrically by the nucleus. The resemblance is only skin-deep.

Now examine the sodium atom. If it lost its lone valence electron, then its next lower electron shell would be uncovered and it would look like neon. This will be more evident if the reader consults the picture of the atom shown in figure 6.1. Again the resemblance to a noble element is only skin-deep, and, on the loss of the electron, the atom of sodium becomes positively charged because of one unbalanced proton in its nucleus.

7. 4. Electrovalence. The tendency for octet formation indicated in the preceding paragraphs for the two elements, chlorine and sodium, can be satisfied if they join each other in the formation of a molecule of sodium chloride:

$$Na\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \rightarrow Na^{+}\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$$

In the resulting compound, both atoms assume the appearance of noble elements, but the transfer of the electron leaves one side of the molecule positively charged and causes the other end to be negatively charged. This is the ionic type of molecule described in chapter 4, and the bond between the atoms is an electrovalence bond.

Notice particularly that the valence bond consists of a pair (or doublet, or duplet, or duet) of electrons. The electron pair (:) takes the place of the straight line in the usual formula Na–Cl. It takes two electrons to constitue one valence bond. Each atom in this case contributes *one* of the electrons of the duet, and each of these atoms is said to have a valence of *one.*

Here is another example:

Cl—Mg—Cl	$\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot^{-}\ Mg^{++}\ \underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:^{-}$
Ordinary formula	Electron formula

In this salt the magnesium atom loses two electrons and is able to satisfy two chlorine atoms. The magnesium atom has a valence of two in magnesium chloride.

To explain the formation of these molecules we made a definite statement for which, of course, an apology is due to the physicists. We stated that the elements go through their chemical combinations for the sake of acquiring an outer coat similar to that of a noble gas. We do not know enough about the atom, as yet, to ascribe any mental processes to it. As chemists, however, we cannot help feeling that all atoms like to look like noble gases because this conception assists us so much in our understanding of chemistry.

7. 5. Covalence. It was difficult for a chemist to explain to a physicist how the two atoms of chlorine can combine to form a molecule of chlorine, Cl–Cl. Both atoms in this molecule are alike, and it does not seem likely that one becomes positive and the other negative

just for the sake of mating. For this reason the covalent bond remained largely a matter of conjecture for many years after the usefulness of the electron theory of valence had become established through the efforts of chemists.

The physicists, however, took over with their calculations in quantum mechanics and showed that two like atoms can be held together by an electron pair with opposite spins. This spin is similar to that of the earth on its axis. If the two electrons in the pair are of the same directional spin the atoms repel each other. The formation of the covalent link is, therefore, as follows, the two electrons in the shared pair spinning in opposite directions:

$$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \rightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

In this case, no transfer of an electron is supposed to occur. The two atoms complete their octets by means of a close union in which the outer shells partially coalesce. The valence of chlorine is one, because each atom contributes one electron to the electron pair which is the valence bond. This type of union is covalent, as pointed out in figure 4.4.

The formulas of a few other common molecules of the covalent type are as follows:

$\mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}$ H	$:\ddot{\mathrm{Cl}}:$ $:\ddot{\mathrm{Cl}}:\ddot{\mathrm{B}}:\ddot{\mathrm{Cl}}:$	$:\ddot{\mathrm{Cl}}:$ $:\ddot{\mathrm{Cl}}:\ddot{\mathrm{C}}:\ddot{\mathrm{Cl}}:$ $:\ddot{\mathrm{Cl}}:$
Ammonia	Boron trichloride	Carbon tetrachloride
$(:\dot{\underset{\cdot}{\mathrm{N}}}\cdot + 3\mathrm{H}.)$	$(:\mathrm{B}. + 3.\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:)$	$(:\dot{\mathrm{C}}. + 4.\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:)$

These compounds will be referred to again near the close of the next chapter.

7. 6. Exceptions to the Rule of Eight. In the introduction to this chapter it was said that the rule of two is more important than the rule of eight. One of the numerous reasons for this statement is that there are many exceptions to the rule of eight (see index). An example is given in the preceding paragraph in the structure of boron trichloride, in which it will be seen that only six valence electrons on the boron atom are required to form the stable molecule.

It is equally important to observe, however, that exceptions to the rule of eight are rare among the hundreds of thousands of compounds of carbon.

7. 7. Atomic Orbitals. To understand the mechanism of electron sharing, which was said in section 7.5 to be the basis of the formation of molecules, and to understand why molecules have the characteristic shapes to be illustrated in section 8.4, it is necessary to learn some of the details of electron habits that are not made apparent by figure 6.1. We must also modify the concept that an electron is a "planetary" object rotating around the nucleus in an orbit like that of the earth around the sun. Instead of referring to an *orbit* we now introduce the term *orbital,* which means the region in space occupied by the electron.

The shape of the space (orbital) occupied by a so-called "electron cloud" can be calculated by wave mechanics; different electrons in a given electron shell may occupy orbitals of different shapes. The fundamental shapes of orbitals are very familiar: a tennis ball (the spherical shape), and an hourglass (the nodal shape), as shown in figure 7.1.

The crossover junction between the two halves of an hourglass is a node. In the corresponding atomic orbital we refer to a *nodal plane* which separates the two parts of the orbital and contains the nucleus of the atom. Thus, the nodal plane of the p_x orbital is the plane which contains the y and z axes in figure 7.1. In the nodal plane, the probability of finding the electron is said to be zero.

In the explanation of the pictures of the atoms in figure 6.1 we referred to shells of electrons. We may also refer to those shells as energy levels. For example, the oxygen atom has two electrons in the lowest energy level (the first shell, principal quantum number 1), and six electrons in the next energy level (the second shell, principal quantum number 2). Larger atoms than those shown in figure 6.1 have more electron shells, the principal quantum numbers ranging from 1 to 7. The shells may also be found labeled alphabetically from K to Q, a practice originally started by spectroscopists, who can follow by means of spectral lines the movements of electrons as they get bounced from one level to another when the atom is deliberately excited to an energy level higher than that of the normal "ground" state.

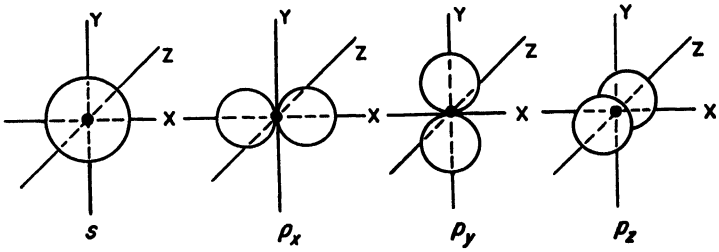


FIGURE 7.1. Representation of atomic orbitals. Black spot is a nucleus. The *s* orbital is spherical, without directional effect. The *p* orbitals are at right angles to one another, that is, 90° apart, on the conventional *x*, *y*, and *z* axes of solid geometry. Each of the *p* orbitals consists of two parts, with a nodal plane between them. All these orbitals can be occupied by a single electron or by two.

The nucleus is *enveloped* by an *s* orbital. It is *in a plane* which separates the two parts of a *p* orbital. The two parts of a *p* orbital represent opposite phases of the wave function, calculated from quantum mechanics (compare figure 17.3*b*).

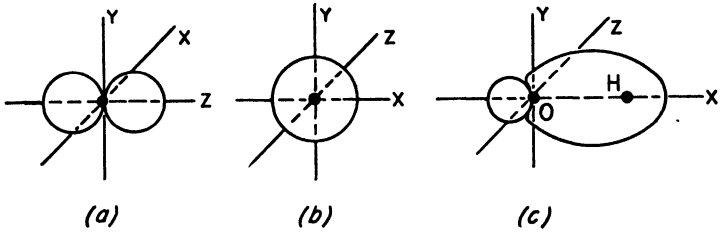


FIGURE 7.2. Formation of one of the $\cdot\ddot{O}:H$ bonds of water, $H:\ddot{O}:H$, through overlapping of *s* and *p* atomic orbitals. The black spot is a nucleus.

(a) The $2p_z$ atomic orbital of oxygen, occupied by one electron. See text (section 7.8) for the reason why the z axis is drawn in the plane of the paper.

(b) The 1*s* atomic orbital of hydrogen, occupied by one electron.

(c) An *s*-*p* molecular orbital, occupied by two electrons with opposite spin. This is a *sigma* (σ) type of bond.

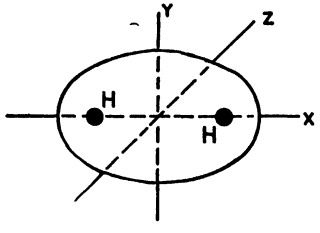


FIGURE 7.3. Formation of an *s*-*s* type molecular orbital, occupied by two electrons, through overlapping of two *s* type atomic orbitals (see figure 7.2*b*) each with one electron. This is a *sigma* (σ) bond.

H:H Molecule
(from H. + .H)

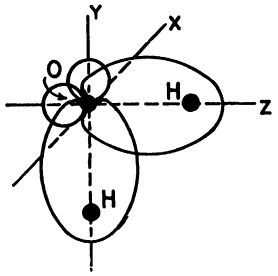
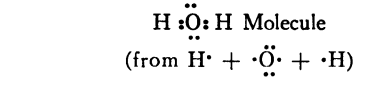


FIGURE 7.4. Formation of two *s-p* molecular bonds (see figure 7.2*c*) at right angles. See text (section 7.8) for position of third **2***p* orbital and of the **2***s* orbital. These are *sigma* (σ) bonds.



H :Ö: H Molecule

(from H· + ·Ö· + ·H)

An important rule to remember is that the electrons in a given principal shell do not necessarily all have exactly the same energy. There are subshells (sublevels of energy), the number of which is equal to the number of the shell. Thus, the second shell of the oxygen atom (principal quantum number 2) contains two subshells, but this was not indicated in figure 6.1. The spectroscopists have labeled these two sublevels of energy with the letters *s* and *p*. An electron in the *s* energy level occupies a spherical orbital, as shown in figure 7.1. The *p* energy level is higher than the *s*, and electrons in that level occupy a nodal orbital shown in figure 7.1.

[Atoms larger than those which we shall discuss have a wider variety of energy levels and orbitals. Thus, the fourth principal shell of a larger atom has four subshells of energy, labeled *s, p, d,* and *f*. The letter system was originated by spectroscopists to relate electronic energy levels to the characteristics of corresponding spectral lines, which are called *sharp, principal, diffuse,* and *fundamental.*]

Another important rule to remember is that the *square* of the principal quantum number tells us how many orbitals are permissible in an electron shell. The second shell of the oxygen atom has the principal quantum number 2, and from $2^2=4$ there are, accordingly, four possible orbitals. The four orbitals are shown in figure 7.1. Since the quantum number is 2 in the second shell, there are two levels of energy in that shell, according to the other rule which was cited previously; some of the electrons are in the *s* orbital, and others are in a *p* orbital at a higher energy level.

We may now proceed to distribute the electrons of the oxygen atom, as follows:

$$\mathbf{1}s^2;\quad \mathbf{2}s^2,\ \mathbf{2}p^2_x,\ \mathbf{2}p_y,\ \mathbf{2}p_z$$

Boldface number is the principal quantum number.
Letter shows type of orbital. Superscript shows number of electrons in c bital.

According to this shorthand expression the first shell of the oxygen atom has a pair of electrons; this shell has only one energy level (principal quantum number 1), and has only one orbital ($1^2=1$). That orbital is the *s* type in figure 7.1 and contains both electrons. An orbital can hold no more than two electrons, and these must be of opposite spin, that is, affected oppositely by a magnetic field.

In the second shell, the *s* energy level fills up its quota of electrons before electrons can enter the higher energy level of the *p* orbitals. Electrons are rather exclusive. An electron already in a *p* orbital will not take a partner unless the other *p* orbitals have at least one each. All three of the **2***p* orbitals are occupied in the oxygen atom, with an electron pair in one of them.

To obtain a picture of the outer shell of the oxygen atom, the reader should visualize the six electrons distributed as just indicated and occupying orbitals as shown in figure 7.1. The two *s* electrons completely encompass the nucleus. The four *p* electrons are in three orbitals at right angles to each other, and the probability of finding a *p* electron at the nucleus is zero.

[As an illustration of the complexity of larger atoms, the fourth electron shell of a large atom has four subshells (*s*, *p*, *d*, and *f*). From $4^2=16$, it has sixteen orbitals (one *s*, three *p*, five *d*, and seven *f*), but the space relations of the *d* and *f* atomic orbitals are beyond the scope of this elementary discussion. Electrons in those orbitals do not take part in the formation of the simpler molecules.]

7. 8. Molecular Orbitals. In reviewing the preceding remarks on *atomic* orbitals it should be understood from figure 7.1 that an electron in an *s* orbital has no directional effect; its energy is greatest at the nucleus, is distributed symmetrically in a sphere which encompasses the nucleus and diminishes to a negligible value at the periphery of the sphere. An electron in a *p* atomic orbital is oriented in a definite direction, at an angle of 90° to other *p* orbitals; its energy

is zero at the nucleus, and negligible at the boundary surface of the hourglass (see figure 17.3*c*).

We can now use this information in building up molecules, and we start with the simplest, namely, hydrogen. The hydrogen atom has the electron distribution $1s$, which means that it has only one electron shell, that the orbital is *s* type, and that it has one electron in that orbital. Figure 7.2*b* shows the H atom and figure 7.3 illustrates how two H atoms combine; the two nuclei act together and the spherical orbitals overlap to give a molecular orbital which is now eggshaped. The *s*-*s* bond is often referred to as a σ-type molecular orbital (σ, *sigma*, is the Greek letter *s*), because it resembles an *s* type atomic orbital which *encompasses* the nucleus.

In section 7.2, the symbols of the first nineteen elements are written so as to show the paired and unpaired electrons in the outermost (valence) shell. Those symbols will be better understood by referring to a specific example, which again will be oxygen :Ö: for which we have already used the electron distribution

$$1s^2;\quad 2s^2,\ 2p^2_x,\ 2p_y,\ 2p_z$$

From this we see that in the **2** shell there are two orbitals already filled with electron pairs. These do not take part in reactions (except as described in section 8.5). Two of the $2p$ orbitals, however, contain only one electron each and can take part in the formation of normal covalence bonds. Such bond formation is illustrated in figure 7.2, where, for the sake of clarity, we have shown only one of the three $2p$ orbitals. We have also taken a liberty in that we have swung the *z* axis into the plane of the page in order to draw more clearly an orbital to which only one electron is allotted.

The *s*-*p* molecular orbital in figure 7.2*c* is known as a *hybrid*, and bond formation from *dissimilar* atomic orbitals is called *hybridization*. The hybrid bond has the hourglass feature of a *p* atomic orbital, with a nodal plane at the nucleus (in this case, the plane of the *y*-*x* axes). The bond also shows the characteristic of an *s* atomic orbital, which encompasses its nucleus; this is illustrated in the diagram by placing both nuclei (O and H) inside the egg-shaped part of the orbital, and extending the egg just past the oxygen nucleus in the normal plane of the *y*-*x* axes.

From the electron distribution in the oxygen atom, we observe that the p_y orbital is incomplete, and can enter into bond formation just like the p_z orbital. The two OH bonds are shown in figure 7.4, where it will be observed that the bond angle O–H should be 90°; deviations from this angle will be commented on in section 8.4. Not shown in figure 7.4 are the **1***s* orbital and the **2***s* orbital of the oxygen atom, which encompass the nucleus, but contain satisfied electron pairs and do not take part in this compound formation. We have also omitted the $2p_x$ orbital, because it already possesses an electron pair; it should be visualized, however, as a pure *p* type atomic orbital (hourglass) at right angles to the plane of the paper.

7. 9. Quadrivalent Carbon Atom. This title means a carbon atom with a valence of four. The valence shell of the carbon atom (see figure 6.1) is the second shell; the electron distribution for both shells according to the scheme outlined in sections 7.7 and 7.8 is written:

$$1s^2;\quad 2s^2,\ 2p_x,\ 2p_y$$

The pair of **1***s* electrons can be disregarded in the chemistry of carbon. The valence shell has four electrons, but they are not equivalent; two of them are already paired and have energy corresponding to a **2***s* orbital, and the other two are in the somewhat higher energy level of a **2***p* orbital. The problem is to explain how the four electrons become equivalent, which is a condition we should expect on the basis of the chemistry of carbon in compounds such as methane, CH_4, carbon tetrachloride, CCl_4, etc. We shall use for illustration the methane molecule (chapter 9).

The electron distribution just cited is for the *ground* state of the carbon atom, its most stable state. When a C atom reacts with four H atoms there is a considerable evolution of energy (section 18.3), more than enough to promote the C atom to an "excited" state in which the pair of *s* electrons is "uncoupled" and one of them raised in energy to the *p* level. The electron distribution in the valence shell then becomes

$$2s,\ 2p_x,\ 2p_y,\ 2p_z$$

In the following discussion, in order to avoid confusion, we shall omit the use of the quantum number 2.

The four electrons now pool their energy to become equal in character, by the process of hybridization. The nature of a hybrid *molecular* orbital was described in section 7.8 and illustrated in figure 7.2*c*, where an *s* orbital from one atom overlapped the *p* orbital of a different atom to form a valence bond. In the case of the carbon atom, it is considered that an *s* orbital and a *p* orbital in the same atom will hybridize. The result is a hybrid *atomic* orbital, which is shown in figure 7.5 and looks like figure 7.2*c* except that this atomic hybrid orbital has only one electron whereas the molecular hybrid orbital has two.

The types of hybrid orbitals possible in the carbon atom are summarized in table 7.1. It is apparent from the table that hybridization in the atom is simply a process by which the several atomic orbitals reach an *average* energy level; for example, an *s* and a *p* orbital will behave like two *sp* orbitals. This specific example of hybridization takes place in certain types of carbon compounds, but our interest at present is only with the sp^3 hybrid, since that is the nature of the hybrid developed when the carbon atom forms compounds of the CH_4 type.

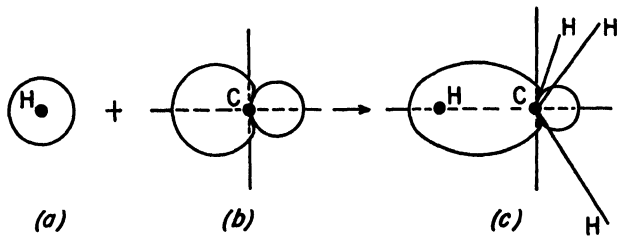


FIGURE 7.5. Formation of a C:H orbital of methane, CH_4. Similar s-sp^3 molecular bond orbitals are formed with the three other H atoms shown. This is a σ type orbital.

(*a*) The hydrogen atom, with one electron in an *s* atomic orbital.

(*b*) One of the four sp^3 hybrid atomic orbitals of carbon, with one electron in the orbital.

(*c*) One of the four molecular orbitals constituting methane.

TABLE 7.1. HYBRIDIZATION OF ORBITALS IN THE CARBON ATOM

The ground state	s^2	p_x	p_y		
Excited state	s	p_x	p_y	p_z	
The s orbital hybridized with:					Example
One p orbital	sp	sp	p	p	Ethyne (section 15.1*b*)
Two p orbitals*	sp^2	sp^2	sp^2	p	Ethene (section 15.1*a*)
Three p orbitals*	sp^3	sp^3	sp^3	sp^3	Methane (this section)

*The superscript shows how many of the p orbitals pool their energy with the s orbital.

Since all four of the sp^3 hybrid orbitals of the carbon atom are equivalent, in the molecule of methane (Figure 7.5) the four C:H bonds radiate from the nucleus of the carbon atom at equal angles of 109° 28′. The solid figure is a tetrahedron which will be described in greater detail in Section 12.2 and may be referred to at this time. The s-sp^3 molecular orbital of figure 7.5 is exactly like the s-p molecular orbital in figure 7.2*c*; in both cases there is considerable σ character, that is, a tendency to *encompass* the nuclei the way an s atomic orbital encompasses a single nucleus.

The reader should refer to the index for other topics related to the subject of orbitals.

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Mayer, M. G., "The Structure of the Nucleus," *Scientific American,* **184**, no. 3, 22 (1951).

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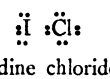
Also, see references to Chapter 4.

8. NORTH POLES AND SOUTH POLES

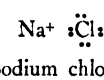
8. 1. Nonpolar, Polar, and Ionic Molecules. This is the last chapter in our elementary study of the structure of atoms and molecules. In preceding chapters we gave most of our attention to the kinds of valence bonds that hold the atoms together in the molecule. In this chapter we shall consider the molecule as a whole, and find out how the type of the valence bond affects the properties of the molecule.

There are two kinds of valence, namely, electrovalence and covalence. There are three principal types of molecules, and their general nature can be illustrated by the following examples:

Chlorine
I. Nonpolar molecule
(covalence)

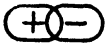


Iodine chloride
II. Polar molecule
(covalence)



Sodium chloride
III. Ionic molecule
(electrovalence)

Electrically symmetrical



Partial transfer of electric charge

Complete transfer of electric charge

In a covalence bond, as we have already learned, the atoms share electrons in such a way that there is no definite transfer of electrons from one atom to the other. The compound we have constantly used for an illustration of this phenomenon is chlorine, Cl–Cl. This type of compound is said to be *nonpolar,* but the reason for this

name will not be apparent until we examine the second compound in our list, which is labeled a *polar* molecule.

The iodine chloride molecule, I–Cl, contains two atoms that belong to the same chemical family and are very much alike in behavior. The properties of chlorine, however, show that it is more electronegative than iodine. By this, we mean that it exerts a stronger pull on the electron pair (:), which is the valence bond.

In order to picture the greater influence of the Cl atom on that electron pair which it shares with the I atom, we write the formula of iodine chloride with a space between the atoms and the electron pair shifted closer to the Cl atom (see the preceding illustrative formulas). This is equivalent to a partial transfer of electric charge to the Cl atom, making it more negative. The I atom, because of the partial removal of the negative electron pair from its vicinity is left slightly positive.

One end of the I–Cl molecule is accordingly negative and the other end is positive. The molecule may be looked upon as having a north pole and a south pole. It is a polar molecule, as distinguished from the nonpolar Cl–Cl molecule, which is electrically symmetrical.

The third principal type of molecule is the *ionic* variety. In this case, there is a complete transfer of an electron from one atom to the other, as in the molecule of sodium chloride. The structure of this molecule is to be represented by two ions, Na^+ and Cl^-, held together by their opposite electrical attraction. In a crystal of salt there are no NaCl molecules; instead there is a lattice-work of Na^+ and Cl^- ions, as shown in figure 8.1. This is a model of a crystal of ordinary table salt, as determined by means of X-ray photographs. If the black balls are sodium ions the white balls are chlorine ions, or vice versa. The symmetrical way in which these simple ions arrange themselves at right angles to each other in space indicates why ordinary table-salt crystals are perfect cubes.

A crystal of salt is a giant molecule in which one Na^+ ion affects six Cl^- ions, or one Cl^- affects six Na^+ ions. Each of these ions is said to have a co-ordination number of six. The co-ordination number depends on the size of the ion, that is, on the number of oppositely charged ions with which it is surrounded.

In figure 8.1, it should be observed that there is no such simple entity as an ionic "molecule," or electrovalence bond, which we have been representing in this book by $Na^+ :\ddot{Cl}:^-$. Although it may not

actually exist, the electrovalence bond is used throughout this book. It is useful to consider it as the extreme case of separation of the atoms from the normal valence bond, which is the covalence bond as in :$\ddot{\text{Cl}}$: $\ddot{\text{Cl}}$:

Figure 8.2 is a model of silver bromide Ag^+ Br^- which has the same type of crystal structure as sodium chloride. This model was built to scale, showing the relative sizes of the ions in the crystal (the small white balls represent silver ions and the larger, black balls are bromide ions). Although the ions are mostly empty space as indicated by figure 4.2, the white and black balls show the relative effective distances from the positive nuclei of the ions to the outer electrons. Observe that each ion (as in figure 8.1) has a co-ordination number of 6.

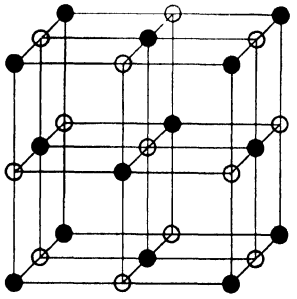


FIGURE 8.1. Arrangement of ions in the sodium chloride crystal.

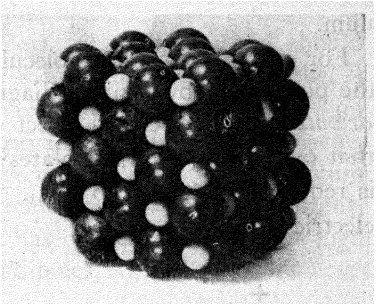
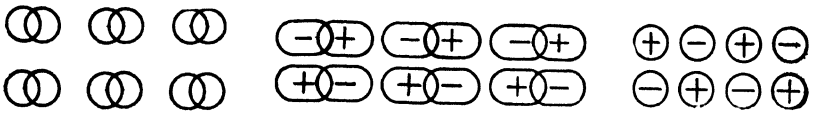


FIGURE 8.2. Arrangement of ions in the silver bromide crystal [E. A. Hauser, *J. Chem. Education*, 18, 165 (1941)].

We have described the structures of ionic, polar, and nonpolar molecules before considering their properties, although, actually, the chemist has developed his theory of their structures from a knowledge of their properties.

We shall now consider some of those properties of molecules that lead us to picture the essential differences between them by the following symbols:



Nonpolar Cl—Cl Polar I—Cl Ionic Na^+Cl^-

. These pictures indicate the general position of the molecules in the lattice of the crystalline material. It will be noticed that polar molecules are "dipoles," — they have a "north" and a "south" end. The absence of + and — signs on the nonpolar molecule should be understood as meaning that the atoms in the molecule are electrically concentric, that is, the total effects of their positive and negative charges coincide.

8. 2. Dielectric Constant. The dielectric constant is a simple physical property that has served as a useful tool in recent years for the study of the nature of molecules. In figure 8.3, imagine first that the charged plates are separated by a vacuum, and that the strength of the electric field between the plates is E_{vac}. If a vaporized substance is placed between the plates, the value of E will fall because of the better conducting ability of the molecules than that of a vacuum.

For example, if polar molecules are employed they will swing into the positions shown in the diagram. It is said that the molecules are *oriented.* The electrical effect of the molecules is then opposite to that on the two charged plates and the strength of the electric field is reduced from E_{vac} to E_{mol}. The ratio E_{vac}/E_{mol} is called the dielectric constant.

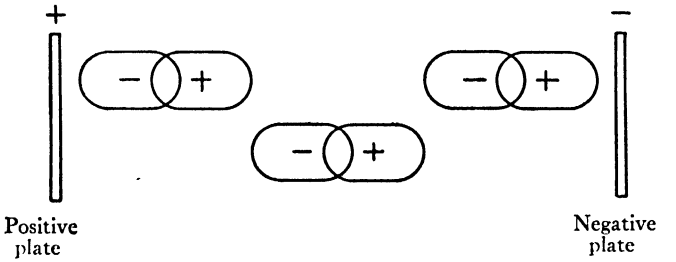


FIGURE 8.3. Polar molecules between charged plates.

The word dielectric conveys the idea of transmitting or holding an electric force without actually serving as a conductor.

Polar compounds have a high reducing effect on the field strength between the plates and, consequently, have a fairly high dielectric constant. This is illustrated further in section 8.9*c*.

Even nonpolar compounds have appreciable dielectric constants. When such a compound as chlorine, which we have represented by

, is placed between oppositely charged plates, the two parts of the molecule are distorted by the electric field, and assume the "induced dipole" state represented by . These molecules then become oriented as shown in figure 8.3, and reduce the field strength. Although the dielectric constant is appreciable for nonpolar compounds, it is of a very low order. It is only with difficulty that the component parts of such a molecule can be distorted to the state of an induced dipole.

The dielectric constant of a polar molecule is due to two principal factors: first, the *permanent dipoles* already present in the molecule, and second, the *induced dipoles* caused by distortion. It is the first factor that brings about the higher dielectric constant of polar compounds. Effects due to induced dipoles are very small compared to those caused by natural dipoles in the molecule.

Ionic compounds, of course, have permanent dipoles and should have high dielectric constants. Since most salts are nonvolatile, it is not possible to measure their dielectric constants by the vacuum method we have illustrated. Certain organic solvents, like benzene, however, are nonpolar and can often be used in place of the vacuum for dielectric measurements. Silver perchlorate is soluble in benzene, does not ionize in such a solution, and has been found to have a high dielectric constant due to its permanent dipoles, $Ag^+ ClO_4^-$.

8. 3. Dipole Moment. The dipole moment of a molecule is calculated from dielectric constant measurements. The meaning of dipole moment is quite simple although the method of calculation may be rather complex. In a molecule that consists of two poles the dipole moment is obtained by multiplying the distance d between the poles by the electric charge e on one pole. The electric charge, of course, is the same on each pole although of opposite sign. The dipole moment, accordingly, is simply de.

The average value of d, the distance across a molecule, is 10^{-8} cm., and the charge on one electron is 4.80×10^{-10} esu (*esu* is the electrostatic unit of electricity, the quantity repelled by a force of one dyne when placed one centimeter from an equal charge in a vacuum). Accordingly, the dipole moment (de) of a highly polar molecule is in the vicinity of 4.80×10^{-18} esu-cm., whereas for a nonpolar molecule it is either zero or close to zero.

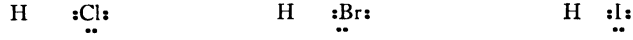
The dipole moments of several types of compounds are shown in table 8.1, where the data are in Debye units (one such unit is equal to 1×10^{-18} esu-cm.).

TABLE 8.1. DIPOLE MOMENTS (IN DEBYE UNITS)

Hydrogen, H_2	0.0	Hydrogen chloride, HCl	1.04
Carbon dioxide, CO_2	0.0	Hydrogen bromide, HBr	0.79
Carbon disulphide, CS_2	0.0	Hydrogen iodide, HI	0.36
Carbon tetrachloride, CCl_4	0.0	Iodine	0.0
Chloroform, $HCCl_3$	1.15	Bromine	0.0
Water, H_2O	1.85	Chlorine	0.0
Ammonia, NH_3	1.55	Silver perchlorate, $Ag^+ClO_4^-$	4.7

When we properly interpret the data in this table, we get some idea of the immense value of dipole moments as a research tool in solving the problems of molecular structure.

8. 4. The Shapes of Molecules. The H_2 molecule has a zero moment and is, therefore, a perfectly symmetrical compound, H:H, with no displacement of the electron pair toward either atom. If we inspect the data for the series of compounds HCl, HBr, and HI, it will be noticed that the moment is greatest for HCl and least for HI. This indicates that the relative spacing of the atoms must be as follows:

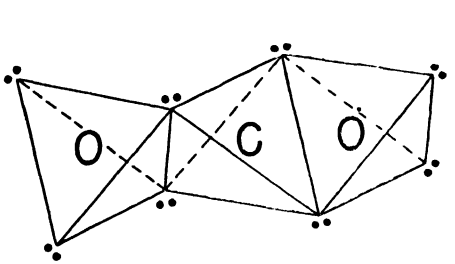


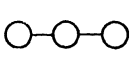
the Cl atom being the most electronegative in this family and, therefore, exerting the greatest pull on the valence pair of electrons which unites these elements with hydrogen.

In section 7.7 it was shown that certain valence electrons are restricted in their movements to definite positions in space with respect to the nucleus. These space positions (p orbitals) are 90° apart on conventional x, y and z axes. Valence-bond formation through the p orbitals accounts for the fact that bond angles are not far from 90°. The deviations from this angle are due to various factors, principally the repulsion of the nuclei at the ends of the bonds. For example, the bond angle in the water molecule (figure 8.5) is about 105°.

Both water (H-O-H) and carbon dioxide (O=C=O) appear to be straight-line molecules as they are normally written. The dipole moment of water is 1.85, which agrees with the angular, unsym-

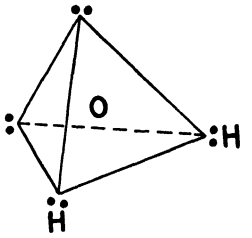
metrical structure developed in figures 7.4 and 8.5, as well as with the fact that the bonds are polar in nature. We are just as certain that

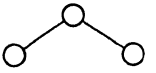




O=C=O or :Ö: :C: :Ö:

FIGURE 8 4. Straight-line molecule.





H—O—H or H:Ö:H

FIGURE 8.5. Angle molecule.

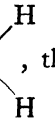
the valence bonds in carbon dioxide are polar and, on that basis, it should be expected to have a fairly high dipole moment; however, the absence of dipole moment is proof that the three atoms are arranged in a straight line as shown in figure 8.4. There are actually two dipoles, O=C and C=O, but they act in opposite directions and the net dipole moment of the molecule is zero.

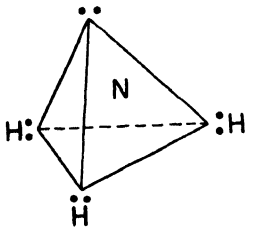
From the hybridization data in table 7.1, and the method of orbitals described in section 7.7, we can give a more convincing account of the straight-line structure of carbon dioxide. However, it is best to postpone that demonstration (see section 18.5) and to employ the useful convention of the tetrahedral models shown in figure 8.4. These models are based on the rules that (1) the atoms in a compound, generally, but not always, attain a cloak of eight electrons, and (2) the electrons act in pairs when forming compounds and are generally symmetrically situated.

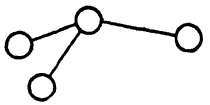
As to the ammonia molecule, the reader should be able to apply the principles of bond orbitals illustrated in figure 7.4. The electron distribution *in the valence shell* of the nitrogen atom is

$$s^2,\ p_x,\ p_y,\ p_z$$

Single electrons are available in all three of the p orbitals, so that an N-H bond can be formed on the z axis as well as on the x and y

axes of figure 7.4. The result is a pyramid molecule as shown in figure 8.6, in which the actual bond angle (H–N–H) is about 108°. Note the "lone pair" of s^2 electrons still present on the nitrogen atom in the diagrams of figure 8.6. If ammonia had the symmetrical flat structure  , the polar valences would balance to give a zero





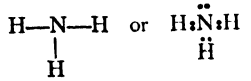
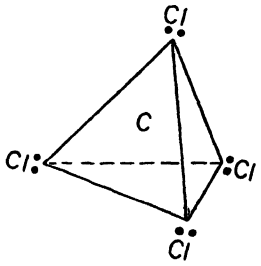
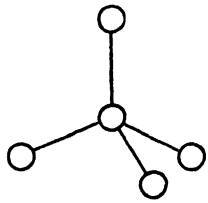


FIGURE 8.6. Pyramid molecule.





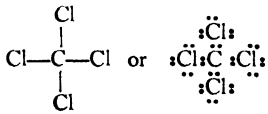


FIGURE 8.7. Tetrahedron molecule.

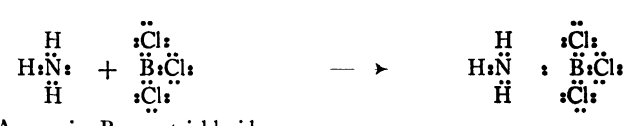
dipole moment. Since it has a high dipole moment, it seems likely that the hydrogen atoms are in one plane, with the nitrogen atom elevated at some distance from the plane of hydrogen atoms.

The CCl_4 molecule shown in figure 8.7 has a zero dipole moment, whereas the dipole moment of $CHCl_3$ is 1.15. From this information, it is safe to assume that the C–Cl bond is polar, but in CCl_4 the four polar valences balance one another because of the symmetrical nature of the molecule. The $CHCl_3$ molecule is necessarily unsymmetrical and consequently has an appreciable moment; the Cl–C–Cl

angles are close to 112°. The reader should review section 7.9 and figure 7.5 on the formation of a tetrahedral carbon compound through four equal hybridized atomic orbitals.

8. 5. The Dative Bond. In discussing the electron theory of valence in the preceding chapter, we stressed the statement that there were two kinds of valence, namely, electrovalence and covalence. This is a good place to point out the fact, however, that there are some exceptions to this general rule.

At the end of section 7.5 we wrote electronic formulas of NH_3 and BCl_3. These two compounds unite easily to form a stable substance of the composition H_3NBCl_3, but, according to the older theories, there was no satisfactory way to account for its formation. On the basis of the electronic structures, however, this type of compound formation is easy to explain:

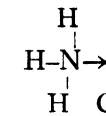


Ammonia Boron trichloride

The N atom in NH_3 has two unshared electrons, whereas the B atom in BCl_3 has room for two more in its valence shell. The N atom donates the electron pair, and is called the *donor* atom. The B atom is the *acceptor.*

The reader should observe that in this valence bond both electrons come from the same atom, whereas in a normal covalence bond, such as in :Cl:Cl:, one electron comes from each atom. The first type of bond is called co-ordinate valence, and is a special kind of covalency.

In this book the co-ordinate bond which we have just described is nearly always referred to as a dative bond, from the Latin verb for *give.* This name indicates that an electron pair has been donated by one atom and accepted by the other, the formula being written



H–N→B–Cl. The arrow is often used as a symbol for a dative

bond, whereas a dash is the conventional symbol for the ordinary covalent bond. Phenomena explained by means of dative bonds will be found listed in the Index.

8. 6. Mobile Electrons. The molecular structures described in section 8.4 have definite shapes due to pairing of electrons which become *localized.* Later we shall describe molecular systems in which certain of the electrons have considerable mobility. This will be discussed principally in connection with the theory of resonance (section 18.5). It will also be referred to in the study of the structure of benzene and of graphite (section 19.7), where the mobile π electrons have much importance. The electrical conductivity of graphite is made possible by these mobile electrons.

The electron configurations in metals have also been made clear by the principles of wave mechanics that were briefly reviewed in chapter 7. A metal is a lattice of positive ions. The electrons in the space around these ions can occupy certain energy levels. If the valence levels are not filled the electrons become mobile and the metal is an electrical conductor. If all the levels are filled the substance is an insulator.

8. 7. The Electronegativity Scale. In section 5.2, it was explained that the electric charge of the chlorine atom is really positive and, for this reason, it strongly attracts electrons. It is, therefore, called strongly electronegative. Conversely, the sodium atom has only a weak positive surface charge, and since its attraction for electrons is feeble it permits electrons to be stolen rather easily. We should call sodium a weakly electronegative element, but in practice it is called strongly electropositive.

TABLE 8.2. ELECTRONEGATIVITY SCALE OF THE ELEMENTS

Cs	0.7	I	2.4
Na	0.9	S	2.5
Li	1.0	C	2.5
Mg	1.2	Br	2.8
Al	1.5	Cl	3.0
Si	1.8	N	3.0
B	2.0	O	3.5
H	2.1	F	4.0

A roughly quantitative scale of electronegativity is shown in table 8.2, which is based principally on the work of Pauling. The elements in this table should be looked up in the chart on the back cover of the book, and their positions studied with reference to figure 5.2.

8. 8. Partial Ionic Character of Covalent Bonds. In figure 5.2, we attempted to show qualitatively how electronegativity varies in the periodic system of the elements. From a generalization like that in figure 5.2, we can estimate the strength of the chemical bond between any two elements; a compound formed from an element in the lower left of the table and an element in the upper right should be not only very stable but also *ionic,* as illustrated by the formation of Na^+Cl^- in figure 4.3. Intermediate elements were not discussed fully in the earlier chapter, except to show that they had amphoteric or "weakminded" tendencies and that the element, carbon, had a halfway position exemplified by its preference for *covalent* linkages.

We shall now examine the intermediate elements more closely, from the point of view of transition from covalent to ionic bonds.

When the separation of any two elements in table 8.2 is less than 1.7 units, the compound that they form can be considered covalent. Thus, the HCl molecule ($3.0 - 2.1 = 0.9$ units) is to be considered covalent, but as already described in this chapter, it is a polar molecule in which the electron pair has shifted toward the more electronegative chlorine atom.

When the separation of two elements is greater than 1.7 units, the compound they form can safely be written as ionic, as in the case of Na^+Cl^- where the data from table 8.2 give $3.0 - 0.9 = 2.1$ units.

It is clear from these examples that there is a gradual transition from covalent to ionic character of a bond. Rough quantitative estimates can be made of degree of ionic character of a bond by reading from a smooth curve which can be plotted through these data (from Pauling):

	HI	HBr	HCl	HF
Separation units (table 8.2)	0 3	0.7	0.9	1.9
Ionic character of bond	5%	11%	17%	60%

According to Pauling a separation of 1.7 units corresponds to about 50% of ionic character, based on a curve such as that just described.

We have already seen that HCl is covalent, as in I, below, and that

I

II

III

its dipole moment shows it has a polar nature as in II, but we must also consider that the molecule has characteristics of III to the extent of about 17 per cent. This is not to be construed as meaning that the HCl molecule is occasionally ionic, but that the *covalent bond* in HCl has *partial ionic character.* The molecule acts as a hybrid which can vary in accordance with its environment (that is, with the solvent in which it is placed, etc.). This will be better understood when the phenomenon of resonance is discussed in section 18.5.

The calculation of the degree of ionic character of HCl can be made as follows. From spectroscopic measurements, the distance between the atoms is 1.28 A, and, if the molecule is completely ionic, the dipole moment should then be 1.28 multiplied by 4.80×10^{-10}, that is, 6.14 Debye units. Actually, the dipole moment is found to be 1.04 Debye units. If we arbitrarily say that the covalent molecule H:Cl has a zero moment (whereas the ionic molecule H^+Cl^- should have a moment of 6.14), then the molecule is actually $1.04/6.14 = 0.17$ or 17 per cent ionic.

This can be visualized by assuming distortion polarization. As stated before, the atoms in HCl are separated by a distance of 1.28 A. However, the hydrogen ion is simply a proton (+), which distorts the electron atmosphere of the $:\ddot{Cl}:^-$ ion in such a way that the center of gravity of the negative charges is pulled toward the center of gravity of the positive pole. This is proved by the dipole moment measurement, which shows that the length of the effective dipole is only 0.21 A, which is 17 per cent of the distance between the atoms, determined spectroscopically to be 1.28A.

8. 9. The Forces between Ions and between Molecules. Since ions are charged particles, those which are oppositely charged are held together by an electrostatic attraction whereas similarly charged ions exert a mutual repulsion. This force can be calculated by Coulomb's law (consult a textbook of physics); that is, it is proportional to the product of the two charges and falls off with the square of the distance between them. Interionic forces are often called *Coulomb forces* and they are quite large. Typical giant molecules built up from ions are shown in figures 8.1 and 8.2.

Intermolecular forces are those which control most of the physical characteristics of typical covalent compounds like NH_3 and CCl_4

(figures 8.6 and 8.7). Textbooks of physical chemistry explain that the molecules in a gas are in constant thermal motion, that is, random motion due to their temperature. When cooled to below a certain *critical temperature,* pressure can bring the molecules close enough together so that they attract each other and reach the liquid state. The laws governing this phenomenon were so completely described by van der Waals that intermolecular forces are now known as *van der Waals forces.*

Intermolecular forces are relatively weak. They are due to the electrostatic attraction of the positive nuclei in a molecule for the electrons in the electron envelopes of neighboring molecules. This force of attraction falls off very rapidly with about the seventh power of the distance between molecules (contrast with the second power for Coulomb force), so that it is not effective until the molecules are within a few molecular diameters of each other. When the molecules begin to interpenetrate, the attractive force between them is balanced by repulsion of the electron clouds around the molecules.

8. 9a. Melting Point and Boiling Point. Since interionic forces are powerful, ionic compounds generally have high melting and boiling points. The process of melting means the break-up of the structure of a giant molecule, and boiling means complete rupture of the strong electrovalent bonds. Since intermolecular forces are weak, the simple covalent compounds have comparatively low melting and boiling points; it is relatively easy to separate the molecules of such a compound. These principles are illustrated by the following chlorides of elements from the first two horizontal series of the periodic system:

	Ionic		*Covalent*	
	NaCl	*$MgCl_2$*	*BCl_3*	*CCl_4*
Melting point, °C.	804	712	−107	−23
Boiling point, °C.	1413	1412	12.5	76.8

Although the simple covalent molecules of carbon tetrachloride (see figure 8.7) are easy to separate, it is important to remember that it is possible to build giant molecules with covalence bonds (such as the diamond molecule in figure 19.1, and the starch molecule in figure 46.3) which are just as difficult to break up as the giant ionic salt molecule in figure 8.1.

8. 9b. Electrolytes. When ionic compounds are melted, the ions are free to move about and are then able to carry an electric current.

Ionic compounds are, therefore, called electrolytes. It is generally said that acids, bases, and salts are electrolytes, but this does not mean that they are necessarily ionic compounds. For example, boron trichloride (see preceding paragraph) is covalent although it is called a salt and an electrolyte; because it has considerable ionic character it reacts readily with water to form ions which make the resulting solution an electrolyte.

Similar reasoning applies to the electrolyte, hydrochloric acid, which is a "strong acid" although a covalent compound; it reacts with water to form an electrolyte as described in section 31.5.

8. 9c. Ionic Dissociation. This is a term which can be applied to dissolution of compounds, like Na^+Cl^-, when placed in liquids, like water, which have high dielectric constants. Water is highly polar and has a dielectric constant of 80; this means that the electrostatic attraction between oppositely charged particles (Na^+ and Cl^-), when placed in water, is weakened eighty-fold over the force of attraction in air or in a vacuum. The act of dissolving sodium chloride in water simply means its dissociation into ions. It is analogous to raising the temperature of a crystal of Na^+Cl^- to its melting point.

8. 9d. Association and Related Factors. Just as certain types of molecules are readily torn apart into smaller units (ions), other types of molecules tend to combine with each other to form larger units by the process of association. At one time, this was vaguely attributed to their polar characteristics, that is, mutual attraction of oppositely charged poles on dipoles, such as illustrated by the molecule of I–Cl at the end of the section 8.1. At present, the phenomenon of association can often be better explained on the basis of *hydrogen bonding,* as in the case of water (section 27.7) and of acetic acid (section 31.12).

It is also useful to refer to polar characteristics for explaining solubility. Polar and ionic molecules usually dissolve readily in water, which is also polar. The solute and solvent molecules are surrounded by electric fields which exert a mutual attraction. A nonpolar molecule like Cl–Cl (see illustrations at end of section 8.1), has a very weak field around it. Consequently, it is only slightly soluble in a polar liquid like water, because there is no opportunity for mutual attraction. The nonpolar substances dissolve more readily in nonpolar solvents, like benzene. Most organic compounds are nonpolar

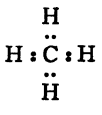
or, at most, only slightly polar and, therefore, dissolve best in nonpolar liquids. "Like dissolves like."

8. 10. Polarity and Chemical Reactivity. It is convenient to think of molecules as either covalent or ionic, but it must be remembered that there can be no sharp dividing line between them. As we have seen in this chapter, a covalent bond can have considerable ionic character, as illustrated for HCl in section 8.8. The important observation we introduce now is that a greater chemical reactivity is associated with greater polarity, or with greater ionic character.

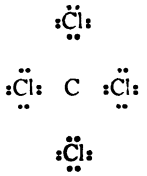
In chapter 5 it was pointed out that the carbon atom occupies a unique position among the elements. The information contained in succeeding chapters makes it possible to understand this unique position more clearly. It has been shown that the tendency for atoms to gain or lose electrons, to form a noble gas structure, is due largely to the charge on the kernel (section 5.2 and figure 6.1). The kernel charge of oxygen, for example, is $6+$ as compared with $4+$ for carbon. Therefore, oxygen has greater attraction for additional electrons by which to complete the octet and give the neon type of structure. Oxygen is said to be more electronegative than carbon. In fact, carbon stands in the unique position of either gaining four electrons to form the neon structure, or losing four electrons to yield the helium structure. As a result, it tends to share electrons rather than to acquire them or to lose them.

The first point we emphasize in this résumé, therefore, is the position of the carbon atom in the periodic table (figure 5.2). It stands at the head of column 4, and it has a valence of four. The picture of the carbon atom for textbook purposes is, therefore, usually $-\overset{|}{\underset{|}{C}}-$; four bonds must always be present, regardless of whether they are drawn as straight lines or as electron pairs. In only a few exceptional cases (sections 26.2 and 33.14) does this valence ever drop below four.

The principal characteristic of the carbon atom is that the valence bonds which it forms with other elements are generally nonpolar or slightly polar, and are chemically very stable. As representative compounds, we may take the following simple molecules, to be described more fully in the next chapter:



Methane



Carbon tetrachloride

The dipole moment is zero for both these molecules. This indicates a symmetrical arrangement of the atoms around the central carbon atom, as pictured for the CCl_4 molecule in figure 8.7.

In these formulas for methane and carbon tetrachloride, the spacing between C and H, and between C and Cl indicates the relative polarity of the valence bonds. The C : H link is nonpolar; if any displacement of the electron pair were shown at all, it would only be a slight displacement in the direction of the carbon atom, since the carbon atom is more electronegative than the hydrogen atom, as shown in table 8.2. The reader must not forget that this nonpolar, covalent link is the common type of bond in organic chemistry.

The C :Cl bond, however, is polar and the reason why we know this is true is given in section 8.4. Polar bonds of this type (and these, also, are covalent bonds) occur often among carbon compounds. They are not as stable, chemically, as the nonpolar bonds. This is an important factor in the study of organic chemistry.

SUGGESTED READING

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Also, see references to chapters 4 and 7.

PART 2

The Architecture of Carbon Compounds

The principal reason why organic chemistry sometimes appears to become difficult is that the student tends to lose track of the meaning of valence.

Every once in a while, the student forgets that the carbon atom must be pictured with four bonds, thus, $-\overset{|}{\underset{|}{C}}-$, and the process by which we can build molecules from these carbon atoms suddenly seems to lose its simplicity.

For this reason, in part 1 of this book we did no more than try to develop a conception of the meaning of valence, that is, of the means by which atoms are joined together.

Now that we have made a study of the various ways in which atoms can be built into molecules we can proceed to the study of the organic chemist as an architect. What we *must* remember is that the carbon atom has a practically constant valence of four.

> "Structural organic chemistry, although developed without mathematics, except of the most elementary sort, is one of the very greatest of scientific achievements . . . It is this system of structural chemistry that served chiefly as my basis when I advanced my theory of valence."
>
> G. N. Lewis, *J. Chem. Phys.*, 1, 17, 1933.

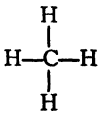
9. METHANE AND THE STRUCTURE THEORY

9. 1. Properties of Methane. We are now ready to consider a very simple compound of carbon called methane. The composition of this substance is expressed by the formula CH_4. It belongs to a family of compounds known as hydrocarbons, because they are composed of hydrogen and carbon, and nothing else.

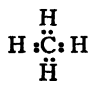
Methane has several other names. It is called *marsh gas,* because it occurs in swamps as the result of the decomposition of organic matter induced by certain bacteria. Its mixture with oxygen or air is also called *firedamp* because its presence in coal mines often leads to serious explosions.

The principal sources of methane are natural gas, which contains about 90% methane, and coal gas, which contains between 30 and 40%. Methane has no color or odor, is only slightly soluble in water, and is only about one-half as heavy as air.

Since the molecular weight of methane has been found to be 16, in round numbers, it contains only one C atom and four H atoms (C = 12 and 4H = 4). The structure of methane can, therefore, be represented by the following formulas, in which carbon is given its usual valence of four and hydrogen, its valence of one:



or



These formulas agree with the general principles which were stressed in the study of valence, that is:

First, in order to understand the chemistry of carbon compounds it is necessary for us to know the positions of all the atoms in the molecule (section 2.2).

Second, the carbon atom has a valence of four; it should always be thought of thus, $-\overset{|}{\underset{|}{C}}-$.

Third, organic compounds are generally nonpolar or polar.

From now on, the reader will encounter less often the electrons which have been stressed so much up to this point. Formulas will usually be written in the customary fashion with straight lines for valence bonds, but care will be taken to keep the attention directed to the rule of the duet of electrons (:) which constitutes one bond.

We shall find that the important thing in organic chemistry is the ease or difficulty with which the bonds between atoms can be broken in order to permit chemical changes. It is usually difficult to break the nonpolar valence bond, but the polar bond is relatively reactive and is more easily broken by chemical reagents.

From now on, the reader must examine the molecule from these angles: How the atoms are bound, how easily the bonds are broken, and how the molecule can be altered by breaking these bonds through a chemical reaction.

Methane is a very stable substance and is not even affected by chemical reagents which destroy most other substances. For example, it is not easily acted on when bubbled through sulphuric acid, nitric acid, strong alkalies, or powerful oxidizing agents.

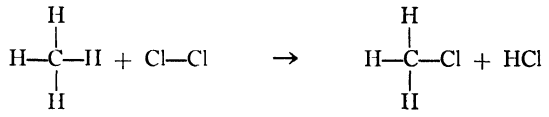
Since methane is so inactive, we see at once that the union between carbon and hydrogen (the C:H or C–H union) is a very strong one. This is a fact which we shall refer to frequently during the rest of our study of carbon compounds. Occasionally, it is true, we may have to amend this rule slightly because we shall find that in larger molecules the presence and structural position of other atoms may weaken the C–H bond, but, in general, the rule of the great strength of the C–H bond is one which must always be kept in mind.

Although methane is so very stable, there are a few things we can do with it. In the first place, it will burn in oxygen, but this is a

common property of many carbon compounds and we need not pay much attention to it. The most noteworthy characteristic of the burning of methane is that its heat of combustion is very high and it is consequently a valuable fuel.

It is possible to make methane react with nitric acid to form a nitro compound (sections 20.4 and 33.15).

A more important property of methane and, from our elementary point of view in this book, its only chemical property of importance, is its reaction with chlorine or bromine (it does not react with iodine):

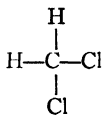


Methane

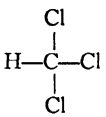
Chloromethane
Methyl chloride

This is one of the very few methods at our disposal for breaking the C–H bond in methane.

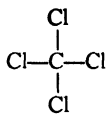
The reaction between methane and chlorine takes place readily when the two gases are mixed and placed in diffused sunlight. Under properly controlled conditions other products may also be obtained, as follows:



Dichloromethane
Methylene chloride



Trichloromethane
Chloroform



Tetrachloromethane
Carbon tetrachloride

Each of these substances (made by other, cheaper processes) is of commercial importance. Methyl chloride is a gas used in refrigeration machines, methylene chloride is a solvent, chloroform is an anesthetic as well as solvent, and carbon tetrachloride is used as a fire-extinguisher, solvent, and "dry-cleaner" for soiled clothing.

As stated before, iodine, the least active of the halogens, does not react with methane. Fluorine, the most active halogen (in fact the most active of all the elements), explosively decomposes methane, even at very low temperatures. In order to prepare fluorine compounds of methane, it is necessary to use indirect methods (section 25.7). For example, the reaction between carbon tetrachloride, CCl_4,

and antimony fluoride, SbF_3, yields dichlorodifluoromethane, CCl_2F_2, when SbF_5 is employed as a catalyst. This product is one of the nontoxic Freons used as refrigerants.

9. 2. Structure Theory. The chlorine derivatives of methane, which we have just tabulated, illustrate a theory which has been of great importance in the development of organic chemistry. We wrote the molecule of methane with the various atoms in a certain space relationship. When we replaced the hydrogen atoms successively by chlorine atoms no appreciable change was indicated in the structure of the molecule.

The amazing progress in organic chemistry since 1850 has been due largely to this belief among organic chemists that *the structures of carbon compounds are not appreciably altered by minor changes in composition.* This conception has generally been known as the structure theory.

Beginning the study of organic chemistry with a description of the properties of methane is, therefore, valuable, because methane illustrates the usefulness of the way an organic chemist looks at a molecule (see chapter 2).

9. 3. Substitution. The direct replacement of one atom in a molecule with another atom is called substitution. As the reader has already observed, these substitution products are named by using the name of the parent molecule as the last name of the compound.

Thus, dichloromethane means that two atoms of chlorine have been inserted in the methane structure in place of two hydrogen atoms. Besides these *systematic* names, certain *common* or *trivial* names are often employed. For example, trichloromethane is more often called chloroform.

9. 4. The Importance of Substitution. The substitution process, by means of which we replace an H atom in a carbon compound with another element, is one of the most important features of organic chemistry.

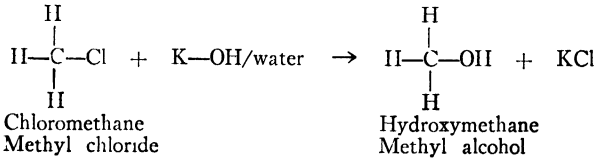
Before we have finished this chapter, it will be evident to the student that the simple molecule $H-\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H$ can be used as the starting point for making a large number of more complex substances. In

fact, methane is regarded as the mother substance of organic chemistry, in that all of the carbon compounds, of which there are now probably about 700,000, can be theoretically derived from methane.

As we have just indicated in the past few pages, the nonpolar C–H bonds in the methane molecule, CH_4, are so stable that we cannot alter the molecule by any *simple* means except by the reaction with chlorine to give CH_3–Cl, chloromethane. (The reaction with nitric acid, described in section 20.4, is much more drastic.) Since the CH_4 molecule is very stable, it does not lend itself for use in the building of the many carbon compounds that were just mentioned. The CH_3–Cl molecule, however, is more active and undergoes a large number of chemical changes, of which several examples will be given in the next section.

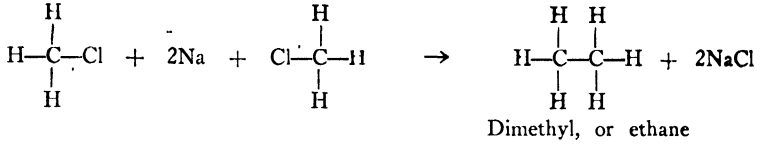
The substitution of a Cl atom for an H atom is, therefore, very often the first step in the preparation of more complex compounds. The Cl atom acts as a "hot spot" in the molecule, and the molecule can then be made to react with other substances.

When methyl chloride is shaken with a warm solution of potassium hydroxide in water the –Cl is slowly replaced by –OH:



This is a general method for replacing the halogen atom in a molecule by the hydroxy group (–OH). Organic compounds containing the –OH group are called alcohols. The fact that the KOH is dissolved in water is so important that it is stressed in the equation by writing KOH/water. Later (section 14.2), we shall find that in organic solvents a different type of product is obtained and that the reaction takes place more smoothly than this one.

If methyl chloride is dissolved in ether and pieces of metallic sodium are added to the solution, the following reaction takes place when the resulting mixture is heated for several hours:



Dimethyl, or ethane

A significant feature of the organic compounds containing chlorine is the fact that they can usually be depended on to react with metals or metallic compounds.

9. 5. Reactivity of Chloromethane. Let us compare once more the formulas of methane and its halogen derivative:

Methane (nonpolar)

Chloromethane Methyl chloride (polar)

In methane, we have nothing but C–H links, which, as we have already pointed out, are nonpolar and are very stable. In the CH_3–Cl molecule there are three nonpolar C–H links, and one C–Cl link which is polar. In this molecule, the Cl atom has the greater pull on the electron pair (:), which means that a slight negative charge rests on the Cl atom and the $-CH_3$ group is, therefore, correspondingly electrically positive.

In many of its reactions CH_3–Cl acts as if it broke up into CH_3^+ and Cl^- ions, behaving just like Na–Cl, the typical inorganic compound. For instance:

$$Na^+ Cl^- + Ag^+ NO_3^- \rightarrow AgCl + NaNO_3$$

$$CH_3-Cl + Ag-NO_3 \rightarrow AgCl + CH_3NO_3$$

The reaction between salt and silver nitrate takes place best in water, in which solvent they both ionize, and an instantaneous reaction takes place between the ions Ag^+ and Cl^- to form insoluble AgCl.

Methyl chloride is insoluble in water, but if it is dissolved in alcohol and mixed with an alcohol solution of silver nitrate, the corresponding reaction takes place, as we have just indicated.

The difference between Na–Cl and CH_3–Cl is that the Na–Cl solution contains Na^+ and Cl^- ions, whereas the CH_3–Cl solution contains CH_3–Cl molecules which break up into ions only as reaction takes place. The CH_3^+ ion has only a brief existence. A polar molecule like CH_3–Cl can be regarded as "potentially ionic"; it becomes ionic under certain conditions. In general, we associate a greater chemical reactivity with a greater polarity.

9. 6. Radicals. In the discussions of this chapter the reader will have noticed that we use the group of atoms CH_3– as a definite unit. It apparently remains intact during a chemical reaction.

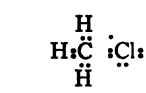
A group of atoms which goes through a series of chemical changes without any change in structure or composition is known as a radical or group.

The radical CH_3– is called *methyl* from its relationship to methane, CH_4. Here are the formulas of some representative compounds in which the methyl radical is present:

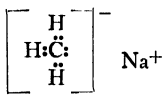
CH_3—H	CH_3—Cl	CH_3—CH_3	CH_3—OH	CH_3—Na
Methane	Methyl chloride	Dimethyl, or ethane	Methyl alcohol	Methylsodium

The methyl radical, it will be seen, has a valence of *one,* in that it combines with only one atom of univalent elements, like Na or Cl, or with one univalent radical like –OH.

We mention some of these compounds derived from methane in order to stress once again the unique position of carbon among the elements. It was shown in chapter 5 that the carbon atom is situated at the border line which divides electropositive from electronegative elements. To some extent, it shows amphoteric properties, since compounds are known in which it is combined with both types of elements. For example, in CH_3–Na the carbon atom is linked to a metallic (electropositive) element, whereas in CH_3–Cl it is linked to an acidic (electronegative) element. These compounds are pictured on the electron basis as follows:



Chloromethane
Methyl chloride



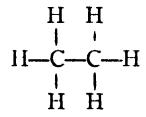
Methylsodium

The electronic structure of methyl chloride is typical of most carbon compounds in that the bonds are all covalent, but there is a slight shift of the electron pair toward the Cl atom in C :Cl because of the much greater electronegativity of the Cl atom.

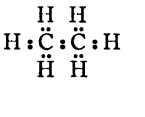
In the case of CH_3–Na we have a compound which behaves like an inorganic salt. The CH_3– group in this molecule is really a negative ion; an electron is actually transferred from sodium to carbon, and we have a true electrovalence bond just as in sodium chloride (section 8.1).

These illustrations emphasize the principle that an increase in polarity of a molecule generally results in an increased chemical activity. Methylsodium is very reactive, igniting spontaneously when exposed to air. It is a relative of tetraethyllead, a substance used to improve gasoline for motor cars.

9. 7. Ethane. This substance, just like methane, is a hydrocarbon and is a gas. It is found dissolved in crude petroleum and is also found in some natural gas wells. The structure of ethane has been proved to be, in most respects, similar to that of methane,



or



the larger part of the molecule consisting of C–H bonds.

The C–H union we have already explained in detail; it is a very stable union and all that can be done to it *readily* is to replace an H atom by halogen. Theoretically, then, we should be able to prepare the following compounds:

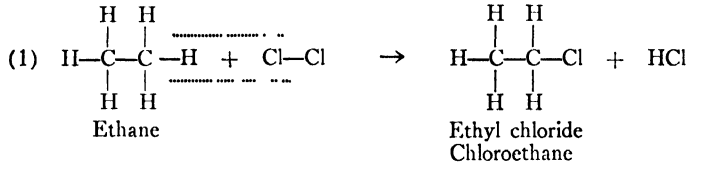
C_2H_5Cl	$C_2H_3Cl_3$	C_2HCl_5
$C_2H_4Cl_2$	$C_2H_2Cl_4$	C_2Cl_6

and in fact all are known. Not all of them, however, can be made by the direct action of chlorine on ethane.

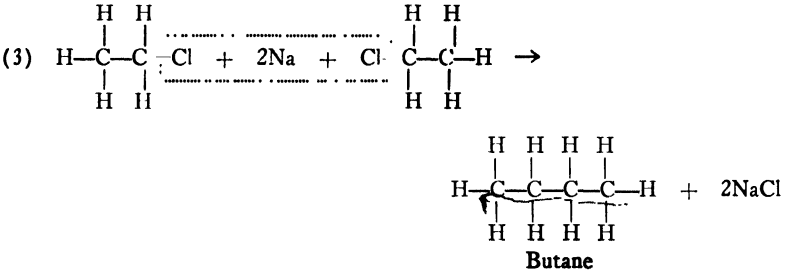
The only part of the ethane molecule with which we are not familiar is C–C, the bond between the two carbon atoms. This valence bond, like C–H, is very stable, and all we need remember about it is that ordinarily it is not acted on by chemical reagents.

In these few paragraphs on ethane, the idea which we wish to impress on the student is that the organic chemist, by inspection

of the formula of the substance, can predict most of its chemical properties. Ethane contains the same elements as methane, linked together in the same way, and, therefore, should behave in the same way. Accordingly, we are not surprised to find that the following reactions take place:



From the names given to these two products, it will be seen that the group CH_3–CH_2– is known as the *ethyl* radical. The condensed formulas of ethyl chloride and ethyl alcohol are usually given as C_2H_5Cl and C_2H_5OH, respectively.

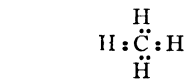


This last equation leads us directly to the subject matter of the next chapter.

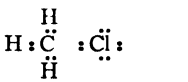
10. CARBON CHAINS

10. 1. Introduction. In this chapter the student becomes acquainted with the real "spirit of organic chemistry." The organic chemist is to be described primarily as an architect. It will be found that the construction methods used by this builder of molecules are seldom more intricate than the simple principles we have learned from the study of methane and its related compounds.

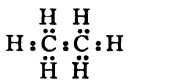
In the last chapter a few simple compounds were described which consist, for the most part, of only carbon and hydrogen, and in some cases chlorine also:



Methane
(very stable)



Chloromethane
(reactive)



Ethane
(very stable)

From the properties of these compounds we arrived at the following rules:

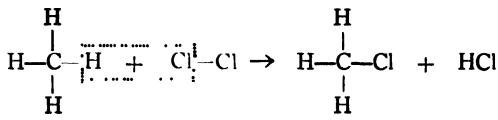
1. The C–H bond is relatively inactive and is not affected by most reagents. An important property of the C–H union, however, is the replaceability of the hydrogen atom by chlorine and bromine.

2. The C–Cl bond is a very reactive one. As explained in the last chapter, it is to be considered as a polar bond, in which the Cl atom is held more loosely to the carbon than are the hydrogen atoms. The chlorine atom in this combination is electronegative, and

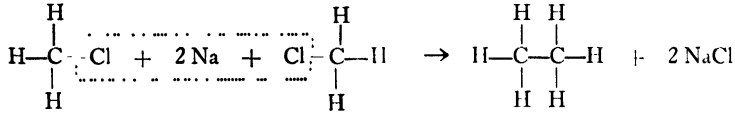
enters into reactions especially with those reagents which contain electropositive elements, such as metals.

3. The C–C union is a very firm one. It is not broken by the action of most reagents, not even by chlorine which does disrupt the C–H bond. Later, some cases will be found in which the C–C bond is broken, but the rule of great stability can be safely applied to most compounds like ethane, in which two carbon atoms are connected by a single valence bond.

The ability to interpret and apply these three simple principles is all one needs in order to be able to build a seemingly infinite number of compounds. For example, we have already seen how easy it is to pass from methane, CH_4, to ethane, C_2H_6:



This reaction follows rule 1 on the ability of chlorine to replace the hydrogen atom in C–H.



This reaction follows rule 2 on the reactivity of Cl, in the C–Cl bond, with metals.

In this chapter a large number of compounds will be mentioned, the construction of which requires no more knowledge on our part than the rules given in the preceding paragraphs.

10. 2. Synthesis. The reaction between CH_3Cl and Na was discovered a long time ago by a chemist named Wurtz and since then any reaction of this type is known as a *Wurtz synthesis.*

The dictionary defines synthesis as the building up of a substance from two or more constituents. From this standpoint, the formation of a hydrate,

$$CuSO_4 + 5\,H_2O \rightarrow CuSO_4 . 5\,H_2O$$

would be a synthesis, since the resulting compound is more complex than its constituents.

The organic chemist, however, usually looks at it differently. He more often limits his use of the word synthesis to the special case in which a more complex compound is formed containing *more carbon atoms,* and in which the carbon atoms of the simpler compounds become *directly linked to each other.*

In the Wurtz synthesis, which we just pictured graphically, a two-carbon compound is built up from a one-carbon compound.

The meaning of the word synthesis will be brought up again in a later chapter (section 30.5*d*) when we take up the problem of condensation.

10. 3. Free Radicals. Later in this book (sections 17.12 and 26.2), we shall discuss free radicals more fully. It is of interest to introduce reactions of free radicals rather briefly in this chapter, because it will help us understand the Wurtz synthesis as well as the reaction which will be studied in section 17.13.

If we refer back to the structure of the chlorine molecule (figure 4.4), we find that if it is divided into its constituent atoms, these atoms would have an electron structure shown in table 10.1.

TABLE 10.1

MOLECULES, FREE ATOMS, AND FREE RADICALS

Molecule		*Free Atom or Free Radical*	
Chlorine	:$\ddot{\text{Cl}}$:$\ddot{\text{Cl}}$:	2 $\cdot\ddot{\text{Cl}}$:	(free atom)
Sodium	Na.	Na.	(free atom)
Ethane	H:$\ddot{\text{C}}$:$\ddot{\text{C}}$:H (H H)	2 $\cdot\ddot{\text{C}}$:H (H)	(free radical)

In the case of sodium (figure 4.3) the molecule is also the atom; it has but one valence electron.

There is considerable evidence that the methyl radical can exist for infinitesimal, but measurable, periods during a reaction in the form of a *free radical* which resembles the two *free atoms* which are described in table 10.1. The free methyl radical has one electron which is not used in a valence bond, just like that in the sodium atom, and it is extremely reactive. The free methyl *radical* should be carefully distinguished from the positive methyl *ion* which is be-

lieved to be present in chloromethane when it is in an activated state at the instant before it reacts with silver nitrate (section 9.5), and from the negative methyl *ion* normally present in methylsodium (section 9.6).

Chloromethane (ionized state) Methylsodium

In the Wurtz synthesis, it is believed that the metallic sodium, that is, atomic sodium, reacts with chloromethane to form a free methyl radical:

$$Cl:CH_3 + Na. \rightarrow .CH_3 + Na^+ :Cl^-$$

The sodium may also react with the free methyl radical:

$$.CH_3 + Na. \rightarrow Na^+ :CH_3^-$$

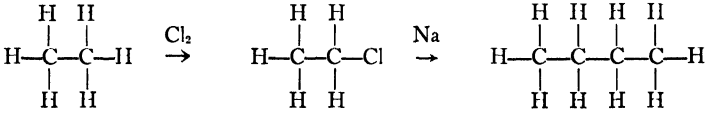
The following reactions will then presumably take place between these highly reactive entities:

$$.CH_3 + .CH_3 \rightarrow \underset{\text{Ethane}}{H_3C:CH_3}$$

$$Cl:CH_3 + Na^+ :CH_3^- \rightarrow H_3C:CH_3 + Na^+ :Cl^-$$

10. 4. Straight Chains. Perhaps the most remarkable thing about the carbon atom is the ease with which it unites with itself to form a chain and, in the Wurtz synthesis, we have an example to study this phenomenon so characteristic of carbon.

We have already seen how a one-carbon compound, CH_4, can be changed into a compound with two carbon atoms, CH_3–CH_3, and by the same procedure we can build higher:

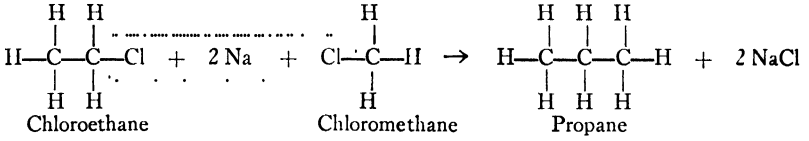


Ethane Chloroethane Butane

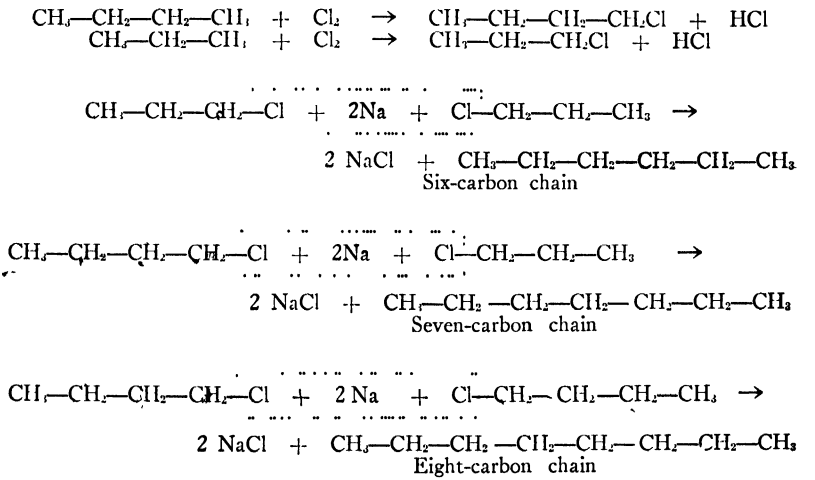
As before, this series of reactions indicates that ethane has been *chlorinated* in order to introduce a reactive halogen atom into the molecule. Two molecules of the resulting chloroethane, when treated

with sodium under the proper conditions, will condense to form a straight-chain compound with four carbon atoms in the chain.

If we want, instead, a chain of three carbon atoms, all we need to do is couple a two-carbon chain with a one-carbon compound:



And the following reactions (see paragraph in italics, section 25.2) constitute the corresponding steps in the preparation of six-, seven-, and eight-carbon chains:



By a method analogous to this one, a carbon compound has been prepared with seventy carbon atoms in a straight chain.

In table 10.2, there is a list of the first twelve of these straight-chain hydrocarbons, with some of their properties. The student should memorize the names of these members of the series of straight-chain compounds, for many compounds to be met with later are related to them, and bear similar names. This memory task is rather simple, because, starting with the fifth compound, their names are derived from words in Greek and Latin (mostly Greek) which indicate how many carbon atoms there are in the chain.

It is unfortunate that the originators of these names did not use a uniform number system for all the compounds. The first four members of the series (methane, ethane, propane, and butane) were not named in this systematic way because they were known before organic chemistry was systematized.

TABLE 10.2. STRAIGHT-CHAIN HYDROCARBONS (PARAFFINS)

Name	*Molecular Formula*	*Structure*	*Melting Point °C*	*Boiling Point °C.*
Methane	CH_4	CH_4	−182 6	−161 58
Ethane	C_2H_6	$CH_3—CH_3$	−172 0	−88.5
Propane	C_3H_8	$CH_3—CH_2—CH_3$	−187.1	−42.2
Butane	C_4H_{10}	$CH_3—CH_2—CH_2—CH_3$	−135 0	−0.5
Pentane	C_5H_{12}	$CH_3—(CH_2)_3—CH_3$	−129 7	36.08
Hexane	C_6H_{14}	$CH_3—(CH_2)_4—CH_3$	−94 0	68 8
Heptane	C_7H_{16}	$CH_3—(CH_2)_5—CH_3$	−90 5	98.4
Octane	C_8H_{18}	$CH_3—(CH_2)_6—CH_3$	−56 8	125 6
Nonane	C_9H_{20}	$CH_3—(CH_2)_7—CH_3$	−53 69	150.71
Decane	$C_{10}H_{22}$	$CH_3—(CH_2)_8—CH_3$	−29.72	174 04
Hendecane	$C_{11}H_{24}$	$CH_3—(CH_2)_9—CH_3$	−25 61	195 8
Dodecane	$C_{12}H_{26}$	$CH_3—(CH_2)_{10}—CH_3$	−9 65	216 2

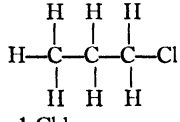
10. 5. Isomerism. Poets often make use of words that do not fit the rules of grammar, and they excuse themselves with the phrase "poetic license." In the same way, teachers must often employ ideas which do not agree with their rules, but the poor teacher has no such trite phrase as poetic license to cover his shortcomings.

For instance, in the preceding section we wrote this reaction:

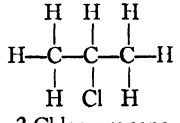
$$\underset{\text{Propane}}{CH_3—CH_2—CH_3} + Cl_2 \rightarrow \underset{\text{Chloropropane}}{CH_3—CH_2—CH_2Cl} + HCl$$

This is a case of "teacher's license," for it does not tell all the truth.

It is practically impossible to control the experimental conditions so closely that the chlorine atom should enter the propane molecule only as indicated. There really are two possibilities:



1-Chloropropane



2-Chloropropane

From the product of the reaction the two different compounds can be separated by distillation, for they have different boiling points. These two chloropropanes furnish an example of the phenomenon of isomerism.

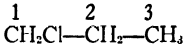
Isomers are compounds of the same composition and molecular weight, but with different properties. The word isomer comes from the Greek, *isos,* meaning equal, and *meros,* meaning measure. In this example of isomerism, the two molecules have an equal measure of materials, namely C_3H_7Cl, but in one case the Cl atom is on an end carbon atom and in the other case it is on the middle carbon atom.

Because the atoms in the molecules are arranged differently, the two compounds have different densities, boil at different temperatures, and react at different rates of speed with other substances.

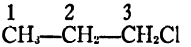
An elaborate system has been devised by which such compounds can be named so that no confusion (at least, very little confusion) arises when we refer to them. This system of nomenclature is too complicated for us to absorb all of it at one time, but we can take it piecemeal whenever occasion demands that part of it is explained.

The two chloropropanes which have just been mentioned are named in such a way as to indicate that they are derived from a straight chain of three carbon atoms, in which the carbon atoms are numbered consecutively 1, 2, and 3.

1–Chloropropane is exactly the same as 3–chloropropane,



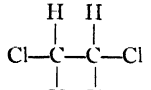
1–Chloropropane



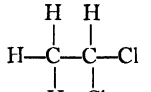
3–Chloropropane

the only difference being the end of the molecule at which the numbering of the carbon atoms is begun. The convention is to *start at that end of the chain where a substituting elem nt appears;* it is better to say 1–chloropropane than 3–chloropropane.

Here is another case of simple isomerism:



1,2–Dichloroethane



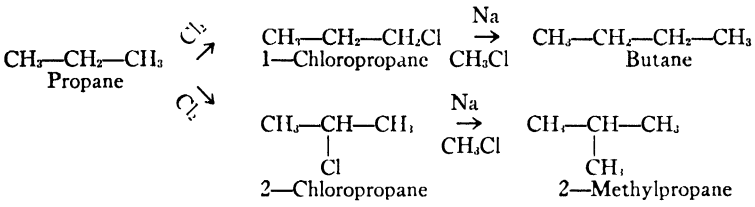
1,1–Dichloroethane

These compounds are made by methods which we cannot discuss at this point. From their methods of preparation, however, it is certain that in one case both Cl atoms are on the same carbon atom, whereas in the other case they are on separate carbon atoms. They have different properties, although the same composition, $C_2H_4Cl_2$;

the difference in structure is apparent from the names we have given them.

10. 6. Branched Chains. In this section, we shall explain how chains of carbon atoms may branch off from the main stem, and form the so-called branched-chain compounds.

Suppose we start with propane, a chain of three, and build it up to a compound with four carbon atoms by means of the Wurtz synthesis. First, propane is treated with chlorine, and then the two chloro-products are coupled with CH_3Cl so as to introduce one more carbon atom:



As a result of these operations, we obtain two compounds of the composition C_4H_{10}. One of them is a straight-chain hydrocarbon and the other is a branched-chain hydrocarbon.

These two compounds are *isomers*. They have the same composition, but by consulting tables 10.2 and 10.3 it will be seen that they have different properties.

We can explain one more detail in the systematic way of naming compounds of carbon. The *last name* of a chain compound is obtained from the name of the *longest straight chain* which is present. In the preceding example of 2—methylpropane, it is clear that the longest chain contains three carbon atoms, C–C–C, and there is a methyl group, CH_3, on the second carbon atom in the chain.

Just as we found there are two isomers of C_4H_{10}, we can also work out the structures of three isomers which have the composition C_5H_{12}, and five isomers of the composition C_6H_{14}. We shall give only a tabulation of the formulas of these branched-chain compounds in table 10.3, without showing the details of their preparation.

This leads to a general observation on theoretical organic chemistry which probably has already become apparent. We are so cer-

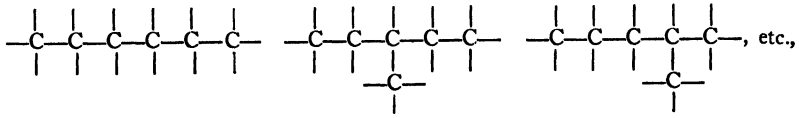
TABLE 10.3. BRANCHED- CHAIN HYDROCARBONS (Paraffins)
(Isomers of the straight-chain compounds in table 10.2)

Molecular Formula	*Name*	*Structure*	*Boiling Point, °C.*
*C_4H_{10}	2—Methylpropane	$CH_3—CH(CH_3)—CH_3$	−12.2
C_5H_{12}	2—Methylbutane	$CH_3—CH(CH_3)—CH_2—CH_3$	28.0
	2,2—Dimethylpropane	$CH_3—C(CH_3)_2—CH_3$	9.5
C_6H_{14}	2—Methylpentane	$CH_3—CH(CH_3)—CH_2—CH_2—CH_3$	60.2
	3—Methylpentane	$CH_3—CH_2—CH(CH_3)—CH_2—CH_3$	63.2
	2,3—Dimethylbutane	$CH_3—CH(CH_3)—CH(CH_3)—CH_3$	58.0
	2,2—Dimethylbutane	$CH_3—C(CH_3)_2—CH_2—CH_3$	49.7

*Branching cannot occur when there are less than four carbon atoms in the molecule.

tain that the chemistry of carbon can be represented by the symbol –C– that we feel we can arrange these atoms on paper at will to build up molecules that can be prepared in the laboratory.

To illustrate, we can write out a string of six carbon atoms, thus,



, etc.,

and arrange them in all the possible ways, filling in the necessary hydrogen atoms on the unused valence bonds. When the puzzle has

been finished, we feel certain that these new compounds which we have worked out on paper can actually exist.

In this example of the possible compounds containing six carbon atoms, it will be found that five arrangements are possible; their structures are listed in tables 10.2 and 10.3 with some of their properties.

In like manner, it has been calculated that there are 355 isomers of the composition $C_{12}H_{26}$. Only a few of these isomers have been prepared, because organic chemists have been too busy with other problems to worry about this one. It is possible that some of these isomers cannot exist because of space considerations of the molecule with which we are not yet familiar, but it is certain that not more than 355 isomers are theoretically possible. It is of interest to note, however, that the nine possible C_7H_{16} compounds, the eighteen possible C_8H_{18} compounds and the thirty-five possible C_9H_{20} compounds have all been made.

The branched-chain hydrocarbons in the table are in all respects similar to their analogous straight-chain compounds, except for the variations in physical properties, such as boiling point, and for minor variations in chemical reactivity.

In most books, the straight- and branched-chain compounds are usually considered in one category as the open-chain compounds, to distinguish them from the ring structures (closed-chain compounds), described in the next chapter.

10. 7. Paraffin Hydrocarbons. All the hydrocarbons mentioned in this chapter belong to the same family.

This is usually the first family studied in organic chemistry, because most other families of compounds can be built up by some ingenious trick of chemical architecture from these simple chain compounds.

Let us see, now, what is meant by a *family* of carbon compounds.

1. All the hydrocarbons described in this chapter will, on examination, be found to agree with the general formula C_nH_{2n+2}. For example, in a compound of three carbon atoms, $n = 3$, and the formula then is $C_3H_{2\times3+2}$ or C_3H_8. If there were sixty carbon atoms in a certain compound, its formula would be $C_{60}H_{122}$.

2. As already explained, these compounds are called hydrocarbons because they consist of nothing but hydrogen and carbon. They were originally called *paraffin* hydrocarbons in order to set them apart from the families of hydrocarbons which will be described later in chapter 16, as well as to indicate their general nature. The name was probably intended to mean slight reactivity but the Latin words *parum affinis,* from which the name was derived, can be more accurately translated to mean too poor in kinship. The description of paraffin hydrocarbons as having only slight reactivity is not taken literally by the modern organic chemist. Although the two building units, C–C and C–H bonds, are relatively inert, we have already seen that the C–H bond is sensitive to the action of the halogens (section 9.1) and later we shall find that it can be attacked through the processes called *nitration* (section 20.4) and *sulphonation* (section 20.3). An example of the reactivity of the C–C bond toward chemical reagents can be found in section 12.6, and the effect of *pyrolysis* on this bond is described in section 20.7.

In addition to being called the paraffin hydrocarbons, this family is also known as the *methane,* or *marsh gas* series. Most families of carbon compounds, as we shall find out later, are named from the first or simplest member of the series, which in this case is methane, or marsh gas, CH_4.

All the members of the paraffin hydrocarbons have names ending in *-ane*. This is the family symbol, the rest of the name simply indicating the number of carbon atoms in the molecule. For example, from the name *hexane,* we can at once tell that there are six carbon atoms in the compound (*hex*), and that it is a member of the paraffin series (*-ane*).

3. This family of compounds also constitutes what is known as a *homologous series,* a term applied to a series of compounds in which the successive members differ by a constant factor. For example,

$CH_3—CH_2—CH_3$ (C_3H_8) and $CH_3—CH_2—CH_2—CH_3$ (C_4H_{10})
Propane Butane

differ by CH_2, and the same increment represents the difference between any other pair of successive members of the family. The members of a homologous series are said to be *homologs.*

4. In a homologous series, the physical and chemical properties generally show progressive variations. The gradual increase in boiling point and density of the successive members of the straight-chain series is evident in table 10.2. The lowest members are gases, intermediate members, beginning with C_5H_{12}, are liquids, and members containing more than sixteen carbon atoms (not shown in the table) are solid at room temperature.

Chemical reactivity, in general, decreases with an increase in molecular weight in this series. Thus, methane and chlorine react with explosive violence when placed in direct sunlight, but the succeeding members, with a higher carbon content, react much more slowly and quietly with chlorine.

10. 8. Petroleum. This is an oil occurring widely in nature. About 90 per cent of the crude petroleum is a complex mixture of several types of hydrocarbons. The open-chain hydrocarbons described in this chapter form a high percentage of the crude oil found in this country, especially in the Pennsylvania oil fields.

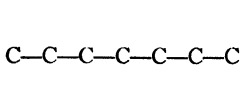
The many hydrocarbons in petroleum can be partially separated by careful distillation. The fraction which boils between room temperature and 70°C. is used largely as a solvent and is called *ligroin* or *petroleum ether. Gasoline* is the mixture of compounds which distills from the crude oil between 70 and 200°C. and *kerosene* is the 200 to 300°C. fraction.

When the more volatile compounds, comprising gasoline and kerosene, are removed from Pennsylvania petroleum, a heavier liquid remains which can be further separated into *lubricating oils,* and *paraffin wax.* The "mineral oil" sold by the druggist for use as a laxative costs more than that used in a motor car because it is more highly purified by removal of coloring matter and sulphur compounds.

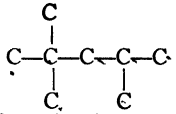
The residue from petroleum of the western states is of an "asphalt" nature as compared with the "paraffin-wax" nature of the residue of eastern petroleum. Each type of petroleum has its advantages for certain uses.

Because of the great importance of gasoline in our national economy, much research has gone into improving its performance in engines. The efficiency of an engine depends largely on the extent

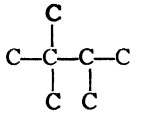
to which the fuel used is free from knock. Long, straight-chain molecules knock badly, but the short, branched-chain compounds knock relatively little. The outline structures of the formulas of certain important gasoline compounds are shown here, with their common names in quotation marks:



Heptane



2,2,4-Trimethylpentane
"Isooctane"

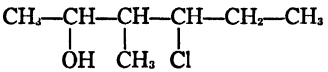


2,2,3-Trimethylbutane
"Triptane"

Heptane is one of the poorest fuels with respect to knock. It was once thought that isooctane was the perfect knockless fuel, but triptane is even better. Although isooctane is not useful alone as a fuel (because of its low volatility), it is used as an antiknock ingredient and as a standard. A gasoline equivalent in performance to isooctane has a 100-octane rating; if equivalent to heptane it has a zero-octane rating; if equivalent to a mixture containing 40 per cent heptane and 60 per cent isooctane it has a 60-octane rating, and so on. Addition of tetraethyllead to a gasoline acts like a high content of the antiknock hydrocarbons.

10. 9. How to Name the Open-chain Compounds. When an architect erects a modern skyscraper, he first builds a steel framework. This serves as an outline to which he later adds the necessary parts for a useful building.

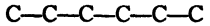
In the same way, the organic chemist regards a chain hydrocarbon as the skeleton framework on which organic compounds are built. Take the following compound, for example,



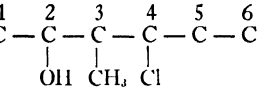
This is a formidable looking substance at first glance. To the uninitiated, it would seem to be a hopeless problem for anyone to write an intelligible name for such a substance.

To the initiated, however, this structure is very simple. In any office building or skyscraper the floors are numbered, and in order to visit a tenant it is merely necessary to whisper the name of the tenant to the elevator operator and he whisks us to the proper floor and lets us out.

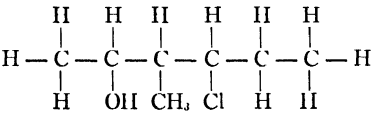
We treat carbon structures the same way. Suppose we count the carbon atoms in the straight chain we have just written, starting from the left end. Then on the second floor we find –OH, on the third $-CH_3$, and on the fourth –Cl. And suppose we call it the *hexane* building. To locate the tenants, we just write out the list of tenants like this, 2–hydroxy–3–methyl–4–chlorohexane. Any organic chemist, given this name as the name of a compound, can sit down and write its complete structure. The first thing he would do is write out a chain of six carbon atoms, for the last name of the compound tells him it is a 6-story building.



Then he would number the atoms from 1 to 6 and place the tenants –OH, $-CH_3$, and –Cl in the proper positions.

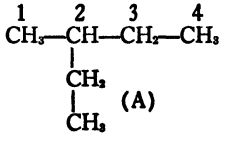


Finally, he would fix up the molecule with enough valence bonds and hydrogen atoms to give each carbon atom its usual valence of four.

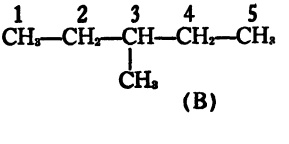


This is a general rule for any chain compound. The last name is obtained by counting the number of carbon atoms in the longest straight chain. In this case, the longest chain is six and we consider the compound as a derivative of the paraffin hydrocarbon, hexane.

There are occasions when the longest chain in a compound is not apparent at first. These two formulas represent one compound in which the longest chain is five carbon atoms:



(A)



(B)

It should be named 3–methyl*pentane* and not 2–ethyl*butane*, although an organic chemist would recognize what is meant from either name. Structure (A) shows it as the butane derivative, while (B) shows it more correctly as a derivative of pentane.

10. 10. Functional Groups. In the preceding section we showed how easy it is to name rather complex compounds, in which the framework is a chain hydrocarbon, by using the name of the hydrocarbon as the last name of the compound. When the frame contains six carbon atoms in a chain (C–C–C–C–C–C) the last name is hexane, with all the substituents, such as –Cl, $-CH_3$, and –OH, listed as prefixes.

We have indicated that the general chemical activity of such a compound is due more to the substituents, such as –OH, than to the hydrocarbon part of the molecule. The organic chemist likes to refer to the –OH group as a "functional" group, meaning that it takes part, to a great extent, in the chemistry of the molecule in which it appears. If there are several such functional groups in the molecule, he picks out one of them and calls it the "chief function" and includes the name of this function in the last name of the compound.

The hydroxy (–OH) group is called a chief function, and compounds with –OH groups attached to the carbon chain are called *alcohols*. The names of alcohols terminate in *-ol;* an example is ethanol (section 27.1). The compound under discussion is considered to be an alcohol, more specifically as *2–hexanol*, since the last name of the compound should correspond to the longest chain containing the functional group. The numbering is begun at that end of the chain which gives the chief function the smallest number; on the basis of these rules the compound might be called 3–methyl–4–chloro–2–hexanol.

The student may argue that the Cl atom is quite active in such a molecule and may also properly be called a functional part of the compound. It has been agreed, however, to regard the Cl atom as a substituent in such a molecule, so the term *chloro* is usually seen as a prefix in the name of a compound.

The compound which we are describing poses still another problem in nomenclature, namely, the order in which the substituents are to be listed. At present, it is the policy to follow the rules used by editors of chemical journals (see the next section) who prefer an alphabetical sequence in a case like this in order to assist them in their indexing. Our compound on this basis is 4–chloro–3–methyl–2–hexanol.

10. 11. Old Nomenclature. Before the organic chemist became the efficient architect that he is today he did not look at structures in the systematic way explained in the preceding section. The early chemists had developed systems that are still in use for simple substances, but are not adequate for complex compounds. Molecules were called *normal* (represented by *n*–) when the carbon atoms were arranged in a straight chain. When the chain had a fork arrangement at one end, with a methyl group on a carbon atom adjacent to a *terminal* methyl group, it was called *iso*. If a carbon atom had four hydrocarbon radicals attached to it the resulting structure was *neo*. These designations can be illustrated by reference to the isomers of pentane which are listed in table 10.3, where 2–methylbutane can be called *iso*pentane, and 2,2–dimethylpropane can be called *neo*pentane (also, see names in section 26.1).

Another old system was to relate all structures to methane. Thus, in table 10.3, the compound 2-methylbutane can also be called ethyldimethylmethane, with the substituents in alphabetical order.

10. 12. New Nomenclature. For information on the naming of various types of compounds, the reader should refer to the index of this book under "nomenclature." The subject is too complex to be discussed in detail in a book of this kind. However, the system used in naming compounds follows closely that which is popularly called *systematic nomenclature*. This was first outlined by a committee meeting in 1892 at Geneva, Switzerland. It was modified in the period 1922–1930 by the International Union of Chemistry, whose recommendations are generally referred to as the I.U.C. Rules.

NOMENCLATURE*

"No phosphorus in phosgene gas,"
The puzzled chemist said,
There's no Cu in copperas,
Plumbago has no lead.

Ind. & Eng. Chemistry News Edition 12, 161 (1934).

"Things are not always what they seem,
'Twas so in days of old.
There's no Au, in spite of gleam,
In ore that's called 'fool's gold.'

"In selenite Se's not found
And more the pity be.
In German silver, I'll be bound,
One cannot find Ag.

"That magnetite has no Mg,
Would not be hard to guess;
But platinite without Pt,
Seems odd, I must confess."

The chemist hung his weary head.
"Enough, enough," cried he,
"Now after this, I'll read instead
Organic chemistry."

But to the patient man's dismay,
Before he had gone far,
He found chromone, 'tis sad to say,
Containing no Cr.

The chemist sighed, and said goodbye,
"At least one thing I ken
That, when I find I want to die,
There's death in KCN."

—C. S. Powell

As intimated by the stanza in italics, the chemist feels that in organic chemistry compounds have names which tell him their chemical composition correctly. Nomenclature is supposedly more systematic in organic than in inorganic chemistry.

But even in organic chemistry it is possible to be misled by the *common* names. For example, chromone (see index) received its name from the Greek word chroma, meaning color, although this name might unfortunately lead us to believe that the compound contains chromium, Cr.

SUGGESTED READING

Gilbert, E.E., "The Reactive Paraffins," *J. Chem. Educ.*, **18**, 435 (1941).

Kettering, C.F., "The Effect of the Molecular Structure of Fuels," *Ind. Eng. Chem.*, **36**, 1079 (1944).

Waters, W.A., *The Chemistry of Free Radicals,* Oxford University Press, New York, 1948.

American Chemical Society Committee on Nomenclature, "Nomenclature, Spelling and Pronunciation," *Chem. Eng. News*, **30**, 1766 (1952). This reference lists the pamphlets available on the subject of nomenclature.

11. CARBON RINGS

11. 1. Formation of Closed Chains. Now that we have seen how the organic chemist can tie together a large number of carbon atoms into a chain, we have acquired a good insight into the methods he uses for building more intricate designs. The chain, ...–C–C–C–C–..., is his fundamental toy. The rest of this book is a description of the remarkable things he can do with it.

The first trick we shall explain is the formation of closed chains, or rings.

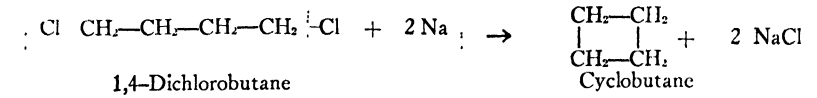
It is possible to make a dichloropropane in which the two Cl atoms are at the ends of the chain, as in the following illustration. Under the proper conditions, the effect of a metal on this compound is to remove both Cl atoms from the same molecule:

$$\underset{\text{1,3—Dichloropropane}}{Cl{-}CH_2{-}CH_2{-}CH_2{-}Cl} + 2\,Na \rightarrow \underset{\text{Cyclopropane}}{\begin{matrix} CH_2 \\ / \quad \backslash \\ CH_2{-}CH_2 \end{matrix}} + 2\,NaCl$$

This is an application of the Wurtz synthesis, which we discussed in chapter 10. At that time, we showed how two molecules can be linked to form a larger one:

$$CH_3{-}CH_2{-}CH_2{-}Cl + 2\,Na + \underset{\text{Chloropropane}}{Cl{-}CH_2{-}CH_2{-}CH_3} \rightarrow \underset{\text{Hexane}}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3} + 2\,NaCl$$

When both Cl atoms are in the same molecule, instead of in separate molecules, a ring can be formed instead of a longer chain. In a similar manner, we can prepare cyclobutane,



1,4-Dichlorobutane Cyclobutane

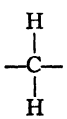
and also cyclopentane, but cyclohexane is better made by a different process. Rings of this type have been reported containing more than thirty carbon atoms.

11. 2. Cycloparaffin Hydrocarbons. It is easy to see that these ring structures are nothing more than the paraffin *straight*-chain compounds tied together at the ends of the chain. For this reason we call them the *cyclo*paraffin hydrocarbons.

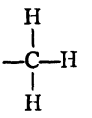
In the process of tieing up the ends of a chain it is necessary to remove, indirectly, one H atom from each end. Now the general formula of a paraffin hydrocarbon is C_nH_{2n+2}. Accordingly, the general formula of a cycloparaffin hydrocarbon is C_nH_{2n}. This is another family of hydrocarbons.

This ring family is also known as the *naphthenes*.

A third name for the family is the *polymethylenes*. This is probably the best of the family names, for it completely describes their structure. The $-CH_2-$ group occurs in many compounds and it has been named the *methylene* group, as a matter of convenience. This is a group with a valence of two, and must not be confused with methyl which has a valence of one:



Methylene

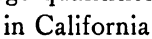
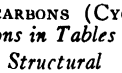
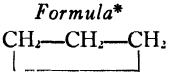


Methyl

These closed-chain compounds are nothing more than a circle of methylene groups and are, therefore, aptly named the *polymethylene* hydrocarbons. Thus, the compound C_3H_6 can be written $(CH_2)_3$ and be called trimethylene as well as cyclopropane. Except for one outstanding characteristic to be discussed in the next chapter, all we need remember is that these closed-chain compounds behave, in general, like their corresponding open-chain brethren.

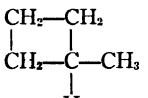
The cycloparaffins are found in large quantities in Russian petroleum, and in the petroleum obtained in California and other western states.

TABLE 11.1. CLOSED-CHAIN HYDROCARBONS (CYCLOPARAFFINS)
(*Compare the open-chain hydrocarbons in Tables* 10 2 *and* 10.3)

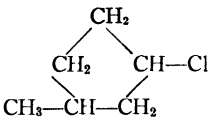
Molecular Formula	*Name*	*Structural Formula**	*Boiling Point °C.*
C_3H_6	Cyclopropane		—34 4
C_4H_8	Cyclobutane		13
C_5H_{10}	Cyclopentane		49.5
C_6H_{12}	Cyclohexane		81.4

*No attempt is made to portray the spatial configuration of these ring compounds, beyond indicating the cyclic structure.

11. 3. How to Name the Closed-chain Compounds. The naming of the cyclic compounds will be illustrated with a few examples:



Methylcyclobutane



1-Chloro-3-methylcyclopentane

In the case of compounds with several substituents, the convention is to number the atoms in the ring in a clockwise direction, with the 1 position assigned to the substituent with the highest alphabetical priority. Thus, chloro is 1 because *c* for chloro precedes *m* for methyl. Although this compound could be called 1-chloro-4-methylcyclopentane, the convention is to use the name with the smallest possible numbers.

11. 4. The Different Kinds of Formulas. We have now collected so much information about the nature of carbon compounds that we

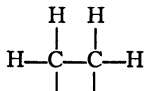
must pause a moment to think a little more carefully about the formulas we have been using.

The *empirical* formula represents merely the ratio in which the atoms have combined to form a molecule; this ratio is found by a quantitative analysis. For example, C_nH_{2n} or $(CH_2)_n$ represents the ratio in which carbon and hydrogen are combined in the polymethylenes.

The *molecular* formula indicates not only the ratio of the atoms in the molecule, but also the total number of atoms in the molecule. Whereas CH_2 is the empirical formula for a series of compounds, the formula $(CH_2)_3$ is the molecular formula of just one compound in that series, the molecular weight of which was measured and found to be 42 (36 for three carbon atoms, and 6 for six hydrogen atoms). This molecular formula may be written either $(CH_2)_3$ or C_3H_6. It is the formula of cyclopropane.

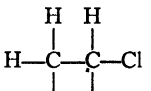
Structural formulas are often preferred to molecular formulas in organic chemistry because they supply more information. For instance, $C_2H_4Cl_2$, at first glance, is simply the molecular formula of a compound derived from ethane, C_2H_6, but we know that there are really two compounds with the formula $C_2H_4Cl_2$. Their structural formulas are CH_2Cl–CH_2Cl and CH_3–$CHCl_2$. These are sometimes also spoken of as *constitutional* formulas.

The *graphic* formula is one in which the atoms are written out completely, instead of only indicating the various groups in the molecule. The graphic formulas of the two compounds corresponding to the formula $C_2H_4Cl_2$ are



1,2-Dichloroethane

and



1,1-Dichloroethane

It should be clear from these examples why structural or graphic formulas are used so extensively in organic chemistry, instead of the molecular formulas which serve the purpose so well for inorganic chemistry.

12. MORPHOLOGY OF CHAIN AND RING COMPOUNDS

12. 1. Introduction. Morpheus is the god of dreams in ancient mythology. His name is obtained from the Greek word *morphe,* which means shape.

The Greeks were not the only people interested in dream shapes. One of the greatest achievements in the history of organic chemistry was the result of a dream in which the principal shape was a molecule of benzene (section 19.1).

The word *morphe* is present in many technical terms. For example, lampblack is said to be amorphous, meaning that it is without shape. Snow is polymorphous; its crystals occur in many shapes. Morphology, then, may be defined as the study of shapes or structures, and the shapes with which we are now concerned are those of the carbon compounds.

Up to this point, our carbon structures have been perfectly flat figures written in the plane of this sheet of paper in only two dimensions. Now we must begin to see the molecules in space in order to understand them. We must examine the molecule as a thing which occupies space in three dimensions. A molecule has thickness as well as length and breadth. Unless we acquire the habit of visualizing the shapes of carbon compounds it will be impossible to understand clearly the problems in the next few chapters.

12. 2. The Tetrahedral Carbon Atom. In chapter 7 we discussed the mechanism by which atoms build up to molecules by the process of electron sharing. In section 7.9, at the close of the chapter, it was

shown that the electron distribution in the valence shell of the carbon atom in its most stable state is not symmetrical. Table 7.1 shows how the electron distribution is modified by excitation when the carbon atom is subjected to chemical reaction with other elements; in the highest energy state, all four electrons are in hybridized sp^3 atomic orbitals which are equivalent. The four orbitals radiate symmetrically from the nucleus of the carbon atom at equal angles of 109°28′. This was illustrated in figure 7.5 for the reaction with four hydrogen atoms to give methane.

The symmetrical figure created when the carbon atom reacts with four hydrogen atoms is called a tetrahedron (figure 12.1). The carbon atom in methane is, therefore, referred to as a *tetrahedral* carbon atom and it is more often written as in figure 12.2, with the four valence bonds directed from the nucleus to the corners of the tetrahedron.

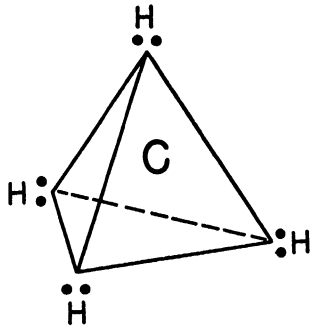


FIGURE 12.1. The four electron pairs at the corners of a tetrahedron.

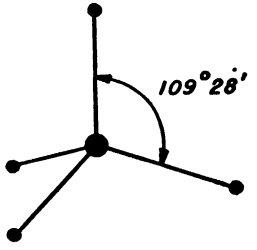


FIGURE 12.2. The four valence bonds directed to the corners of a tetrahedron.

It is generally agreed that the carbon atom retains this tetrahedral shape in all of its compounds of the methane type, and that the valence angles vary only slightly with the nature of the attached atoms. For example, if a hydrogen atom in methane is replaced by a chlorine atom to give CH_3Cl, the valence angles will not be appreciably changed even though the Cl atom is larger than the H atom and has a different pull on the electron pair.

The rest of this chapter will be devoted to a study of the various shapes of carbon compounds, in so far as these shapes are determined

by the tetrahedral nature of the carbon atom as shown in figure 12.2. At this point, the student may profitably review the subject matter associated with figures 8.4 to 8.7.

12. 3. The Shapes of Chain and Ring Compounds. First let us see what carbon compounds look like when the carbon atoms are arranged in what we have been calling a straight chain. If we add two carbon atoms to each other and fill up the empty valence bonds with

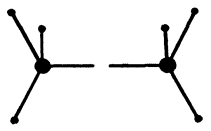


FIGURE 12.3. Ethane.
CH_3–CH_3

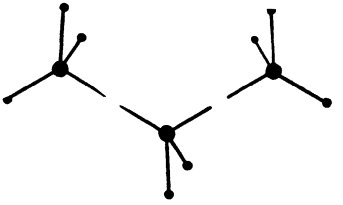


FIGURE 12.4. Propane.
CH_3–CH_2–CH_3

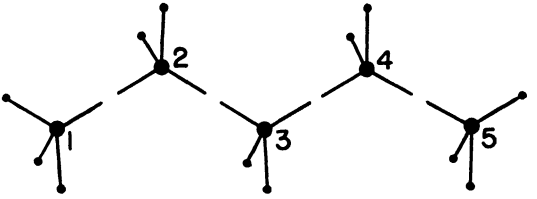


FIGURE 12 5. Pentane, zigzag pattern.
CH_3–CH_2–CH_2–CH_2–CH_3

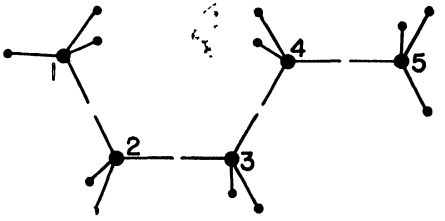


FIGURE 12 6. Pentane, meander pattern.

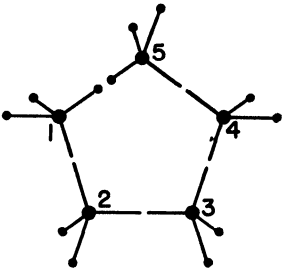


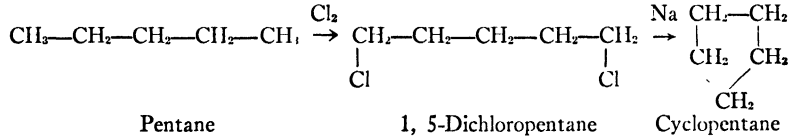
FIGURE 12.7. Pentane, ring pattern.

H atoms we obtain ethane (figure 12.3). Add another C atom to the chain to form propane (figure 12.4) and the chain develops quite an angle. And when we stretch the chain to the five-carbon compound (figure 12.5) several angles appear. This zigzag shape, which

we predict for a carbon chain on the basis of the tetrahedral carbon atom, has been proved by X-ray evidence to be the actual structure of chain hydrocarbons. This is discussed further in section 12.7.

In the crystals of the hydrocarbons, the atoms are frozen into fixed positions at definite valence angles, although the *molecules* may rotate at temperatures considerably below the melting point (section 13.12). In the liquid state, the molecules have complete freedom for rotation, but rotation of the atoms around the valence bonds is still restricted. The zigzag pattern prevails until sufficient energy is introduced, as in a chemical reaction. For example, from the zigzag pattern of the C_5H_{12} molecule we can obtain the *meander* pattern by a simple rotation of the bond between atoms 2 and 3. (The name meander means that the chain takes a "winding" course.) When the pentane molecule is sufficiently agitated carbon atoms 1 and 5 can almost clasp hands, they are that close together. This nearly complete ring arrangement takes place by rotation between atoms 3 and 4.

As a matter of fact, these end carbon atoms do sometimes join up as we indicated in the last chapter when describing the formation of ring compounds:



Pentane 1, 5-Dichloropentane Cyclopentane

When these reactions leading to the formation of a ring compound were first described in the preceding chapter, it probably appeared to the reader that the organic chemist was forcing a chain of carbon atoms to do quite a little stretching in order to have it bend around far enough for both ends to meet.

12. 4. "Odd" Molecules and "Even" Molecules. The zigzag structure of chain molecules offers an explanation for a phenomenon which puzzled organic chemists for a long time.

If the student will turn back to table 10.2, he will find the melting points and boiling points of the first twelve normal, or straight-chain, hydrocarbons, beginning with methane and ending with dodecane. These melting points and boiling points are shown plotted in figure 12.8. It will be seen that the *boiling points* rise uniformly as the

length of the chain increases. The *melting points*, however, form two smooth curves; the data for "even" molecules fall on curve B, whereas the data for "odd" molecules fall on curve C.

In the solid state, the molecular structure is fixed. The two melting point curves, therefore, are probably due to the molecules forming

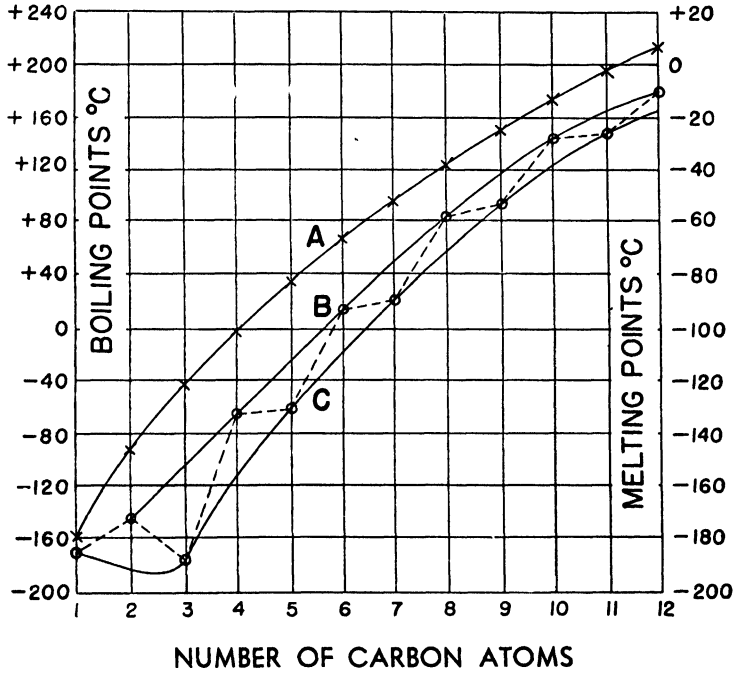


FIGURE 12.8. Melting points and boiling points of straight-chain hydrocarbons.
Curve A: Boiling points.
Curve B: Melting points of even molecules.
Curve C: Melting points of odd molecules.

one type of crystalline pattern when there is an *even* number of carbon atoms in the chain, and a different pattern when there is an *odd* number of carbon atoms. A reasonable explanation of this phenomenon pictures a five-carbon molecule and a six-carbon molecule in this way,

in order to indicate the direction of the attractive forces (review van der Waals forces in section 8.9) which hold molecules together in the

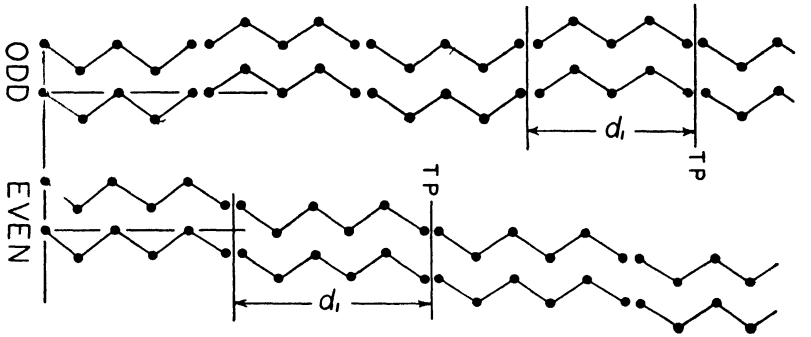


FIGURE 12.9. Layers of hydrocarbon molecules with odd and even numbers of carbon atoms in the chain. The molecules are perpendicular to the terminal planes (T.P.).

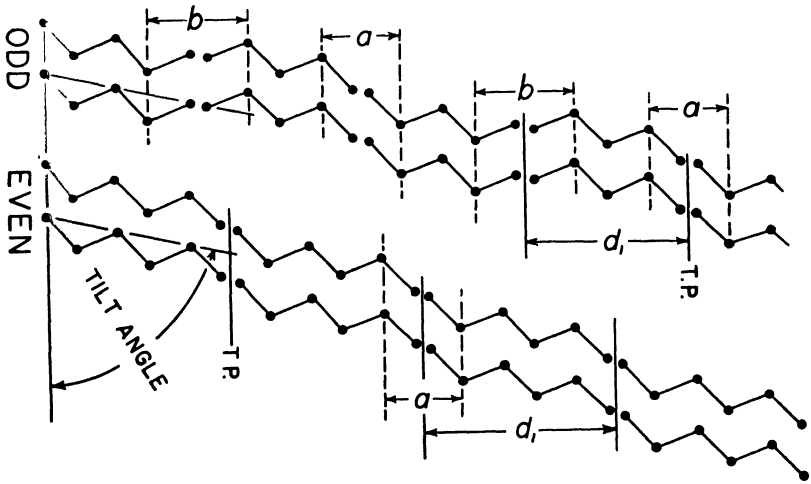


FIGURE 12.10. Layers of hydrocarbon molecules with odd and even numbers of carbon atoms in the chains. The molecules are tilted to the terminal planes (T.P.).

crystal state. The arrows do not indicate the presence of dipoles; hydrocarbons have no dipole moment.

The forces in crystals tend to produce greatest symmetry. The odd and even molecules may thus be expected to align as shown in figure 12.9. In this figure, it is obvious that the odd molecules follow a straight line set up by the first molecule, whereas the even molecules fall away from this line in a step-wise fashion. However, all molecules in figure 12.9 are *perpendicular to the terminal plane,* labeled *T.P.* The distance between terminal planes is d_1, which can be determined by X-ray methods since these are reflecting planes. For paraffin hydrocarbons, the terminal planes consist of CH_3 groups. If the chain is lengthened by inserting a CH_2 group the d_1 spacing increases regularly and at the same rate for both odd and even molecules.

Figure 12.10 shows the behavior to be expected if the molecules are *tilted to the terminal planes* (*T.P.*). The terminal groups uniformly occupy a distance designated *a* in the even chains, but in the odd chains, the terminal groups in alternate planes require a larger distance *b*. When the chains are tilted, the alternate terminal planes of odd chains are less closely packed. The odd-chain compounds are less stable than the even and melt at lower temperatures, as shown in figure 12.8.

From this discussion it is evident that the alternation of properties in a series of compounds depends not only on the zigzag nature of the hydrocarbon chain, but also on whether the chain is tilted to the terminal planes as in figure 12.10. The perpendicular chains of figure 12.9 do not show alternation behavior. A notable example of the alternation of properties pictured in figure 12.8 is the series of straight-chain acids in table 31.3, where most of the even molecules have higher melting points than the next higher members of the series with odd numbers of carbon atoms.

The boiling points in a series of compounds, such as those in figure 12.8 (Curve A), show no unusual behavior. They fall on a smooth curve because of the freedom of motion of molecules in the liquid state.

12. 5. Helical Chains. The reader may refer at this point to section 46.4 where it is shown that long chains in certain giant molecules, such as starch, may be forced into the corkscrew configuration known as a helical chain.

12. 6. The Strain Theory for Ring Compounds. In 1885, Baeyer drew attention to a phenomenon we described earlier in the chapter, namely, that the first and fifth carbon atoms in a chain can presumably unite to form a ring without any strain (section 12.3). He also pointed out that some strain is probably set up when ring compounds are formed with a number of carbon atoms other than five.

We showed in figure 12.2 that in a normal tetrahedral carbon atom, the angle between valence bonds is close to 110° (actually

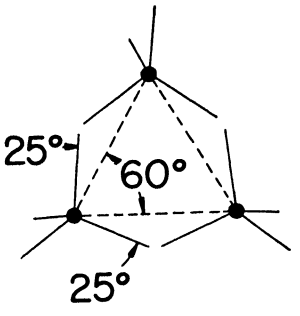


FIGURE 12.11. Illustration of strain in a three-carbon ring.

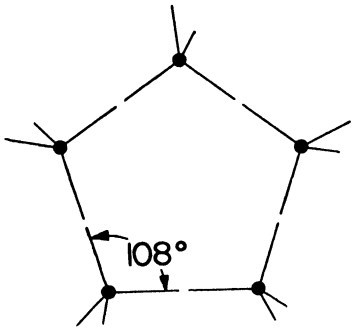


FIGURE 12.12. Illustration of absence of strain in a five-carbon ring (but see section 12.7).

109°28′). Figure 12.11 shows how the valence bonds must be bent away from this usual angle, when there are only three atoms in the ring, in order to form a straight-line union between the carbon atoms.

TABLE 12.1. DATA ON THE BAEYER STRAIN THEORY

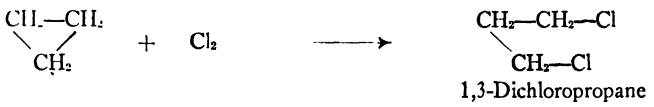
Number of Carbon Atoms in the Ring	*Strain Angle Between Bonds*	
3	24° 44′	
4	9° 44′	
5	0° 44′	
6	—5° 16′	In these cases, the bonds must be bent outward in order to form straight lines between C atoms.
7	—9° 35′	
8	—12° 46′	
9	—15° 16′	

In figure 12.12 the five-membered ring is formed with hardly any strain.

Baeyer proposed the theory that the stability of a ring compound is dependent on the angle through which the valence bonds must be bent in order to make a straight-line bond. This strain for the compound C_3H_6 is close to 25°, but for C_5H_{10} it is less than 1°;

consequently, the second compound is more stable. The calculated tension on the valence bonds in rings of various sizes is shown in table 12.1.

There is a good application of the strain theory in the study of the chemical properties of the cycloparaffin hydrocarbons. For example, in the case of cyclopropane, CH_2–CH_2–CH_2, we have a preconceived idea as to what chemical properties to expect based on what we learned in chapter 10. In the earlier chapter, we found that the H atoms in CH_2 groups are generally easily replaced by Cl or Br atoms. When cyclopropane is treated with chlorine, the substitution takes place, but the ring also tends to open (on account of the strain) and form an open-chain compound:



1,3-Dichloropropane

In this case, the C—C bond breaks, and the two Cl atoms *add on* to the molecule at the point where the ring is fractured.

This is one of the few instances in which it is not difficult to break the C—C bond (see section 10.1). It is very difficult, however, to break the ring of five carbon atoms.

12. 7. Crumpled Rings. The Baeyer strain theory now has more historical than practical interest, but this historical perspective gives us a better understanding of current theories based on modern technics and measurements which will be discussed in the next chapter.

If cyclohexane, C_6H_{12} (the six-carbon ring), is built up from atom models according to the Baeyer principle it will appear, as in figure 12.13, with all the carbon atoms in one plane. Instead of linking the C atoms with the usual wood pegs, which are struck into them at the tetrahedral angle of 109°28′, it is necessary to use springs to complete the ring. (The hydrogen atoms which should appear on the ends of the wood pegs are omitted in the picture for clarity.) The use of springs illustrates the old conception shown in table 12.1 that, with the C atoms in one plane, a strain results if there are more or less than five atoms in the ring.

There is now considerable proof that C_6H_{12} is not a planar structure but has the arrangement shown in figure 12.15, which is known as a *puckered, buckled,* or *crumpled* ring. This crumpling is due to

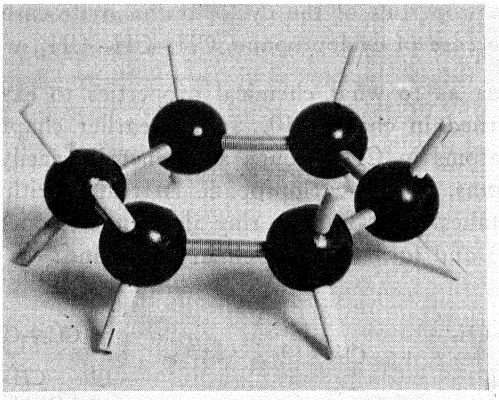


FIGURE 12.13. Cyclohexane.
Planar form.

repulsion forces set up by the hydrogen atoms. In figure 12.13, the H atoms would be as close as possible to each other; because of mutual repulsion, the adjacent $-CH_2-$ groups rotate about the bonds joining the carbon atoms until the H atoms are as far apart as

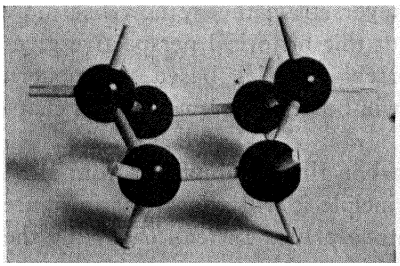


FIGURE 12.14. Cyclohexane.
Cis form, also known as the *boat* form and *tub* form.

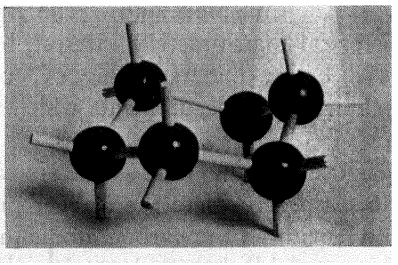


FIGURE 12.15. Cyclohexane.
Trans form, also known as the *chair* form.

possible, as in figure 12.15. This rotation of *adjacent* $-CH_2-$ groups with respect to each other is 60°, that is, each rotates 30° from the plane shown in figure 12.13. From theoretical considerations, there-

fore, the *cis* form shown in figure 12.14 should be less stable than the *trans* form in figure 12.15. Although the evidence shows that cyclohexane is *trans,* the *cis* form has only a slightly smaller stability, and the *cis* type of structure is conceivably present in certain compounds (see *decalin,* section 36.5).

Now we can return to the zigzag structure of an open-chain paraffin hydrocarbon, such as that in figure 12.5, which shows the CH_2 groups (carbon atoms marked 2, 3, and 4) in certain fixed positions. Until very recently it was understood that the CH_2 groups could freely rotate on the C–C bonds (such as between 2 and 3) but now it is known that because of repulsion forces between H atoms this *rotation is restricted.* In their most stable positions, adjacent $-CH_2-$ groups are rotated 60° with respect to each other, just as in *trans* cyclohexane (figure 12.15).

From the preceding paragraph, it will be seen that cyclohexane has stability equivalent to that of an open-chain hydrocarbon (the CH_2 groups rotated 60°). Cyclohexane is free from strain and is the most stable of the cyclic paraffin hydrocarbons, contrary to the data in table 12.1. Furthermore, cyclopentane does not have the flat structure shown in figure 12.12; it must crumple due to repulsion by the hydrogen atoms. Cyclopentane and other cycloparaffins will be less stable than cyclohexane for one or two reasons, namely, the angles between carbon atoms will not be exactly tetrahedral (angular strain), or, the angle of rotation of the $-CH_2-$ groups with respect to each other about the C–C bond will not be exactly 60° (torsional strain).

12. 8. Large Rings. For many years, no ring compounds containing more than six carbon atoms had been discovered in living nature, and no ring compound containing more than nine carbon atoms had been prepared in the laboratory. It was felt that the absence of large rings was due to excessive strain. In 1920–1930, however, large ring compounds containing seventeen and eighteen carbon atoms were recognized in nature (see section 36.1) and, in recent years, cycloparaffins, containing more than thirty carbon atoms in the ring, have been prepared in the laboratory. These large rings are quite stable, contrary to the Baeyer strain theory, and it is believed they are crumpled rings.

It should not be supposed that the mere act of crumpling a ring of carbon atoms leads automatically to a structure free from strain. We must consider the space available for the atoms attached to carbon, for these atoms may have so little room that it will be difficult to form the ring at all. This is illustrated by the model (figure 12.16) of cyclononane, C_9H_{18}, which is shown with the H atoms

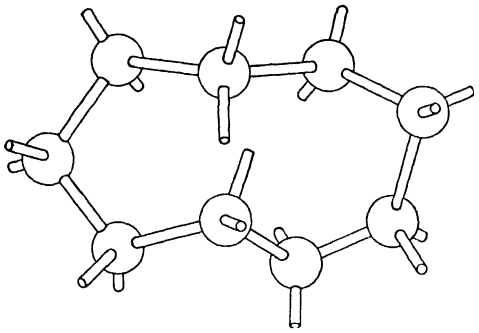


FIGURE 12.16. Arrangement of carbon atoms in cyclononane, C_9H_{18}. One of several possible configurations, in all of which crumpling of the ring takes place.

omitted in order to make the picture clear, but with the valence bonds shown attached to the carbon atoms. It will be seen that when carbon atoms are tied into a nine-membered ring some of the valence bonds on the carbon atoms are twisted in toward the center. The H atoms on these bonds have very little space available in the center of this crumpled ring and there is considerable mutual repulsion and thus a certain amount of strain. This cause of strain, however, is different from that assumed by the Baeyer theory, which pictures rings in which all the carbon atoms are in one plane.

Rings with about fifteen carbon atoms in the cycle are much roomier than the nine-membered ring shown in figure 12.16 and the strain is quite small for these large rings. The very large rings probably have the shape of a circle that has been pulled out to resemble a flattened rubber band. A large ring behaves like two long zigzag chains lying parallel to each other and joined at the ends.

In concluding these remarks on ring compounds, it must be emphasized that the *relative ease of formation* of a carbon ring is not nec-

essarily the same as its *relative stability*. Ease of formation of a ring depends largely on the probability of the end carbon atoms in a chain coming close together, and this probability is very great in a five-membered ring as we have already pointed out in section 12.3.

Once a thirty-membered ring has been formed, however, it may be nearly as stable as a five-membered ring, even though it may have been harder to prepare because of the smaller probability of the end carbon atoms approaching each other.

13. ENERGY AND MOLECULAR STRUCTURE

13. 1. Introduction. The inquiring reader will want to know how it was possible to arrive at some of the conclusions on molecular structure which are indicated by the models of molecules shown in the preceding chapters. Some of the reasoning was given in chapter 8. The further explanations in this chapter belong, perhaps, in the domain of the physical chemist, but the organic chemist can easily afford to read a few pages on such an important aspect of his science. The continuity of this book will not be lost, however, if the reader prefers to skip this chapter and remain aloof in the domain of "pure" organic chemistry.

In order to obtain a real understanding of the theories involved we must review some of the elementary principles of physics. Fortunately, those principles which we make use of are easy to comprehend and even the mathematical equations are quite simple, although it must be admitted that considerable genius was required to put these ideas into expressions which nonmathematical chemists can employ.

13. 2. Energy. When a body is in motion it has a certain amount of energy due to its motion. This is called kinetic energy and is labeled E_k. A body, like a stretched rubber band, has potential energy, E_p, equivalent to the kinetic energy required to put it in the configuration which prevails at a certain instant. This will be discussed later in section 13.10.

Motion in a straight line is referred to in scientific literature as translational motion; consequently, kinetic energy due to straight-line motion is called translational energy, E_{tr}.

The body may also have kinetic energy due to its rotation around one or more axes, like a spinning top; this energy is E_r.

If the body is in constant vibration, like a tuning fork, the energy of vibration is designated E_v. It will be explained later (section 13.7) that energy of vibration consists not only of kinetic energy but also of potential energy.

The total energy, E, is obtained from the equation

$$E = E_{tr} + E_r + E_v$$

Every molecule has structure and occupies space. A molecule like hydrogen, for example, can be represented by a dumbbell like that in figure 13.3*b*, which can move off into space in straight lines in any direction, can rotate on its axis, and can vibrate as if the atoms were held by a rubber band being alternately stretched and relaxed.

Much information with regard to the structure of a molecule can be found by a study of the distribution of its energy among the three types of energy. We shall first discuss E_{tr} rather fully in order to develop the basic line of thought with the simplest of the phenomena. The observations on E_r and E_v will be deferred to sections 13.6 and 13.7.

13. 3. Translational Energy. In order to determine the relation between molecular structure and energy of the molecule, we begin a study of gases in which the hypothetical molecules have no structure at all. The student will recall that this is the kind of molecule employed in developing the kinetic theory of gases, which assumes that molecules are simply "points" in space, that they have no attractive forces, are perfectly elastic, and have only translational motion. After studying this "ideal" gas, we shall return to gases in which the molecules are "real."

We may also recall the *ideal gas law*, a combination of the laws of Boyle and Charles,

$$\frac{PV}{T} = R \qquad \text{or,} \qquad PV = RT \qquad (13.1)$$

where R is a constant which, for 1 mole of gas, shows the relationship of the volume V, the pressure P, and the temperature T in degrees

Kelvin. The constant R can be evaluated in terms of heat energy and is 1.987 calories per mole per degree, but for most purposes, it can be said that R=2 cal./mole/deg. The units of R will be defined in section 13.4.

In any elementary text on physical chemistry we can find another simple equation involving the PV product; it is obtained from the fundamental assumptions given in the first paragraph of this section about the hypothetical "point" molecule, which has only translational energy, E_{tr}. This "kinetic theory" equation is

$$PV = \tfrac{2}{3}E_{tr} \qquad \text{per mole of ideal gas} \qquad (13.2)$$

By combining equations 13.1 and 13.2, we obtain for 1 mole of ideal gas

$$\tfrac{2}{3}E_{tr} = RT, \qquad or \qquad E_{tr} = 3 \times \tfrac{1}{2}RT \qquad (13.3)$$

At the temperature of 27°C. (T=300°K.), the kinetic energy of a mole of ideal gas due to its translational motion is

$$E_{tr} = 3 \times \tfrac{1}{2} \times 2 \times 300 = 900 \text{ calories}$$

This kinetic theory leads to the conclusion that at –273°C. (T = 0°K.) the value of E_{tr} is zero. That is, there would be no translational motion at the absolute zero of temperature (but see remarks in section 13.13*d* on the zero-point energy due to vibrational motion).

13. 4. Molar Heat Capacity of Gases. When heat energy is added to a confined gas, various mechanical disturbances take place in the gas molecules. The nature and extent of these disturbances control the amount of heat energy that can be absorbed. Our hypothetical "point" molecule can move only in straight lines; it is, therefore, limited in the amount of heat energy it can absorb. More complex molecules, which have rotational and vibrational motions, can absorb more energy than a "point" molecule under the same conditions.

The amount of heat, in calories, required to raise the temperature of one molar weight of a gas through a temperature interval of 1°C. (or 1°K.) is called the molar heat capacity.

If the experiment is done with the sample at constant volume the heat capacity is labeled C_v. If the gas is contained in a vessel maintained at constant pressure, so that the sample can expand while

being heated, the resulting heat capacity will be greater and is called the molar heat capacity at constant pressure, C_p. In this book we shall consider only C_v.

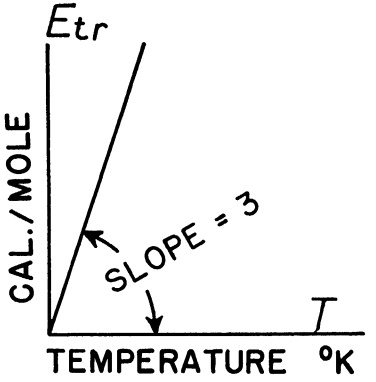


FIGURE 13.1. Graph of equation 13.3, based on the kinetic theory.

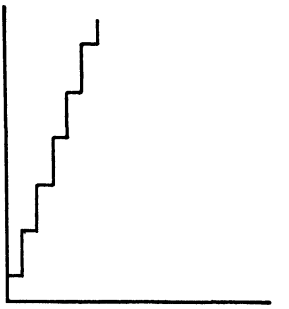
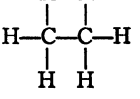


FIGURE 13.2. The equation in figure 13.1, interpreted by the quantum theory (sec section 13.13*b*). *The "steps" are greatly exaggerated.*

Equation 13.3 applies to an ideal gas consisting of "point" molecules. If the temperature of 1 mole of such a gas is raised 1°, it can be calculated from equation 13.3 that the energy due to its more

TABLE 13.1. MOLAR HEAT CAPACITIES OF GASES AT 15°C.

Atoms per Molecule	*Name*	*Formula*	C_v *in cal./mole/deg.*	*Degrees of Freedom at 15°C.*
1	Helium	He	2.98	3
1	Mercury vapor	Hg	2.98	3
2	Hydrogen*	H—H	4 83	5
2	Hydrogen chloride*	H—Cl	4.99	5
3	Carbon dioxide**	O=C=O	6.71	7
8	Ethane**		9.51	-

*See section 13.6. **See section 13.8.

rapid motion is increased to the extent of 3 calories (since R=2, and T=1). The relation is illustrated graphically in figure 13.1, which shows that the translational energy E_{tr} is increased by 3 cal./mole

for a rise in temperature of 1°. At the absolute zero of temperature the E_{tr} value would be zero, as already mentioned. The slope of the straight line is the heat capacity C_v.

This predicted value for an ideal gas of C_v=3 cal./mole/deg. very closely approximates the measured values for gases which are composed of molecules that resemble "point" molecules. Such gases are helium and mercury vapor, which are monatomic (table 13.1). It is apparent that energy supplied to these molecules serves only to

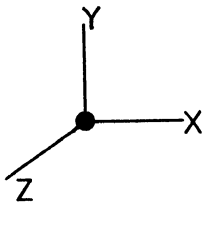


Figure 13.3*a*

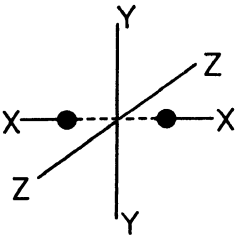


Figure 13.3*b*

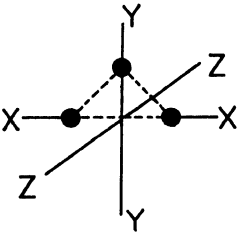


Figure 13.3*c*

FIGURE 13.3*a*. Monatomic molecule, or "point" molecule, with three degrees of translational freedom.

FIGURE 13.3*b*. Two degrees of rotational freedom around axes YY and ZZ for a rigid diatomic molecule (or any *linear* molecule). Total degrees of translational and rotational freedom = 5.

FIGURE 13 3*c*. Three degrees of rotational freedom around axes XX, YY, and ZZ for a rigid, nonlinear, triatomic molecule, such as water, $H\overset{O}{\diagup}H$. Total degrees of translational and rotational freedom = 6.

(Adapted from A. A. Michelson, *Studies in Optics*, University of Chicago Press, 1927.)

increase their translational velocity. For a monatomic gas, therefore, we can substitute for the total energy E the energy of translation E_{tr} and apply equation 13.3.

From table 13.1 it will be seen that the values of C_v for molecules containing more than one atom are greater than predicted by the kinetic theory. The energy required to raise the temperature of 1 mole of polyatomic gases 1° is used not only to increase translational velocity (kinetic energy of translation) but also to raise the energy of molecular rotation and possibly the energy of intramolecular vibration. It was explained in section 13.2 that $E=E_t+E_r+E_v$, and we

can substitute for E_{tr} its equivalent from equation 13.3 and state that

$E = (3 \times \frac{1}{2}RT + E_r + E_v)$ calories per mole, for any gas (13.4)

The student should observe that we have completed one-third of our program. We have found out how to calculate what part of the total energy, E, of a mole of gas is energy, E_{tr}, due to motion of the molecules in straight lines. This motion does not depend on the structure. We shall discuss the E_r and E_v contributions to total energy in sections 13.6 and 13.7, where it will be found that the structure of the molecules is all important.

13. 5. Equipartition of Energy. The motion of a "point" molecule, or of a monatonic molecule, can be represented by three components on axes at right angles to each other, as shown in figure 13.3*a*. The average value of the X component is one-third of the total, and the same is true of the Y and Z components. The total energy of translational motion, from equation 13.3, is $3 \times \frac{1}{2}RT$ calories per mole; each component is equivalent to one-third of this, or $\frac{1}{2}RT$ calories per mole.

A monatomic molecule is said to have three *degrees of freedom* because its motion can be defined by three variables. According to the principle of the equipartition of energy, the total energy is divided equally among these degrees of freedom.

13. 6. Rotational Energy. A diatomic molecule, like H–Cl, is assumed in the discussion in this section to have a rigid dumbbell structure. Since the entire molecule is in translatory motion it has the three degrees of freedom associated with such motion, each of which contributes $\frac{1}{2}RT$ calories per mole to the total energy as just described in section 13.5. In addition, the molecule has energy of rotation (E_r); it can rotate (tumble) about the axes YY or ZZ shown in figure 13.3*b*, so that it has two additional degrees of freedom, a total of five. By the principle of equipartition of energy, each degree of freedom contributes $\frac{1}{2}RT$ calories per mole of energy:

$E = E_{tr} + E_r = (3 \times \frac{1}{2}RT + 2 \times \frac{1}{2}RT) = 5 \times \frac{1}{2}RT$ calories per mole

Now the molar heat capacity (C_v) is the change in energy per degree, and $R = 2$, so that with T equal to unity, we have for the diatomic molecule

C_v(trans. + rot.) $= (3 \times \frac{1}{2}R + 2 \times \frac{1}{2}R) = 5$ cal./mole/degree

This is the experimental value found for diatomic molecules as shown by the data in table 13.1. The possible rotation (spin) around an axis parallel to the bond joining the two atoms in a diatomic molecule is associated with negligible energy requirements.

13. 7. Vibrational Energy. We can consider the atoms in a molecule as separate entities held together by an elastic bond. At a certain temperature (which depends on the molecule) the atoms are displaced with respect to each other, with a consequent restoring force, and vibration at characteristic frequencies sets in. This absorbs energy, so that C_v at a certain temperature rises above 5 cal./mole/degree.

The *act of displacement* of the atoms represents the kinetic energy factor in the oscillation and this constitutes one degree of freedom. The *degree of separation* of the atoms in an oscillation represents a potential energy change (see section 13.10) which is equal to the change in kinetic energy, so that it is equivalent to a second degree of freedom. Each of these degrees of freedom absorbs $\frac{1}{2}RT$ calories per mole, so that vibrational energy is equal to twice this value, or RT cal. per mole. It is convenient to indicate a vibration by the symbol $\rightleftarrows$ in order to keep in mind that such vibration in any one direction is equal to two degrees of freedom. At high temperatures, then, we can have a total of seven degrees of freedom in a diatomic molecule,

$$E = E_t + E_r + E_v = 3 \times \tfrac{1}{2}RT + 2 \times \tfrac{1}{2}RT + 2 \times \tfrac{1}{2}RT$$
$$= 7 \times \tfrac{1}{2}RT \text{ cal. per mole}$$

and the molar heat capacity is

C_v (trans. + rot. + vib.) $= 7 \times \frac{1}{2}R = 7$ cal. per mole per degree.

For hydrogen chloride and chlorine, the values of C_v at different temperatures are as follows:

	0°	100°	200°	500°	1200°	2000°C.
HCl	5.00	5.09	5.27	5.46	6.13	6.9
Cl_2	5.95	6.3	6.7	6.9	7.1	7.2

13. 8. Modes of Vibration. Any linear molecule should have the general characteristics described for a diatomic molecule, as to the three types of translational freedom and two types of rotational freedom. Such a linear molecule is carbon dioxide (figure 8.4).

When referring to vibration of the atoms, the possible motions are called modes of vibration.

Each atom in a molecule considered by itself has three degrees of freedom; if there are n atoms there are $3n$ degrees of freedom. However, if the molecule is diatomic or linear it has five degrees of freedom due to *translation* and *rotation,* so that if we subtract these five degrees of freedom from the total number possible, the modes of *vibrational* freedom are $(3n-5)$. Each mode of vibration is equivalent to RT cal. per mole as explained in section 13.7. For H–Cl, with its two atoms, there is only one mode of vibration $(3n-5=6-5)$; this can be pictured as the knobs of a dumbbell oscillating on the line which joins them. For O=C=O, we can similarly calculate that there are four modes of vibration. One mode can be pictured as the oscillation of the terminal oxygen atoms toward the carbon; another may be the oscillation of the carbon atom perpendicular to the line joining the three atoms.

Since a nonlinear molecule (figure 13.3*c*) has six degrees of freedom due to translation and rotation, the possible modes of vibration it may have are $3n-6$. For the nonlinear H–O–H molecule, which is shown in figure 8.5, the formula $3n-6$ yields $3 \times 3-6=3$ possible modes of vibration. The total energy of the gas at high temperatures can be calculated from

$$E_{tr} = 3\times\tfrac{1}{2}RT \qquad E_r = 3\times\tfrac{1}{2}RT \qquad E_v = 3\times RT$$

which gives an E value (since $R = 2$) of $12T$ calories. The maximum molar heat capacity C_v is then 12 cal./mole/deg.

Ethane is a nonlinear molecule (table 13.1 and figure 13.7); the maximum value for its heat capacity at high temperatures should be close to 42 cal./mole/deg., based on the reasoning in this section. In such more complex molecules, other factors, such as internal rotation about the bond in the molecule (section 13.11 and 13.16) will alter this calculated value somewhat and also the molecule may decompose at certain high temperatures before the maximum possible C_v is reached.

13. 9. Heat Capacity and Temperature. Only energy which varies with temperature can affect the heat capacity; this follows from the definition in section 13.4. In the case of translational energy, the

variation with temperature is constant, as indicated in figure 13.1 and in equation 13.3, which can be written $E_t = 3T$ since R is equal to 2 cal./mole/deg. In other words, for every rise in temperature of one degree the translational energy increases by three calories. This holds for the ideal gas and for monatomic gases. In figure 13.4 this constancy is shown by the horizontal line labeled translation.

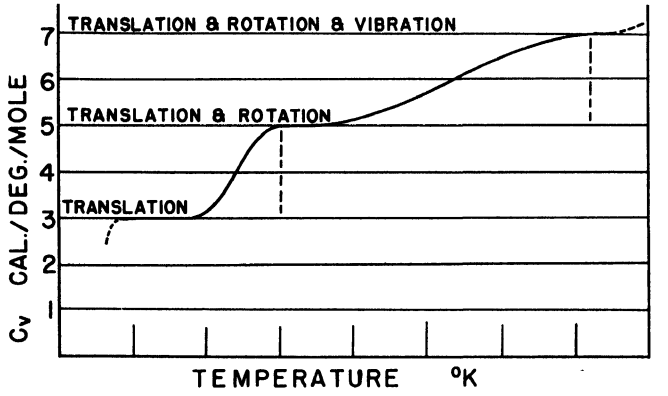


FIGURE 13.4. Effect of temperature on molar heat capacity at constant volume of simple gases. Vertical broken lines are required by classical theory. Slant curves are experimentally found, and predictable by quantum theory. The positions of the vertical lines and of the curves are purely schematic, not data for any one compound.

It has been shown in this chapter that, when a molecule with more than one atom in it absorbs energy, there is an increase not only in translational energy but also in rotational energy. However, according to old established theory, which is now called "classical" theory, diatomic gaseous molecules, like H–H, should not rotate until they have acquired a certain amount of translational energy. At some temperature, represented by the first vertical dotted line in figure 13.4, the molecules should have so much energy that they begin to rotate. The H_2 molecule, in fact, follows classical behavior up to about 50°K., showing a constant C_v of 3 cal./mole/deg. characteristic of a *point* molecule, but, instead of the C_v rising abruptly to 5 cal., experiment shows that there is a long, slow rise to that value. This slow change in C_v can be calculated by means of the "quantum" theory, and the

ability to predict curves such as shown in figure 13.4 was one of the early triumphs of the new theory.

The quantum theory will be discussed in section 13.13*a*, but it may be stated at this point that according to this theory a molecule absorbs energy in small units called *quanta*. This is shown schematically in figure 13.2, where the step-like line indicates absorption of energy in small increments. These quantum increments, however, are so small in the case of translational energy (see section 13.13*b*) that, for practical purposes, translational energy is said to be absorbed continuously, that is, classically, as shown in figure 13.1.

Rotational energy quanta are larger than those of translational energy, but are still small enough so that at ordinary temperatures many molecules have such quanta; the result is the slant curve from the three to five levels in figure 13.4. Vibrational energy quanta, however, are so large that at ordinary temperatures very few molecules have acquired them. For this reason, most diatomic molecules have C_v values of about 5 cal./mole/degree at ordinary temperatures (translational and rotational motion energy only). Vibrational quanta are absorbed gradually as the temperature is raised (since each unit is so large) accounting for the gradual rise in figure 13.4 from the five to seven level. This is also illustrated by the data for chlorine in section 13.7.

13. 10. Potential Energy. The energy of a body due to its position in space relative to another body is potential energy, E_p. It is instructive to compare the *force* and *potential energy* curves in figure 13.5 for a system of two atoms, one of which is at the origin O and the other at some distance d. Both atoms oscillate as compared to each other, but for convenience, we assume a reference atom as fixed. An attractive force which causes the second atom to fall toward the atom which is at the reference position O is assigned a negative value. A repulsive force which tends to separate the atoms is positive. At the equilibrium distance d_e the forces of attraction and repulsion are equal. It will be observed that at that distance of separation the potential energy of the system is at a minimum, marked M. Because of the shape of the curve, this is called the potential energy trough. Adding energy to the system will cause the second atom to oscillate over the distances marked by arrow heads (assuming the reference

atom fixed in position at *O*) until sufficient energy is introduced to separate the atoms to an "infinite" distance over which they no longer affect each other. Another way of looking at it is to consider the height of the "hump" in the force curve as the height of a barrier. If the atoms are close together, enough kinetic energy must be added to overcome the attractive force and carry the system over the hump.

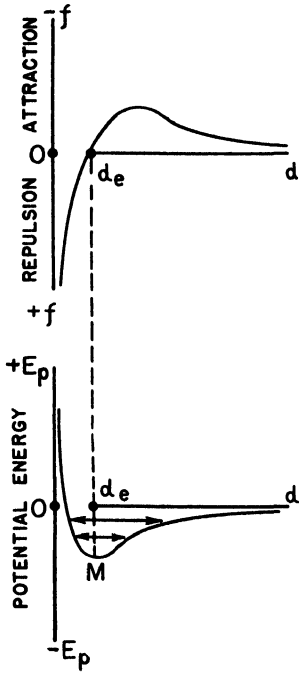


FIGURE 13.5. Forces between two atoms and the potential energy trough between two atoms. (Adapted from R. Houwink, *Elastomers and Plastomers, Their Chemistry, Physics, and Technology. Vol. I-General Theory*, p. 195, Elsevier Publishing Co., Amsterdam and New York, 1950; and from R. Houwink, *Elasticity, Plasticity, and Structure of Matter*, p. 23, Cambridge University Press, New York, 1937.)

13. 11. Potential Energy Barrier. The literature of chemistry contains many references to phenomena involving an energy barrier which can be understood by reference to a potential energy trough, such as that in figure 13.5. For an illustration we may refer to the model of ethane in figure 13.6, which pictures the corresponding hydrogen atoms, on the two carbon atoms, directly opposite each other. There is a mutual repulsion by the hydrogen atoms which causes a rotation of 60° about the C–C bond to give the configuration of figure 13.7 (which is also apparent in the zigzag structures

of figures 12.4 and 12.5). The potential energy of ethane is at a minimum when the hydrogen atoms of one methyl group are opposite the *spaces* between hydrogen atoms of the other methyl group.

Rotation about the C–C bond in ethane is not "free." Energy, the amount of which can be represented by the height of the line from M to d_e in figure 13.5 is required to cause the methyl groups

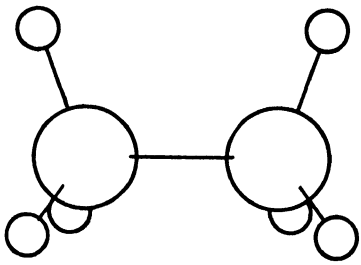


FIGURE 13.6. The ethane molecule (CH_3—CH_3) at maximum potential energy with respect to the methyl groups.

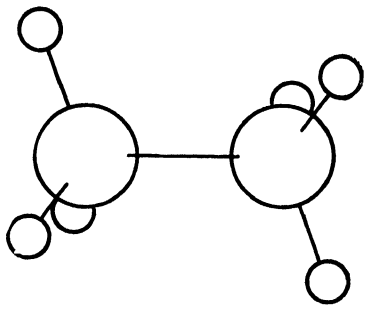


FIGURE 13.7. The ethane molecule (CH_3—CH_3) at minimum potential energy with respect to the methyl group

to rotate from the position in figure 13.6 to that in figure 13.7. (To make figure 13.5 more representative of this phenomenon, the distance on axis *O-d* may be considered to be a measure of angular rotation of the methyl group.) The methyl groups oscillate about the position of minimum potential energy but hindrance to free rotation is great enough at room temperature so that only a few molecules have sufficient energy to rotate past the position of maximum potential energy. The "height of the barrier" for free rotation in ethane is about 3,150 calories per mole; this is much higher than the RT value of 900 cal./mole calculated for a temperature of 27°C. in section 13.3, and explains why most of the molecules are in the potential energy trough. The method of estimating the height of the barrier is briefly described in section 13.16. Once the ethane molecule passes the configuration in figure 13.7, it runs into the barrier again, so that figure 13.5 is not strictly applicable; it should be modified to show a succession of energy troughs at 60° intervals.

The reader should review section 12.7 where it was explained that *trans*-cyclohexane is more stable than the *cis* form. There is a re-

stricting potential (energy barrier) which tends to keep the molecule *trans*, and the effect is large enough to be found through its contribution to the heat capacity of the substance.

13. 12. Heat Capacity of Solids and Liquids. In order to complete the study of heat capacity which is summed up for gases in figure 13.4, a few brief remarks are in order with respect to solids and liquids. The molecules in most crystals are restricted to only one type of molecular motion, that is, *vibration* about equilibrium positions of minimum potential energy. Consider crystals of metals, which consist of atomic molecules capable of vibratory motion in all directions. These motions can be resolved along three axes, in a manner similar to that shown in figure 13.3*a*. The molecules in a crystal can, therefore, be said to have three modes of vibration.

Since it was shown in section 13.7 that each mode of vibration is equal to RT calories per mole, the solid ideal element in crystal form should have an energy content at any temperature of 3 RT calories per gram-atom, and the value of C_v should be $3\times2\times1=6$ cal./gram-atom/degree. This agrees roughly with the empirical rule of Dulong and Petit that the atomic heat capacities of solid elements (with certain exceptions) are about 6.4 cal./degree at ordinary temperatures, the agreement being more satisfactory if the measured value is corrected to constant-volume conditions.

The principle of equipartition of energy, which predicts the heat capacity of solids at ordinary temperatures as explained in the preceding paragraph, does not hold at low temperatures, for the C_v of all solids approaches zero at the absolute zero (0°K.). The theory required to explain this was introduced by Einstein in 1907, who applied the quantum theory in the form of an equation involving a fixed vibration frequency (section 13.13*a*) of the atoms in the crystal lattice. Calculation of C_v by this quantum theory equation gives reasonable values at temperatures close to 0°K. and the equation reduces to classical theory (C_v=3R) at high temperatures.

The Einstein equation was improved in 1912 by Debye, who assumed a variable vibration frequency and showed that C_v is a function of T/θ where θ is related to the maximum vibration frequency, but has dimensions of temperature. The Debye constant θ is known as the *characteristic temperature* of the element. It can be determined

by means of a single heat-capacity measurement and can then be used in a complex (Debye) equation to calculate the value of C_v for the solid element over a wide range of temperatures. Tables of characteristic temperatures for many elements have been prepared, and the Debye calculation is used to extrapolate heat capacities to the absolute zero from measurements made below about 30°K., that is, at temperatures below $\theta/10$. In order to obtain the molar heat capacity of a crystalline compound, the Debye equation is used to calculate the heat capacity per gram-atom, and this is multiplied by the number of atoms in the molecule. Valence forces must also be considered in these calculations, which apply to only a few simple compounds.

As already stated, the molecules in most crystals can only vibrate. In some crystalline compounds, however, the molecules are in "swinging" oscillatory motion (a better word is *libration,* which should be looked up in a dictionary) at low temperatures, but are not able to rotate freely because of the restrictive forces exerted by neighboring molecules. At a sharply defined temperature, sufficient rotational energy quanta are acquired by the molecules to enable them to begin free rotation in the solid phase. The melting point of 1,1,1-trichloroethane (CH_3–CCl_3) is 240°K., but from heat capacity measurements it was found that the molecules start to rotate in the solid phase at 224.3°K. Rotation of benzene derivatives (table 19.1) and of a number of other compounds in the solid phase has been observed. The onset of rotation is accompanied by a decrease in density; the molecules need more room in which to rotate. From this review, it is clear that vibrational and rotational motions are possible in solids, but there is no translatory motion.

Thermal effects on molecular motions of an ideal gas and of crystalline solids are now well understood, but this is not quite so true of the liquid state. At low temperatures, the motion is mostly vibrational and rotational as in the solid state and at high temperatures, it also becomes translatory. Molar heats of liquids at high temperatures approximate those of corresponding gases.

13. 13. Molecular Structure and the Spectrum. The discussion of heat capacity in this chapter has led to the study of translational, rotational, and vibrational motions of molecules and of the atoms in

molecules. No mention was made of electronic disturbances because the energy required to alter electronic motions is so great that usually it does not appear in ordinary heat-capacity measurements. However, we found that quantum theory plays an important part in explaining absorption of energy by molecules, and a brief description of this theory is made easy by reference to the electronic structure of the atom.

13. 13a. Quantum Theory. In section 7.1 it was stated that the electrons in an atom rotate around the nucleus in orbits corresponding to certain energy levels. When the electrons are in their assigned orbits the atom is in its "ground" state, but the atom is said to be in an "excited" state if an electron is sufficiently disturbed to rise to a larger orbit (higher energy level). The energy levels in an atom are fixed; the electron will not jump to its new orbit unless enough energy is supplied for it to reach the new level. This absorption of energy corresponds to a line in the absorption spectrum of the atom. If the electron falls back to a lower energy level, a corresponding line will appear in the emission spectrum. The energies of the various levels are proportional to $1/n^2$, where n is said to be the quantum number. The quantum numbers are small whole numbers, that is, 0,1,2,3,4, etc. In the level where $n=2$ the energy is one-fourth that in the level for which $n=1$.

When the cause of excitement has passed and the electron falls back into its original orbit, it liberates the energy (by radiation) which it acquired when it became excited. It liberates a quantum of energy, the numerical value of which can be calculated from

$$\varepsilon = h\nu \qquad (13.5)$$

where h is a universal constant known as Planck's constant, and ν is the vibration frequency of the energy which is radiated. The wave length λ of the radiation is obtainable from the equation

$$\lambda = \frac{c}{\nu} \qquad (13.6)$$

where c is the velocity of light (3×10^{10} cm. per sec.). If all the particles in a gram-atom or a gram-mole of substance are radiating

energy, the total energy is equal to Nhv, where N is the Avogadro number (see footnotes to table 13.2).

Since h is a constant, it is apparent from equation 13.5 that the size of an energy quantum depends on the vibration frequency of the radiation (or on the wavelength). From table 13.2, it will be seen that the quantum associated with comparatively long (radio) waves is small, but that the X-ray quantum is tremendously large. The outer electrons in an atom are relatively loosely held by the electrostatic attraction of the nucleus and are associated with relatively small quanta of energy. The inner electrons, which are tightly held by the nucleus, require quanta of high energy content to disturb them.

TABLE 13 2. RELATION BETWEEN WAVELENGTH AND ENERGY

Nature of radiation	*Wavelength in Angstroms* *	*Radiation frequency, cycles/sec.* **	*Energy in calories per mole of quanta* ***	*Effect on molecule*
Radio	> 10^8 (1 cm.)	3×10^{10}	2.858	Rotation
Infrared	2,000,000	1.5×10^{12}	142.9	Rotation
	500,000	6×10^{12}	571.6	Rotation and
	10,000	3×10^{14}	28,580	vibration
Visible	8,000			
	7,000	4.29×10^{14}	40,840	Outer electron
	4,000			displacement
Ultraviolet	3,000	1×10^{15}	95,270	Outer electron
	2,536.7	—	112,000	displacement
X-rays	100			
	1	3×10^{18}	2.86×10^{8}	Inner electron
	0.01			displacement
Nuclear	< 0.01			

* An average molecular diameter is about 3 to 10 A (Angstrom) units.

** The symbol for wavelength is λ. The frequency unit used by spectroscopists is generally $cm.^{-1}$ ($=1/\lambda$ cm.). Other conversion units are 1 A$=10^{-8}$ cm., and 1 μ = 10,000 A. The wavelength region most thoroughly studied with respect to molecular motion (vibration) is 2.5μ to 25μ

*** The amount of the quantum in calories can be obtained by dividing these data by the Avogadro number ($N=6.02\times10^{23}$), the number of molecules in one mole.

Chemical reactions take place through disturbance of the external (valence) electrons. The energy of visible light is sufficient, in many cases, to excite these electrons. The wavelength of 2536.7 A in table 13.2 is one of those radiated by incandescent mercury atoms. The energy of this radiation is more than enough to dissociate hydrogen

molecules, in which the valence bond is exceptionally strong, as shown in table 17.1.

The effects of translational motions of molecules cannot be detected spectroscopically. However, rotational, vibrational, and electronic motions give rise to characteristic absorption spectra consisting of bands and lines. This is discussed in the following section in some detail. (The student is also advised to read the opening pages of chapter 42 on dyes, in which absorption spectra are discussed.)

13. 13b. Quantum Theory and Translational Motion. Just as a person listening to music may be induced to tap his feet on the floor in unison with the music, if the music is "right," a molecule in translatory motion if subjected to radiant energy may be induced to accept the energy. Since energy (according to modern theory) is always radiated in small packages (quanta) this is the way they will be absorbed by the molecule; however, the quanta will not be accepted unless they are of the right magnitude for the molecule to assimilate.

The ideal gas law, which we reviewed in section 13.3, applies to a *gram-molecular weight* of substance, and we found that, from the equation $PV=RT$ for one mole of gas, we could proceed to an expression which indicates that the energy content is a function of RT. This is the classical-theory way of looking at things, and the RT product will be found in many equations derived by classical methods in texbooks of physical chemistry.

In quantum theory, however, attention is directed to the *individual* molecule, and in quantum-theory equations the product kT is more often found. The constant k is the Boltzmann constant, which can be calculated very simply from $k=R/N$ where N is the (Avogadro) number of molecules in a gram-mole.

The quantum level of energy of a molecule is generally represented by ε. Thus, ε_0 is the lowest permitted state of energy, called the zero-point energy, and ε_1, ε_2, etc., are the energy states at quantum levels, 1, 2, etc. The translational energy at any quantum level n (in any one direction as in figure 13.3a) is given by

$$\varepsilon_{tr} = \frac{n^2 h^2}{8ml^2} \qquad (13.7)$$

where h, as usual, is the Planck constant, m is the mass of the molecule, and l is the length of an edge of a cube holding the substance.

Now, the total translational energy content ε_{tr} of a molecule at any temperature T is equal to $3 \times \frac{1}{2}kT$ (by analogy to equation 13.3), but along any one axis, as shown in figure 13.3*a*, it is equal to $\frac{1}{2}kT$. We may compare this actual energy content of the molecule with the difference in energy levels from, say, quantum level 1 to quantum level 2. In equation 13.7, this means calculating ε_t, when $n=1$ and when $n=2$. It will be found that ε_t, is about 10^{17} times as big as the difference between the two quantum levels of ε_{tr}. In other words, not only are the quanta of translational energy rather small, but also the quantum levels are so closely spaced that absorption of such energy is apparently continuous and "classical." The effect is shown by the continuous straight line in figure 13.1, since the quantum steps in figure 13.2 are actually infinitesimally small.

Translational energy levels cannot be determined spectroscopically; the energy levels are so close that they would form a continuous band in a spectrum. In section 13.3, we found that the kinetic energy of translation of a mole of a gas at ordinary temperature is about 900 calories. Translational energy is sometimes called external energy, because it can do work, such as pushing a piston in an engine. It is also called thermal or heat energy. By contrast, the rotational and vibrational energies of a molecule are referred to as its internal energy.

13. 13c. Quantum Theory and Rotational Motion. Much larger quanta are required to affect the rotational motion than the translational motion of a molecule. This quantized energy is furnished by radiation in the infrared region (see table 13.2); such energy causes a change in molecular rotation which, for many molecules, can be detected by the spectroscope in the form of simple absorption bands.

The rotational energy at any quantum level n for a diatomic molecule, such as H—H, or for any linear molecule, assuming it to be a rigid rotator as in figure 13.3*b*, is given by

$$\varepsilon_r = \frac{n\,(n+1)\,h^2}{8\pi^2 I} \qquad (13.8)$$

where h again is the Planck constant, and I is the moment of inertia of the molecule. For most simple gases, the calculation of total rotational energy by quantum theory is in agreement with that by classical theory, showing that the rotational quanta are quite small, even though they are larger than translational quanta. An exception is hydrogen, for which the moment of inertia I is so small and ε_r is proportionately so large (from equation 13.8) that the quantum levels are fairly widely spaced. At 50°K., all hydrogen molecules are in their zero rotational level of energy. The rotational quanta, being fairly large, are not completely acquired by hydrogen molecules in a gram-mole until the temperature of 300°K. is reached, at which temperature it has a classical C_v of 5 calories. This is shown schematically in figure 13.4.

13. 13d. Quantum Theory and Vibrational Motion. The general equation for vibrational energy for each vibrational mode of a molecule in terms of quantum levels is

$$\varepsilon_v = (n+\tfrac{1}{2})\ h\nu \qquad (13.9)$$

where n has its usual whole number values of 0,1,2,3,... etc. In figure 13.5, one of a pair of atoms is indicated as being in constant vibration (oscillation) about the equilibrium distance d_e. At absolute zero (0°K.), there is no motion, and the system at point M is in the lowest vibrational state (that is, n is zero). From equation 13.9, it is seen that the oscillator at 0°K. has an energy of $(0+\frac{1}{2})$ $h\nu$; in other words, it still retains a half quantum of energy. This is called the zero-point vibrational energy. The horizontal lines above point M in figure 13.5 show the higher quantum levels that prevail at temperatures above 0°K. The vibration frequency is high (about 10^{13} to 10^{14} cycles per second), the same order of magnitude as the frequency of the infrared radiation in table 13.2.

Since translational quanta are small, all gases, even at very low temperatures, have acquired such quanta of energy. Rotational quanta are also small enough so that all the molecules of most gases at ordinary temperatures have acquired at least the first few levels of rotational energy. With respect to translation and rotation, therefore, most gases behave classically, as shown in figure 13.4; thus,

for a diatomic molecule where $E = E_{tr} + E_r + E_v$ we can substitute for E_{tr} and E_v as follows:

$$E = (3 \times \tfrac{1}{2}RT) + (2 \times \tfrac{1}{2}RT) + E_v$$

and since $R = 2$ cal./mole/degree, the molar heat capacity $C_v = 5$ cal./degree.

At relatively high temperature, such as 1000 to 2000°C., the value of C_v goes up, because vibrational motion occurs and the energy used to raise the temperature by 1° is absorbed not only by translational and rotational motion, but also by vibrational motion. The factor E_v which must be added to the last equation, to account for the vibrational contribution to heat capacity, can be calculated if the vibration frequency is known from spectroscopic measurements. The calculations are carried out with the help of tables of "Einstein functions." These functions, for each mode of vibration, are

$$E_v = RT \frac{x}{e^x - 1} \quad \text{and} \quad C_v = R \frac{e^2 x^2}{(e^x - 1)^2} \qquad (13.10 \text{ and } 13.11)$$

The equations are made easier to manipulate by using x to represent the quantum energy factor $h\nu/kT$. The tables give values of x for any temperature T, and any vibration frequency ν. All the other symbols stand for known constants.

At ordinary temperatures, the fraction $h\nu/kT$ is so large for most diatomic molecules that they are in the quantum level ε_0 for vibrational energy. Their vibrational contribution to E_v and C_v is, therefore, zero. An exception is chlorine, which starts to acquire vibrational quanta at temperatures close to normal, as shown in section 13.7.

13. 14. Infrared Spectroscopy. If a sample is irradiated by light of a certain vibration frequency, the energy of the incident light will be absorbed if the molecules in the sample can vibrate at two frequencies the *difference* of which is the same as the vibration frequency of the light. Another requirement is that a change must occur in the dipole moment of the molecule (section 22.15). This is the basis for the experimental procedure in obtaining infrared spectrograms, such as those shown in figure 13.8. Essentially monochromatic bands of infrared radiation of gradually increasing wavelength are successively passed through the samples, and the per-

centage of radiation transmitted is plotted against vibration frequency or wavelength. Information on the nature of the atomic vibrations in a molecule can be gleaned from such spectrograms; thus, the two butanes in figure 13.8 show absorption peaks at 1,450 cm.$^{-1}$ due to bending vibration of the C–H bond, and bands at 1,375 cm.$^{-1}$ which are characteristic of CH_3 group absorption. The double band

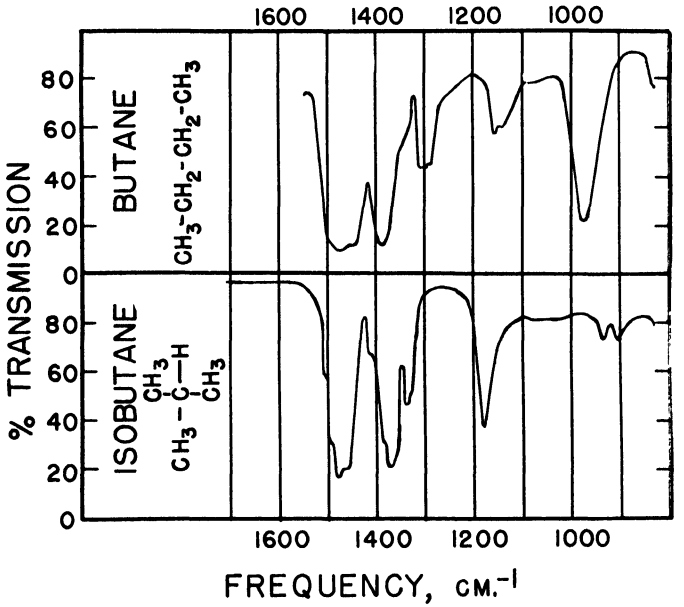


FIGURE 13.8. Infrared absorption spectra of isomeric butanes. [From R. B. Barnes, U. Liddel, and V. Z. Williams, *Ind Eng. Chem. Anal. Ed*, **15**, 659-709 (1943), which is the source of some of the material in this section].

(1,375 cm.$^{-1}$ and 1,360 cm.$^{-1}$) in isobutane has been found to be characteristic of compounds with a terminal isopropyl group, CH_3–CH –CH_3.

We have already discussed the procedure for calculating the "fundamental" modes of vibration of linear and nonlinear molecules (section 13.7). The chloroform molecule, H–CCl_3, has nine modes (from $3n-6=3\times 5-6$) of which we may consider those modes associated with the C–H bond. A model can be prepared in which

the atoms have their relative atomic weights (35.5 for Cl, 12 for C, and 1 for H) and the valence bonds are simulated by springs. Such a model shows clearly the *origin of characteristic vibrations* in the molecule. If the spring between C and H is stretched and released, these two atoms will oscillate at a certain characteristic frequency, but the three Cl atoms are relatively so heavy that they are not affected by this C–H "stretching" vibration. In other words, this mode of vibration takes place independently of other phenomena in the molecule, and study of the spectrograms of many compounds containing C–H bonds shows that this stretching vibration has a frequency of 2,900 $cm.^{-1}$

The frequencies in figure 13.8 do not go as high as 2,900 $cm.^{-1}$ to show the stretching vibration, but that figure does show a characteristic "bending" or "wagging" vibration of the C–H bond at 1,450 $cm.^{-1}$ which can be simulated on our chloroform model. This is done by displacing the H atom in order to bend the spring (without twisting the spring) and when it is released, the weighted atoms will again oscillate with practically no similar movement of the rest of the molecule. It may be mentioned that, for any molecule, there are n–1 stretching vibrations (where n, as usual, is the number of atoms) and the rest are bending vibrations. It is apparent that a catalog of infrared spectrograms of organic compounds (see reference under figure 13.8) is of immense value in elucidating the structure of an unknown compound, by comparison of its absorption bands with corresponding bands of compounds of known structure.

The student should refer to the concluding paragraphs of section 33.6 for a brief discussion of the ammonia molecule, NH_3, which at ordinary temperatures absorbs at a wave-length of about 1.25 cm., in what is known as the "microwave" region. The absorption is due to an intramolecular vibration which figuratively is equivalent to turning itself inside out at the rate of twenty-four thousand million times a second.

13. 15. Raman Spectra. Infrared absorption spectra are obtained by passing a wide range of radiations through a sample and finding out what has been absorbed. Raman (Rah-man) spectra are obtained with monochromatic radiation (usually from a mercury-vapor lamp); this light of single wavelength is generally scattered

by the molecules of the sample through which it passes, giving rise to lines on the spectrogram representative of new wavelengths in addition to that of the exciting radiation. The positions of the new lines relative to that of the exciting radiation is called the Raman shift. The Raman effect is one of the most important tools now being employed in the study of organic structures. The shifts have been quantitatively related to modes of vibration of the atoms in specific groups, are easily recognized, and are often numerically equal to the frequencies found in infrared absorption for the same vibrations. The secondary spectral lines are generally of longer wavelength (lower energy state) than the exciting radiation, because some of the energy is usually absorbed in the molecular vibration. However, the quantum of incident radiation sometimes absorbs a quantum of energy from the molecule it hits and, being then of greater energy, it shows up in the spectrogram as a line of shorter wavelength.

13. 15a. Nuclear Magnetic Resonance. The peaks in a spectrum obtained with visible light or infrared radiation show at what frequencies certain motions in a molecule are in resonance with the radiation frequencies passed through the sample. Nuclear physics has recently given chemists another resonance phenomenon, which can be presented pictorially as a mapped spectrum and is useful in studying molecular structures. For this discovery of nuclear magnetic resonance, or *nuclear induction,* the Nobel prize in physics was awarded to Bloch and to Purcell in 1952 (see references at the end of this chapter).

The nucleus of an atom, when in a constant magnetic field, precesses like a spinning top and the spinning earth (section 26.3). The precession frequency w is proportional to the magnetic field intensity H according to the equation $w = \gamma H$, where γ is a fundamental constant of the nucleus showing the ratio of its spin quantum number to its magnetic moment. For some nuclei, such as C^{12} and O^{16}, this constant is zero, but for most nuclei, such as all the hydrogen isotopes (section 45.3), it is finite and for these the equation can be applied. The precessional rotation frequency w around a constant magnetic field is in the range of radiofrequencies, about 3×10^7 cycles/sec., which is below the range of optical methods for detection (see table 13.2). However, the rotation is accompanied by its own magnetic

field with an alternating component perpendicular to the axis of rotation, which induces a change in voltage in a coil around the sample; this developed voltage is the quantity which is measured (compare figures 22.19 to 22.21).

The sample in a test tube is subjected between the poles of a large magnet to a uniform field of about 10,000 gauss. A coil around the sample also subjects it to a radiofrequency excitation of about 3×10^7 cycles/sec., which induces the nuclei to precess in step rather than at random. A coil at right angles to the constant magnetic field then "sweeps" the sample with a slow change in field strength. When the frequency of the sweep forces is in resonance with the natural frequency of the spin/magnetic moment forces of the nuclei in the sample, a small voltage is developed in a coil which is loosely coupled with the coil that supplies the radiofrequency energy. This induced voltage is amplified and presented on an oscilloscope or recorded on a chart. The spectrum obtained resembles a light-absorption spectrum, but shows voltage peaks plotted against magnetic field intensity.

For a compound like ethyl alcohol, CH_3–CH_2–OH, peaks will be obtained for H atoms in the CH_3 group, in the CH_2 group, and in the OH group, and they are well separated on the spectrum. This separation of peaks shows to what extent the different electron environments of the H nucleus in the three types of chemical groups affect its magnetic moment. The distance between peaks is called the "chemical shift." By this procedure, it is easily possible, through the nuclear induction by hydrogen nuclei, to identify groups of atoms such as CH_3 and OH even though the nuclei of ordinary carbon and oxygen atoms do not give the induction effect. The "intensity" of each peak, that is, its height, corresponds to the absorbancy in ordinary light spectra. The intensity is proportional to the number of equivalent nuclei involved; for example, the peak for CH_3 is three times as high as that for OH. The sample must be in the liquid state for high resolution.

13. 16. Calculated Heat Capacities. In the early pages of this chapter, we defined heat capacity (section 13.4) and indicated that it was a value obtainable by a calorimetric measurement. The data obtained by direct experiment were then evaluated in terms of the possible motions of the molecule.

In these closing pages of the chapter, it has been shown that molecular gyrations can be recognized spectroscopically. Spectroscopic measurements can be made with a high degree of accuracy and the experts in quantum theory and statistical mechanics, by methods which are hinted at in this chapter, are able to use such data to obtain calculated values of the heat capacity which are more reliable than the calorimetric data. It should be observed, however, that the discrepancy between a heat capacity calculated from spectroscopic (molecular) data and that determined calorimetrically sometimes leads to highly important discoveries. For example, the calculated heat capacity for ethane (section 13.11) is a little higher than the calorimetric value. The calculation assumed that the compound is a free rotator about the C–C bond. The discrepancy indicates that the rotation is hindered, and the difference between the two values (about 3,150 cal. per mole) is the energy equivalence of the hindrance to rotation.

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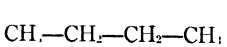
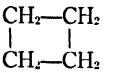
14. DOUBLE BONDS AND TRIPLE BONDS

14. 1. Introduction. In the preceding chapters we have done our best to portray the organic chemist as an architect. We have shown how this architect, using the carbon atom as his principal building block, can erect structures of two general types,



Butane



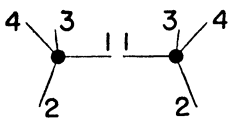
Cyclobutane

which we have designated as the chain type and the ring type, respectively. If this were the sum total of the accomplishments of the organic chemist, his problems would cease to interest us right at this point. But organic chemistry has much more to show us. The carbon chains and carbon rings are only the outline structures on which the organic chemist performs his magic.

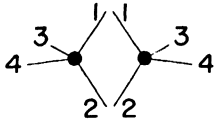
As explained in earlier chapters, the chain and ring hydrocarbons pictured on this page are relatively inactive. Since the chemist, by definition, is primarily interested in the transformations of substances, he would enjoy working with these structures to a much greater degree if he could increase their activity. This, we found, he can do by the simple trick of inserting a Cl atom into the molecule. The presence of the Cl atom permits a series of chemical changes which is limited only by the ingenuity of the chemist.

In this chapter, and the following one, we shall describe carbon compounds that do not depend on a foreign element for enhanced chemical reactivity. The greater activity in these compounds will be found to result from the way in which certain pairs of *adjacent* carbon atoms are linked in the chains and rings. These structural types have not yet been mentioned in this book.

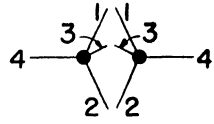
Up to this point, we have been careful to limit ourselves to those compounds in which each carbon atom uses only one of its valence bonds to combine with an adjacent carbon atom. This is called a *single* bond, and is represented as in model I. Model II shows how



I
Single bond



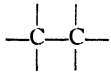
II
Double bond

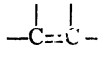


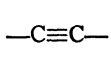
III
Triple bond

the *double bond* is formed when each carbon atom uses two of its bonds, and model III indicates how the *triple bond* is formed by the use of three bonds.

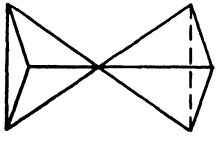
When projected on the plane of a printed page, these three kinds of carbon-to-carbon union are usually written in this way:



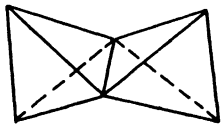




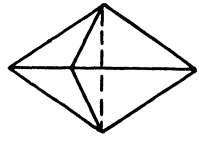
Each carbon atom has four valences, and one, two, or three of these valences may join with a second carbon atom. It should be observed in model II that if four H atoms are attached to the bonds marked



IV
Single bond



V
Double bond

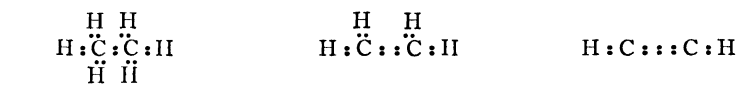


VI
Triple bond

3 and 4 they are in the *same plane* as the two carbon atoms. According to model III the two H atoms attached to the bonds marked 4 are in the *same straight line* as the two carbon atoms.

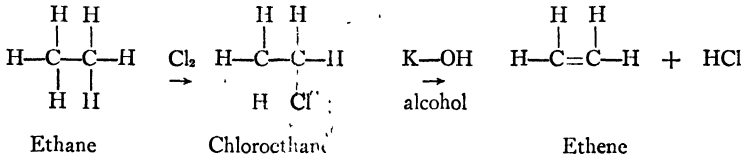
If the full tetrahedral model of the carbon atom is used (chapter 12), another interesting picture can be obtained of these three kinds of carbon-to-carbon bonds, shown in models IV, V, and VI. A single bond consists of a point-to-point union, a double bond is an edge-to-edge union, and in the triple bond the union is face to face.

We should also consider the electronic formulas, in which a pair of electrons represents one bond:



14. 2. Preparation of Compounds with Double and Triple Bonds. It will be an easier task to explain the chemistry of molecules in which the carbon atoms are united by double and triple bonds if we first find out how they are formed. We shall start with the simplest possible case, that is, a compound with only two carbon atoms.

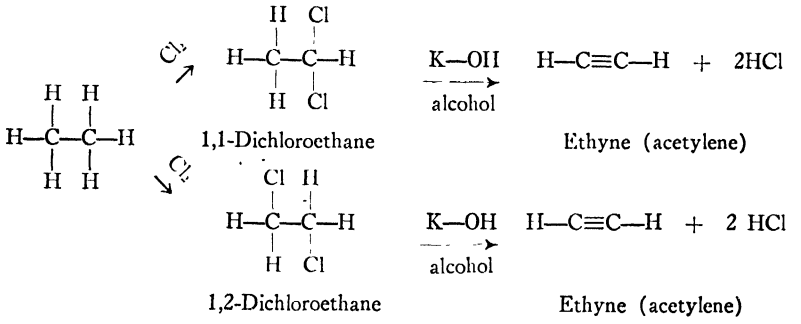
The only two-carbon hydrocarbon we have yet described in this book is ethane, CH_3–CH_3. We found that ethane behaves like methane; it allows its H atoms to be replaced by chlorine or bromine atoms. Suppose we insert one Cl atom into the ethane molecule, and see what we can do with the product:



After one H atom has been replaced by Cl, the compound has a greater reactivity. If we treat the resulting chloroethane with an alkali under certain conditions, a molecule of HCl is split out from *adjacent* carbon atoms and a *double bond* is formed. The conditions for this reaction are quite definite. The KOH must be dissolved in alcohol (not in water) for the reaction to take place as indicated; the reaction also proceeds rather quickly. In section 9.4 it was shown

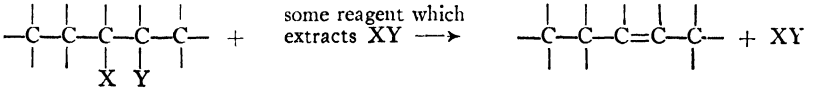
that when the reagent used is a solution of KOH in water a *slow* reaction results, in which –Cl is replaced by –OH. The reader should compare the results obtained.

Now let us see what happens if there are two chlorine atoms in the ethane structure:



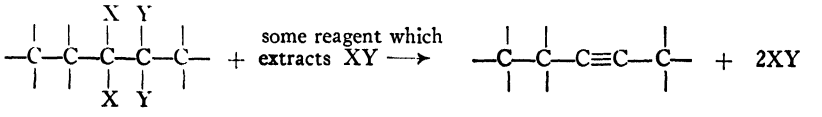
Both dichloroethanes yield a *triple bond* when treated with an alcoholic KOH solution.

These simple cases illustrate the general method by which compounds are formed which contain *multiple bonds*. Two atoms or radicals, must be removed from adjacent carbon atoms in order to make one extra bond. In a general way this can be summarized as:

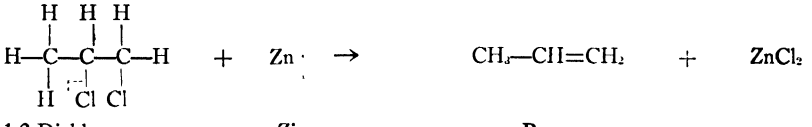


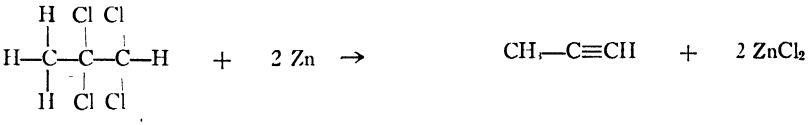
The important thing to remember is that X and Y must be on adjacent (neighboring) carbon atoms.

Similarly, for a triple bond two XY pairs must be removed from adjacent carbon atoms:

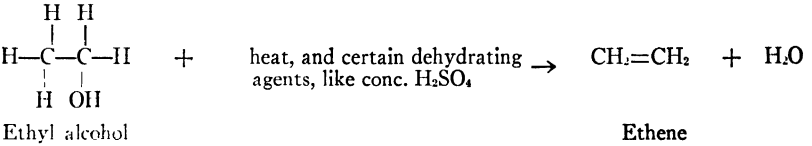


Now that we understand the general mechanism of the creation of a double bond and triple bond, it is easy to think of a number of similar reactions which can be used for the purpose. For example,





And here is one for the double bond only,

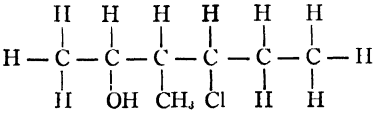


Notice how the organic chemist likes to put a halogen atom into an organic compound, and then use a metal or metallic compound for the next step in the process. Also, notice that he is careful to place four valence bonds on each carbon atom, when writing formulas and reactions. This is as important to organic chemistry as the "balancing of equations" in beginning chemistry.

14. 3. How to Name Compounds with Double Bonds and Triple Bonds. As already hinted, the double bond is indicated by the ending *ene* and the triple bond by *yne,* just as in preceding chapters the single bond was represented by *ane.*

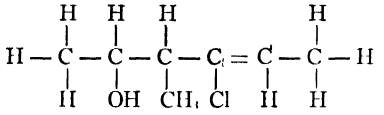
As usual, we consider the chain of carbon atoms as the general framework of the compound, and from the number of carbon atoms in the longest chain containing the multiple bond we derive the parent, or last name of the compound. In section 10.9, we wrote the fol-

lowing formula for a certain compound with six carbon atoms in the longest chain:



4-Chloro-3-methyl-2-hexanol

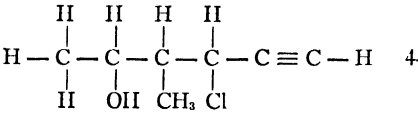
If this compound is altered by introducing a double bond at the fourth carbon atom from the left, the name and formula would be as follows:



4-Chloro-3-methyl-4-hexen-2-ol

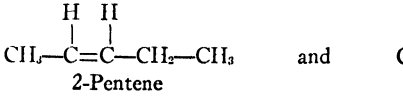
The –C=C– group is regarded as one of the "functional" groups in a molecule (section 10.10) and the presence of this group is, therefore, indicated in the main part of the name of the compound, thus, hex*ene*. The –OH group takes precedence over the –C=C– group, however, so the molecule is numbered from the left end in order to make the number associated with this chief function as small as possible. The compound is a *hexenol,* that is, an olefin (section 16.1) and an alcohol.

Modifying the compound in such a way as to introduce a triple bond will change it to a *hexynol*:



4-Chloro-3-methyl-5-hexyn-2-ol

From what has been said it is apparent that double bonds or triple bonds can be situated in various parts of a molecule. Here are two compounds with a straight chain of five carbon atoms,



2-Pentene and 1-Pentene

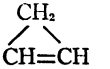
which have the same molecular formula, C_5H_{10}, but different arrangements of the atoms. They therefore have different properties and are isomers (section 10.5).

It is also possible for both double bonds and triple bonds to appear in the same molecule:

$CH_2{=}CH{-}C{\equiv}C{-}CH_3$ 1-Penten-3-yne
(Double bond gets the lower number)

Notice that when the $-C{\equiv}C-$ group is somewhere in the interior of a chain there are no H atoms on those two carbon atoms.

Many cyclic compounds are known in which double bonds are present, for example,

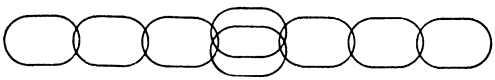


Cyclopropene

but relatively few have been prepared containing triple bonds. The smallest cyclic compound reported with a triple bond in the ring is cyclooctyne, C_8H_{12}, the eight-membered ring, the first apparently unequivocal synthesis of which was published in 1953.

15. PROPERTIES OF CARBON CHAINS WITH DOUBLE AND TRIPLE BONDS

15. 1. Introduction. If we take a steel chain, like one used for lifting a ship's anchor, and weld two links to it where there had been only one before, we find that it is twice as strong at that one place. This is the picture:



The double and triple links in the carbon chains, which we represent by C–C=C–C and C–C≡C–C, apparently have a similar strengthening effect on the physical properties of the molecule. Certain measurements, such as those of absorption spectra (section 15.6), give evidence that the resistance to stretching and compression is about three times as great for a triple bond as for a single bond.

Similarly, thermochemical data (table 17.1) show that more heat energy is required to break the multiple bonds than to break the single bond. In the words of the physicist (or physical chemist) the multiple bonds are thermodynamically more stable.

Now all this may seem contrary to what we said about double bonds and triple bonds in chapter 14, when we introduced these bonds to the reader. At that point, we stressed the fact that molecules containing these bonds are usually much more reactive than those with only single bonds. There is, however, no essential disagreement

in these statements. What we must realize is that relative stability of substances when subjected to physical effects, such as change in temperature, may be quite different from the relative stability when treated with chemical reagents, such as chlorine. Both of these stability factors can be expressed precisely in mathematical terms, and, in a later chapter, we shall compare briefly thermochemical stability and chemical reactivity (section 17.9) from the standpoint of the physical chemist.

For the present, however, we can use the term chemical reactivity in its usual loose sense, that is, the general willingness of a substance (or of its valence bonds) to enter into chemical change. Studying the chemical properties of compounds in which C=C and C≡C bonds are present, we shall find they are to be classed with the relatively reactive substances, and that the double bond or triple bond serves as a reaction center and furnishes the chemist with a point of attack on the molecule.

We can obtain a helpful conception of the reason for the reactivity of the double bond by reviewing the method of its formation:

$CH_3—CH_2Cl$ → $CH_2=CH_2 + HCl$

Chloroethane — Ethene

Much of the progress in the history of organic chemistry has been due to just such a picture of the carbon atom as we have given here, that is, an atom with four symmetrically placed valence bonds. The chemist assumes, further, that the valence bonds tend to act in straight lines. Therefore, he takes it for granted that the ethene molecule closes up as shown in figure 15.1, and that there is a strain in the molecule due to this adjustment of the valence bonds. The strain theory should be reviewed in section 12.6 and it should be observed that ethene can be regarded as the simplest of the *cyclic* hydrocarbons.

Although this conception of the double bond is helpful, it does not find favor with physicists and modern organic chemists for a number of reasons. One good reason is that the double bond is formed so easily that it does not appear likely that it would yield

such an uneasy, strained structure. Also, there are a number of physical properties, such as thermochemical stability (table 17.1), which contradict this theory of the strained bonds.

At any rate, this picture of the double bond does help us to understand why compounds containing such bonds appear to be *unsaturated,* that is, add on other molecules as shown in the following pages (section 15.2).

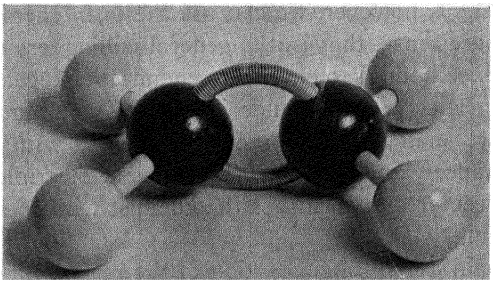
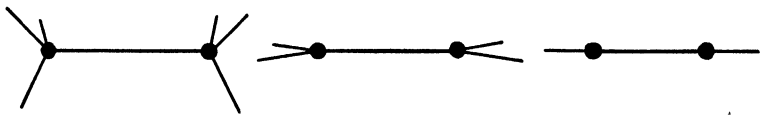


FIGURE 15.1. **Model of ethene, C_2H_4.**

15. 1a. Molecular Orbitals in Ethene. A more accurate picture of the double (and triple) bond than that in figure 15.1 is based on the concept of orbitals described in section 7.9 and table 7.1. Although we shall not use such orbital models in the chemistry to be presented in the introductory chapters on double and triple bonds, they will be illustrated at this point so that we can use them as reference structures in several important phenomena to be described later (sections 17.3, 18.5, 18.10, 19.7).

Let us look once more at models I, II, and III in section 14.1 and then arbitrarily draw single bonds instead of multiple bonds between



I
Tetrahedral

II
Trigonal

III
Digonal

the carbon atoms. In model I, both carbon atoms are tetrahedral (see figures 7.5 and 12.2), and all the H–C–H valence-bond angles are 109°28′. The carbon atoms in II are trigonal; the H–C–H

valence angles are 360/3=120°, and are in one plane. In III the symmetry is digonal; the valence angles are 360/2=180°, and are in a straight line.

In model I, all four valence bonds on each carbon atom are equivalent; this status is reached when three p atomic orbitals are hybridized with an s atomic orbital to give four orbitals of the sp^3 type as explained in table 7.1. The overlapping of an sp^3 atomic orbital of one carbon atom with a corresponding orbital of the other carbon atom is illustrated in figure 15.2; the resulting molecular orbital is sp^3–sp^3 and is σ (sigma) type as defined in section 7.9. The coalescence of a carbon atom sp^3 orbital with the s atomic orbital of a hydrogen atom to yield an s-sp^3 molecular orbital was shown in figure

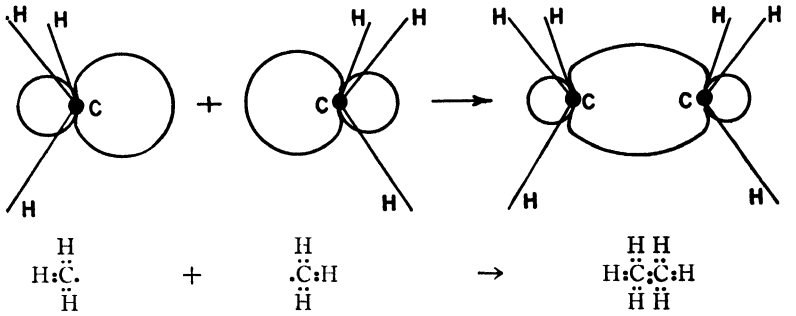


FIGURE 15.2. Formation of the C—C bond in ethane by overlapping of two sp^3 hybrid atomic orbitals. The C—C bond has *sigma* character, both nuclei being encompassed by a molecular orbital containing two electrons.

7.5 and should be referred to again. This, also, has σ character and all the bonds in model I are, therefore, of the σ type.

In table 7.1, it was shown that the atomic orbitals in the valence shell of the carbon atom can hybridize to a state in which only two of the p orbitals are involved and in which the four orbitals can be represented by sp^2, sp^2, sp^2, p. In model II, we use the three sp^2 orbitals on each carbon atom to create the three single bonds that are shown in trigonal symmetry. The C–C link (sp^2–sp^2 molecular orbital) is illustrated in figure 15.3 *(a)*; one of the C–H links (s–sp^2 molecular orbital) in figure 15.3 *(b)*; and the utilization of all three of the sp^2 atomic orbitals on each carbon atom is represented in fig-

ure 15.3 (*c*). Each of these molecular orbitals is of the σ type, in which a pair of nuclei is encompassed by a two-electron egg-shaped orbital.

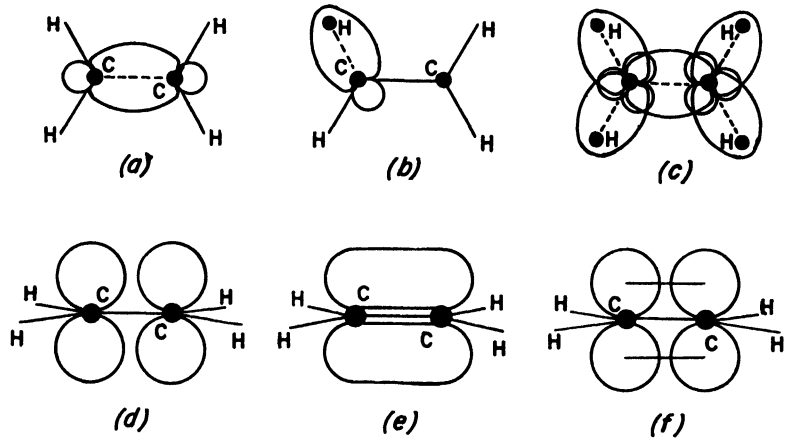
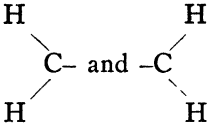


FIGURE 15.3. Disposition of the orbitals in ethene. Upper series of diagrams are top views of molecule, with all atoms in the plane of the paper. All the molecular orbitals are of the *sigma* type. In the lower series, the molecule is viewed from the side (front); the *p* atomic orbitals are in plane of the paper, perpendicular to the rest of the molecule, and the molecular orbital is of the *pi* type.

(*a*) The C–C bond is an sp^2-sp^2 molecular orbital.
(*b*) The C–H bond is an s-sp^2 molecular orbital.
(*c*) The C–C bond and four C–H bonds are in the plane of the paper.
(*d*) The hourglass-shaped *p atomic* orbitals on each carbon atom, before overlapping to form a *molecular* orbital.
(*e*) Overlapping of the *p* atomic orbitals The resulting molecular orbital, containing two electrons, is known as a π orbital.
(*f*) A method of representing the status in (*e*), that is, overlapping of two *p* orbitals, each of which has a single electron. The tie-lines are used to indicate overlapping.
(See comments under figure 17.3*c*.)

The bottom series of diagrams in figure 15.3 shows how the lone *p* atomic orbital on each carbon atom affects the molecule. Each hourglass orbital contains a single electron and is perpendicular to the

-plane. The second bond in the $H_2C{=}CH_2$ molecule is due

to overlapping of the *p* atomic orbitals of the two carbon atoms; the bond is most stable when there is maximum overlapping, and this is the case when  are all in the same plane. The *p* atomic orbitals are then side by side as in figure 15.3 (*d*) and can coalesce to a squat hourglass, more commonly referred to as a pair of fat sausages (figure 15.3 (*e*)). The resulting *molecular* orbital is labeled *p–p;* since it is very similar to a *p atomic* orbital with a nodal plane between the two parts, it is called a π (*pi*) orbital and the two electrons in it are called π electrons. To differentiate between the two types of carbon-carbon bonds in ethene we may write the structure $H_2C{-}{\cdot\cdot}CH_2$, where the line is a σ bond and the dots are a π bond. It is apparent that the carbon atom in ethene has trigonal symmetry; it is connected to three atoms by *sigma* bonds, and these bonds are in the same plane at equal angles of 120°. The electron

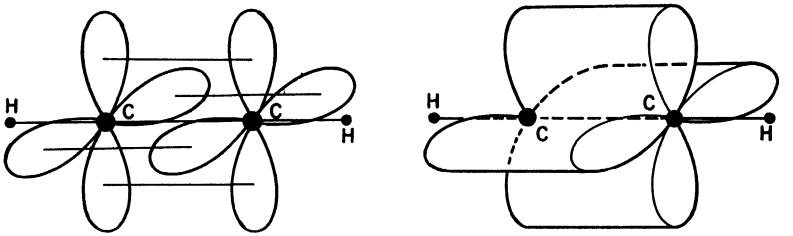


FIGURE 15.4. The two perpendicular π-type molecular orbitals of the ethyne molecule. The atomic orbitals before overlapping are shown as figure-8's rather than as the customary hourglasses. This method has been adopted to make the diagrams easier to comprehend (see benzene in figure 19.3 and the comments under figure 17.3*c*). The σ-type orbitals are not shown.

pairs in these three bonds are said to be *localized.* The two electrons represented by dots are said to be *mobile* electrons. This will be discussed further in section 17.3.

15. 1b. Molecular Orbitals in Ethyne. The ethyne molecule is built up from carbon atoms in which hybridization (see table 7.1) of only one *p* atomic orbital is involved, and the four orbitals of the carbon atom are then represented by *sp, sp, p, p.* In model III the two *sp* orbitals on each carbon atom are used in making the H–C

bond and the C–C bond. The two remaining p orbitals are perpendicular to the straight-line molecule shown in model III; they are also perpendicular to each other. The hourglass p orbitals on the carbon atoms overlap just as illustrated in figures 15.3 (d) and 15.3 (e), except that in the case of ethyne there are four p orbitals. The overlapping results in two molecular π orbitals, as shown in perspective in figure 15.4. This molecule may be represented by HC≒CH, to indicate a σ bond between the carbon atoms enhanced by two sets of π electrons in two π bonds.

15. 2. Addition Reactions to Multiple Bonds. In later chapters, the π electrons of ethene and ethyne will be found to be associated with considerable activity of both chemical and physical nature. For the chemistry to be described in this chapter, however, the simple structure of figure 15.1 will serve quite well. In this section, we shall consider simple addition to the double bond.

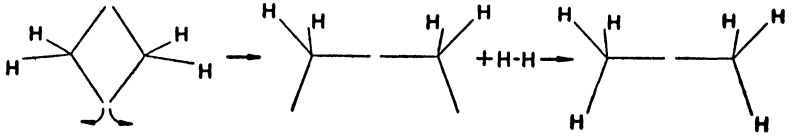
15. 2a. Hydrogenation. Hydrogen can be added directly to compounds containing $-\overset{|}{C}=\overset{|}{C}-$ and $-C\equiv C-$ groups, usually without any difficulty:

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + H_2 \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3}$$

$$\underset{\text{Propyne}}{CH_3{-}C{\equiv}CH} + H_2 \rightarrow \underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H_2 \rightarrow \underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$

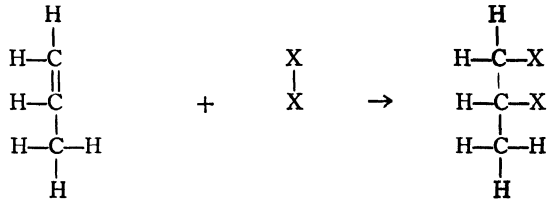
The customary procedure is to mix the vaporized hydrocarbon with the hydrogen and pass the mixture over powdered nickel at an elevated temperature. The process is called *hydrogenation,* and nickel is an excellent hydrogenation catalyst.

The simplest way to explain a reaction of this type is to assume that the bonds open up in this way,



and that the added molecule hooks on to the free valences. This is discussed further in section 18.2.

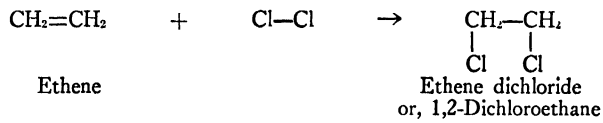
It should be observed that the addition always takes place *across the double bond,*



and that this is the reverse of what takes place in the formation of the double bond, as shown in section 14.2.

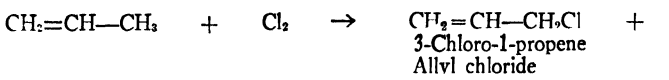
If there is a triple bond in the chain, the addition takes place in two stages, as indicated for the hydrogenation of propyne to propene and then to propane. In some instances, the reaction can be stopped at the first stage.

15. 2b. Addition of Halogen. Halogens, also, add directly to multiple bonds:



The student should notice that the product of this reaction can be named in two ways. It can be named as an *addition* product of ethene or as a *substitution* product of ethane.

The addition of Cl_2 to a double bond is easier at a lower temperature, whereas substitution for hydrogen atoms in the chain is aided by a higher temperature. This is well illustrated by the action of chlorine on propene at temperatures of 250° to 500°C., with yields of up to 90 per cent of the substitution product:



The addition reaction will be explained in section 17.4 as an ionic reaction, whereas the substitution will be ascribed to a free-radical mechanism in section 20.2.

15. 2c. Addition of Hydroxy Groups. Certain oxidizing agents, such as potassium permanganate ($KMnO_4$) in aqueous solution, act on the double bond as follows:

$$CH_2{=}CH_2 + H_2O + O \rightarrow \underset{\text{Ethene glycol}}{\overset{\quad OH \quad OH}{CH_2{-}CH_2}}$$

It will be seen that the action of the oxidizing agent is equivalent to the addition of a molecule of hydrogen peroxide (H_2O_2 or HO–OH) across the double bond. The product of this reaction, containing two –OH groups, is a member of the family of glycols (section 27.5).

The action of ozone (O_3) on the double bond apparently also results in initial products through addition across the bond. The subsequent reactions, however, are too complex to be considered in this chapter (see section 30.2*b*).

15. 2d. Unsymmetrical Addition. In the preceding two examples of addition reactions, the added molecules are the symmetrical substances, hydrogen (H–H) and chlorine (Cl–Cl). Now let us see what takes place in an unsymmetrical addition reaction, where the added molecule is in general represented by H–X. Such unsymmetrical combinations exist in hydrochloric acid (H–Cl) and in sulphuric acid (H–SO_4H). These are inorganic substances which readily ionize by splitting up into a positive part and a negative part.

The addition of an unsymmetrical compound to a symmetrical compound containing a double bond does not offer anything unusual:

$$\underset{\text{Butene-2}}{CH_3{-}CH{=}CH{-}CH_3} + HCl \rightarrow \underset{\text{2-Chlorobutane}}{CH_3{-}CH_2{-}\overset{\quad Cl}{CH}{-}CH_3}$$

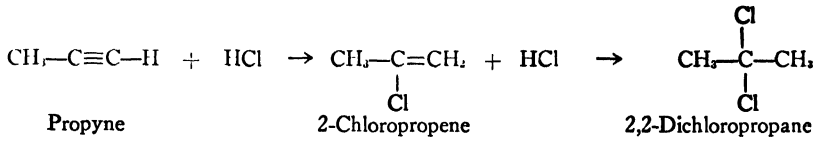
However, if the addition takes place on an unsymmetrical double-bond compound, there are several possibilities:

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + HCl \rightarrow \underset{\text{2-Chloropropane}}{CH_3{-}\overset{\quad Cl}{CH}{-}CH_3} \text{ or } \underset{\text{1-Chloropropane}}{CH_3{-}CH_2{-}CH_2Cl}$$

Experience has shown that the *negative half* of the adding molecule *usually* goes to the carbon atom with the least hydrogen. Therefore, 2-chloropropane is the predominant product in this reaction. This characteristic behavior of unsymmetrical compounds like

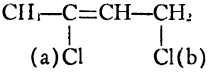
H–Cl, when added to a double bond, is spoken of as "directed addition" to the double bond and will be discussed further in section 17.4. This is not, however, to be taken as an infallible rule.

According to this same principle of "directed addition," when HCl is added to triple-bond compounds, the negative half of the molecule tends to "pile up" on the same carbon atom:



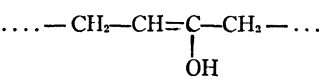
15. 3. Other Properties of Compounds Containing Double and Triple Bonds. Although the most important characteristic of the multiple bond is that it readily adds on other substances, there are a few other properties to be considered which do not come in this category.

15. 3a. Effect on Other Substituents. The presence of a double bond in a molecule makes a profound change in the behavior of the two carbon atoms at the ends of the bond, and often produces changes in other parts of the molecule. For example, in such a substance as this,



it will be found that the two Cl atoms are very unlike in activity. The Cl atom marked (a) is very inactive, showing that the union $=\overset{|}{\underset{Cl}{C}}-$ is stronger than $-\overset{|}{\underset{Cl}{C}}-$. It is difficult to make the (a) halogen atom go through the reactions of the (b) halogen. In fact the (b) chlorine atom is even more reactive than it would be in a compound containing only single bonds (section 25.4).

A good rule to remember is that in such a structure as this,



the compound is unstable, and rearrangements occur which will be described later (sections 31.9, 32.11, and 32.14). There are numerous

exceptions to this rule, however; an example will be found in the vitamin C molecule (consult Index).

15. 3b. Acidity of —C≡C—H Group. In the triple-bond compounds an unusual characteristic arises when the triple bond is at the end of the chain, as in the following:

H—C≡C—H and CH_3—CH_2—C≡C—H

The hydrogen atom in the H–C≡C– group has the properties of the H atom in acids. It can be replaced by metals.

Ethyne, more commonly known as acetylene, has two acidic H atoms, of which either one or both can be replaced:

$$Na^+[C{\equiv}C]^=Na^+ \xleftarrow[200°]{Na} H{-}C{\equiv}C{-}H \xrightarrow[100°]{Na} [H{-}C{\equiv}C]^-Na^+$$

(Acetylene passed into melted sodium)

$$H{-}C{\equiv}C{-}H + 2\,AgOH \rightarrow Ag{-}C{\equiv}C{-}Ag + 2H_2O$$

(Acetylene passed into ammoniacal silver nitrate)

The compounds formed with highly electropositive metals (review section 8.8) are salts, but with certain of the heavier metals, like silver, the structure is believed to be covalent rather than ionic. Salts like the compounds of sodium and calcium are quite stable, but compounds of the heavier metals like silver are unstable and dangerously explosive when dry.

The nomenclature of these acetylene derivatives is confused. Some writers refer to compounds in which one H atom is replaced as *acetylides*, and in which both H atoms are replaced as *carbides*. Other writers call the covalent compounds *acetylides*, and the ionic compounds *carbides*. The most common of these compounds in commerce is calcium carbide, $Ca^{++}(C{\equiv}C)^=$. The crystal structures in this series of compounds are believed to be of various types, leading to different reactions with water. For example, calcium carbide gives acetylene when added to water, whereas aluminum carbide (section 45.3) yields methane.

15. 3c. Oxidation. Oxidizing agents rupture a chain of carbon atoms more easily when the chain contains C=C and C≡C bonds. The initial stage in the reaction is presumably addition of —OH groups across the multiple bond, as described in one of the preceding

paragraphs. Continued oxidation then often breaks the chain at the point between the –OH groups.

An example of this behavior is the oxidation of oleic acid (section 31.9), which is an eighteen-carbon straight-chain compound with one double bond in the chain. Shaking this acid with dilute potassium permanganate breaks it down into two lower acids, each with nine carbon atoms, proving that the C=C bond of oleic acid is in the middle of the chain.

15. 4. Detection of Double and Triple Bonds in a Molecule. By making use of our knowledge of the *chemical* activity of C=C and C≡C bonds, we can easily devise simple methods by which we can find out whether or not a molecule contains these groupings. The simplest method makes use of the ease with which C=C and C≡C can be oxidized.

Suppose we get samples of these three gases: ethane CH_3–CH_3, ethene CH_2=CH_2, and ethyne CH≡CH and we are required to determine which is which. If we successively pass them into a dilute alkaline solution of potassium permanganate, the red color of the solution will rapidly disappear in the case of ethene and ethyne, but not in the case of ethane. In oxidizing the reactive double and triple bonds, the reagent loses its color.

Another method of detection of double and triple bonds is to treat the substances with a weak solution of bromine in carbon tetrachloride. This reagent has a pale red color, and the color gradually disappears as the Br_2 in solution adds on to the double and triple bonds.

A double bond can be usually distinguished from a triple bond by the fact that the triple bond adds twice as much bromine. This requires a quantitative analysis. When the –C≡C– group is at the end of the chain, however, its presence can be detected easily by the formation of a metallic derivative, as explained in the preceding section.

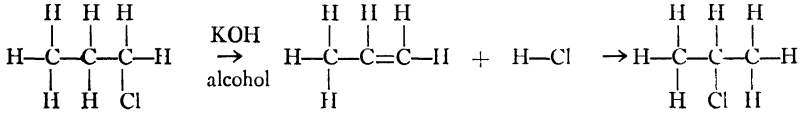
It is also possible to detect double and triple bonds in a molecule by *physical* methods, by applying the principles of infrared spectroscopy described in chapter 13. The vibration frequency of the C=C bond is about 1630 cm^{-1} and that of the C–C bond is about 2000 cm^{-1}. When using such data to identify multiple bonds in the spectrograms of compounds, it must be remembered that the intensity of absorption and the actual frequency at which absorption

takes place will depend, to some extent, on the nature of the rest of the molecule. In section 13.13, it was stated that absorption of light in the infrared region takes place only if the increased amplitude of the atomic oscillations results in a change in dipole moment; in a very symmetrical molecule, like that of ethene, the absorption is nearly nil. The effect of light on molecules containing double bonds will be considered in more detail in the study of dyes (chapter 42).

15. 5. Some Tricks of the Organic Chemist. In section 9.4, we showed how the presence of Cl in a paraffin hydrocarbon gave the relatively inert molecule the ability to react with other substances. In this section, we shall illustrate with some examples the corresponding importance of the multiple bond in the carbon chain.

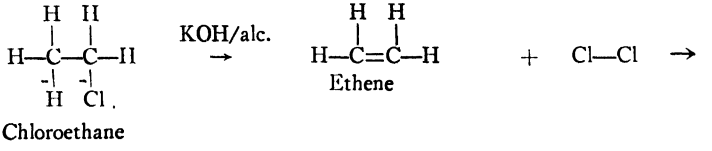
a. Suppose we have the compound $CH_3–CH_2–CH_2Cl$, in which the Cl atom is at the end of the chain, but for some reason we want $CH_3–CHCl–CH_3$, in which the Cl is inside the chain. How can we make the change?

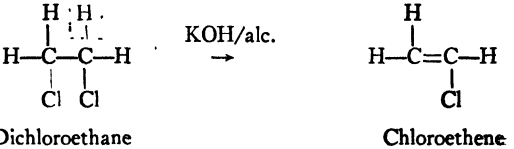
The method is quite simple:



We first remove the HCl from adjacent carbon atoms to form a double bond. Then, when we add a molecule of HCl back again, the Cl atom will go to the carbon atom with least hydrogen, as explained earlier in the chapter.

b. Suppose we have a quantity of $CH_3–CH_2Cl$ and we wish to convert it to $CH_2=CHCl$. One of the possible series of reactions is as follows:





c. In the commercial preparation of gasoline at the oil refineries, it is often necessary to remove chain hydrocarbons which contain double bonds. The procedure followed is treatment with concentrated sulphuric acid:

$$CH_3{-}CH{=}CH_2 \xrightarrow{H{-}SO_4H} CH_3{-}\underset{\displaystyle SO_4H}{\underset{|}{CH}}{-}CH_3 \xrightarrow{\text{steam}} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

The acid adds on across the double bond when such compounds are present, and the resulting products, being insoluble in the rest of the mixture, are easily removed. When steam distilled, these acid addition products are converted into alcohols which have many commercial uses.

d. In the oil and fat industry, the chemist has made extensive use of his knowledge of the double bond and its characteristics. This will be referred to in section 31.9.

15. 6. Force Constants. In such a bond as C–C, the atoms oscillate rapidly about an equilibrium position. Force is required to change this equilibrium distance, that is, to push the atoms closer together or to move them further apart (see figure 13.5); these forces are generally referred to as *compression* and *stretching* forces, respectively. The phenomenon has been treated as a special case of Hooke's law for the simple harmonic vibrations of an elastic medium:

$$\nu = \frac{1}{2\pi}\sqrt{\kappa/m} \qquad (15.1a)$$

where ν is the vibration frequency in cm.$^{-1}$, κ is the displacement, and m is the mass of the oscillating body. The following modification makes the equation adaptable to atomic systems:

$$\nu = \frac{\sqrt{10^5 N}}{2\pi c}\sqrt{f/\mu} = 1302\sqrt{f/\mu}\ \text{cm.}^{-1} \qquad (1\ 51b)$$

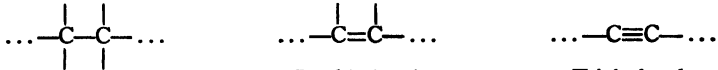
where c is the velocity of light (3×10^{10} cm./sec.), μ is the reduced mass of the two atoms (explained below), and N is the Avogadro number (6.02×10^{23} molecules/gram-mole). The *force constant* between the atoms, f, is the restoring force per centimeter of displacement and is expressed in dynes/cm.$\times10^5$. The fixed constants (π, c, N) are all incorporated in the number 1302.

The reduced mass is obtained from the relation $1/\mu = 1/m_1 + 1/m_2$ where m_1 and m_2 are the relative weights of the vibrating atoms. Thus, when both atoms are carbon, as in the C–C bond, the reduced mass, μ is found to be 6.0, from the relation $1/\mu = 1/12 + 1/12$. With the proper spectroscopic data at hand, it is possible to calculate from equation 15.1*b* the force constant f for various pairs of atoms. It has been found that for atoms united by a single bond (not only C–C, but also C–H, O–H, etc.), the value of f is between 4 and 6×10^5 dynes/cm. For atoms linked by a double bond, the value of f is twice as great (from 8 to 10×10^5 dynes/cm.) and for the triple bond it is three times as great (from 12 to 18×10^5 dynes/cm.).

Since the same type of bond between any two atoms has roughly the same force constant, it is obvious that, from this constant, the approximate value of the vibration frequency of any pair of atoms can be calculated.

16. PARAFFINS, OLEFINS, AND ACETYLENES

16. 1. Introduction. After we found out how to build chains of carbon atoms we learned that the carbon atoms in a chain can be connected in three different ways, as follows:



Single bond Double bond Triple bond

Hydrocarbons in which the chain is formed exclusively of C–C units are named the *paraffin* hydrocarbons. The general formula of this family is C_nH_{2n+2}, and the names of all the compounds in the family end in *-ane*. Before proceeding with this chapter, the reader should review sections 10.7 and 11.2, where the characteristics of the paraffin series of compounds have been outlined.

Now we shall describe the *olefin* family, in which the chain of carbon atoms contains one C=C unit, and the *acetylene* family, in which the chain of carbon atoms contains one C≡C unit.

16. 2. The Olefin Hydrocarbons. The simplest hydrocarbon containing a double bond is ethene, $CH_2=CH_2$. This is a gas, and has been known for several hundred years. It had been known as *ethylene* until systematic methods for naming compounds were recently developed. According to our modern system, when the name of a compound ends in *ene* it indicates that the compound has a double bond in it, but the custom has not yet become universal, and many people still prefer the ending *ylene*.

The early chemists who first studied the properties of ethene discovered that it forms oily compounds when it combines with chlorine or bromine. The reaction will be found written out in section 15.2. Because of the oily nature of the addition product which is formed, ethene was known as the "oil-forming" or "olefiant" gas. This is why other hydrocarbons containing double bonds and related to ethene have been called, in general, *olefins*.

The simpler members of the olefin family are shown in table 16.1. Comparing the compounds in this table with the paraffins in table

TABLE 16.1. OLEFIN HYDROCARBONS

Name	*Molecular Formula*	*Structural Formula*	*Boiling Point °C.*
Ethene	C_2H_4	$CH_2{=}CH_2$	—102.4
Propene	C_3H_6	$CH_3{-}CH{=}CH_2$	—47.7
1-Butene	C_4H_8	$CH_3{-}CH_2{-}CH{=}CH_2$	—6.47
*2-Butene (*cis*)	C_4H_8	$CH_3{-}CH{=}CH{-}CH_3$	+3.73
*2-Butene (*trans*)	C_4H_8	$CH_3{-}CH{=}CH{-}CH_3$	+0.5
2-Methyl-1-propene	C_4H_8	$CH_3{-}C(CH_3){=}CH_2$	—6.6
†1-Pentene	C_5H_{10}	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$	+30.1

*The difference between *cis*- and *trans*-2-butene will be explained in section 22.3.
†Pentene is more often called amylene; four other isomers of the composition C_5H_{10} are known, but are not included in this table

10.2, it will be found that these olefins can be regarded as paraffin hydrocarbons with *one* double bond somewhere in the chain. The olefins form a homologous series of compounds, just like the paraffin series. The olefin series corresponds to C_nH_{2n}, for each compound contains two H atoms less than its analogous paraffin compound.

It is also apparent from the examples given in the table that, because of the double bond, there are more isomers possible in the olefin series than in the paraffin series. If the meaning of isomerism has become hazy to the reader it should be reviewed in section 10.5.

There are four isomers of the composition C_4H_8 in the olefin series, but only two of the composition C_4H_{10} in the paraffin family. Three of the four isomers of C_4H_8 are easy to figure out as being due to a straight-chain or branched-chain arrangement of the carbon atoms, or the position of the double bond. In the case of 2-butene, however,

we find a kind of isomerism which we have not yet met and to which we shall devote a separate section (section 22.3).

16. 3. The Acetylene Hydrocarbons. The simplest hydrocarbon containing a triple bond, H–C≡C–H, is *ethyne,* known more commonly as *acetylene.* Metal derivatives of acetylene are either *carbides* or *acetylides* (section 15.3).

Acetylene is the first member of a family of hydrocarbons, which, as usual, takes its name from that of the simplest member, and is consequently known as the acetylene series. It is a relatively unimportant series of compounds except for the first member, acetylene itself.

TABLE 16.2. ACETYLENE HYDROCARBONS

Name	*Molecular Formula*	*Structural Formula*	*Boiling Point °C.*
Ethyne	C_2H_2	CH≡CH	—83
Propyne	C_3H_4	CH_3—C≡CH	—23 3
1—Butyne	C_4H_6	CH_3—CH_2—C≡CH	+8.6
2—Butyne	C_4H_6	CH_3—C≡C—CH_3	+27 2
1—Pentyne*	C_5H_8	CH_3—CH_2—CH_2—C≡CH	+39.7

*The other possible isomers of pentyne have not been included in this table.

The acetylene hydrocarbons can be regarded as the corresponding paraffin series (table 10.2) with *one* triple bond somewhere in the chain of carbon atoms. Since each triple bond means the loss of four hydrogen atoms (section 14.1), the general formula for this series of compounds is C_nH_{2n-2} as compared with the formula C_nH_{2n+2} for the paraffins.

The names of all the compounds in the acetylene family end in *-yne.*

It is of interest to observe that in table 16.1 four isomeric olefin compounds were tabulated with the composition C_4H_8, but in table 16.2, only two acetylene compounds can be written for the composition C_4H_6. The presence of the triple bond has, in this case, limited the number of possible arrangements of the carbon atoms.

16. 4. Properties of Olefins and Acetylenes. The preparation and properties of compounds containing double bonds and triple bonds have already been described in chapters 14 and 15 and need not be

repeated. The student should keep in mind the following facts about C=C and C≡C groups:

1. They readily add on other molecules.
2. They are easily acted upon by certain oxidizing agents.
3. Their presence in a chain can be detected by agents which make use of the two preceding properties.
4. Their presence in a chain compound usually gives it greater reactivity.
5. The olefin and acetylene families are those compounds which contain only *one* double bond or *one* triple bond in an *open chain.* This is an important distinction, for C=C and C≡C groups can be present in other types of structures, such as ring compounds, which are not members of these families.

16. 5. Poly-enes and Poly-ynes. It is possible, of course, for a molecule to contain several (*poly*) double and triple bonds, as shown by the following examples:

$CH_2{=}CH{-}CH{=}CH_2$ — 1,3-Butadiene

$HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$ — 1,5-Hexa-di-yne

Butadiene will be discussed in section 18.1, where it will be shown to have unusual properties because of its alternate arrangement of double and single bonds. The most interesting thing about hexadiyne is that it is an isomer of benzene (section 19.1) the composition of which is C_6H_6.

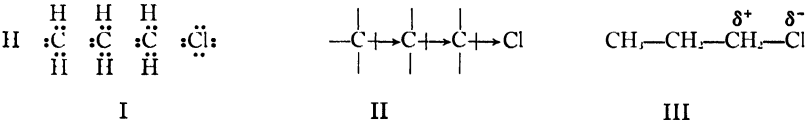
17. HOW MOLECULES REACT – AND WHY

17. 1. Reaction Mechanisms. Since the birth of organic chemistry over 100 years ago thousands of reactions have been tried simply to determine if they would take place. As a result, we now have an enormous literature which tells us what happens when various substances are mixed. As shown by articles in the current journals, the chemist is less satisfied than ever with the mere knowledge that certain reactions go; he also wants to know "what makes them go."

In this book, we have already described the generally recognized types of reaction mechanisms. In section 9.5, it was shown that the reaction between chloromethane (CH_3Cl) and silver nitrate ($Ag^+ NO_3^-$) is *ionic;* and in section 10.3, the action of sodium (Na) on chloromethane was explained as a *free-radical* mechanism. A third mechanism, described in section 8.5 in connection with the reaction between ammonia (NH_3) and boron trichloride (BCl_3), may be called *molecular;* this term may be applied to the simple union of whole molecules to form a larger molecule or to the reverse reaction by which a molecule dissociates to smaller molecules.

If the reactions referred to in the preceding chapters are reviewed, it will be apparent that they can be thoroughly understood only if we know the electron structures of the molecules involved. It is the purpose in this chapter to discuss briefly the language and symbols used in the interpretation of reaction mechanisms.

17. 2. Inductive Effect. From preceding chapters it will be recalled that molecules become more active when an *electron displacement* occurs. Thus, in section 10.1, it was said that CH_3Cl is more active than CH_4 because the Cl atom causes the displacement of an electron pair in such a direction as to make the Cl atom potentially ionic. A displacement, such as that described in section 10.1, makes itself felt throughout a chain of atoms, and the phenomenon can be represented



I II III

FIGURE 17.1. Methods of representing the inductive effect.

in several ways as illustrated in figure 17.1. In formula I, it will be seen that the electron pair between any two atoms is unequally shared; this can be shown, as in III, to be equivalent to a dipole (section 8.3) in which one atom has a minute positive charge ($\delta+$) whereas the atom toward which the displacement occurs acquires a minute negative charge ($\delta-$). The inductive effect can also be illustrated as in II, where the arrowhead points to the negative end of the dipole and the plus sign shows the positive end.

The *direction* of the inductive effect in a molecule can generally be predicted on the basis of the relative electronegativities listed in table 8.2. If an atom (or group of atoms) is more electronegative than the H atom, it is said to have a negative inductive effect ($-I$), whereas if it is less electronegative than hydrogen, and repels electrons more than the hydrogen atom, it has a positive inductive effect ($+I$). This will be discussed in more detail in section 21.7, in the study of benzene derivatives, and in section 31.6, in the study of acids.

The inductive effect prevails in the normal state of a molecule. It is essentially a phenomenon associated with the single valence bond. The electron pair (:), which is the normal valence bond, is displaced slightly when there is an atom in the molecule which exerts a greater or lesser attraction for the electron pair than the other atoms do.

17. 3. Electromeric Effect. When a molecule contains multiple bonds, an electron movement entirely different from that described in the preceding section is possible. In the inductive effect, an atom does not lose or gain an electron pair; it simply loses or gains *partial* interest in it. In what is known as the electromeric effect, however, an electron readjustment takes place which is equivalent to an actual shift of the electron pair from one position in the molecule to another. One atom gains *complete* control of an electron pair which was previously shared by two atoms. This second type of displacement, or electron-pair shift, is of far greater importance in the phenomena to be described in the rest of this book. Very shortly (see figure 17.3*b*), it will be shown that this displacement is due to mobility of certain electrons and that only one of these may be considered as shifted (see part (*e*) under figure 17.3*b*).

In the simple case of ethene, we can write electron structures as shown in figure 17.2, where I is the structure as usually represented

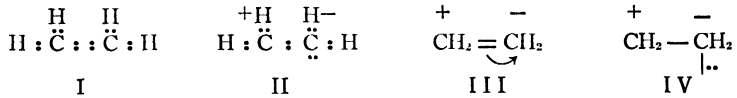


FIGURE 17.2. Methods of illustrating an electromeric effect.

and II is a possible structure in which an electron pair has shifted to a neighboring atom. Structures I and II are *electromers* (compare the term *isomers* in section 10.5). In III and IV methods are shown

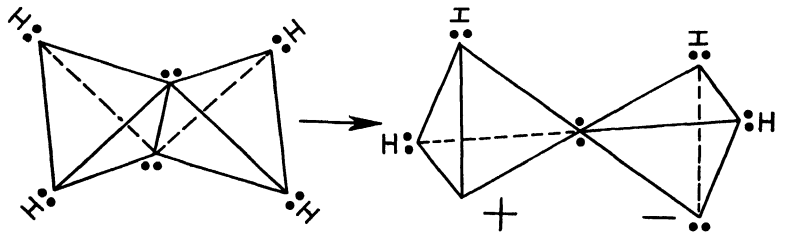


FIGURE 17.3*a*. Mechanical explanation of an electromeric effect in ethene.

for illustrating the new distribution of charges in the molecule; of these methods, IV will be used most in this book. A pictorial representa-

tion of the phenomenon will be found in figures 17.3 *a, b,* and *c* (and in figure 18.3).

The electromeric shift in ethene gives rise to a single bond between the carbon atoms (a point-to-point union shown in section 14.1) and also results in a dipole. The atom to which the electron pair shifts is often shown as in formula IV of figure 17.2, with the electron pair printed next to the new valence bond. A structure such as IV is termed a *polarized* molecule, and the ease with which the electron displacement takes place is called the polarizability of the molecule. It should be understood, of course, that the electromeric shift can occur not only as shown by formula III of figure 17.2, but also by a corresponding shift of the electron pair to the carbon atom on the left. (Still another type of electromeric structure, the *diradical,* will be described in section 26.4).

The fundamental nature of the electron-pair shift to produce a "free" valence bond is better understood by referring to the structure of ethene as arrived at by the method of molecular orbitals (see concluding paragraph in section 15.1*a*). It was shown that ethene may be writtten $H_2C{=}CH_2$ (also see section 26.3), where the straight line bond between the carbon atoms is a σ-type orbital, but the other bond is a pair of *p* electrons (in molecules referred to as π electrons) in a π-type orbital. The bonding energy of the π electron pair is only about 70 per cent of the bonding energy of the σ pair. The σ electrons in the "normal" bond are called *localized* electrons; the π electrons are said to be *mobile.* The π electrons account for the polarizability (and consequently the reactivity) of the ethene type of molecule. In figure 17.3*a* the free electron pair in the structure on the right of the diagram is the pair of π electrons (but see part (*e*) under figure 17.3*b*).

Figure 17.3*b* is a pictorial representation of electromeric effect on the basis of the method of molecular orbitals. This set of diagrams introduces the terms *bonding* and *antibonding* electrons, designations used in spectral analysis to differentiate these electron states in both σ and π types of orbitals. Since we are concerned only with the π electrons, further reference will not be made to the antibonding σ electrons, but figure 17.3*c* is added to give a more exact representation of the difference between the antibonding and bonding types of π orbitals. In the antibonding configuration, the electron surge

is away from the bond, whereas in the bonding state, the electrons are drawn to the region between the two atoms.

Atoms (and groups of atoms) have a positive electromeric effect ($+E$) when they tend to release electrons to the rest of the molecule,

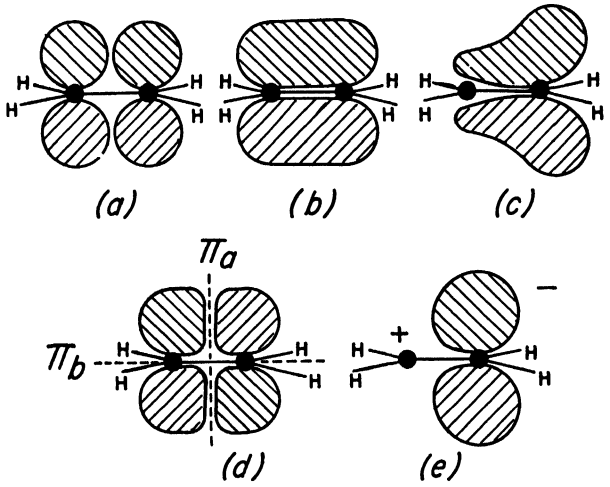
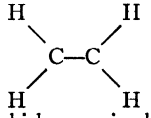


FIGURE 17.3*b*. Molecular orbital explanation of an electromeric effect in ethene.

(*a*) The two *p* atomic orbitals, perpendicular to the  structure. Each hourglass-shaped orbital contains one electron, which occupies both parts of the hourglass.

(*b*) Overlapping of the *p* atomic orbitals to give the π molecular orbital (a pair of sausages). The nodal plane contains the line which joins the two carbon nuclei. The shading represents the opposite (+ and —) phases of the wave functions in the two parts of the orbital. The orbital contains two electrons, both of which are called *bonding* (π_b) electrons.

(*c*) Partial polarization caused by a reagent molecule which raises the effective (positive) nuclear charge at one end of structure (*b*) and increases the electron (negative) density at that end. This *polarized* variation of the *ground* state of the ethene molecule should be distinguished from an electronically *excited* state shown in (*d*).

(*d*) Excitation (for example, by ultraviolet light at 1750 A) leaves one electron in the π_b orbital, but raises the other to a higher-energy orbital in which the electron is called *antibonding* (π_a.) The π_a orbital has a nodal plane which is at right angles to that of π_b orbital and in ethene, it is midway between the nuclei of the two carbon atoms. An excited structure such as (*d*) has a very short life of about 10^{-8} second. Although much energy is required to

create the π_a orbital in ethene, in more complex molecules (see figure 18.4 and 18.8), the π_a orbital may be present in the ground (stable) state. With such a molecule, a reactant particle which raises the effective nuclear charge on one end of the molecule displaces the π_a nodal plane in that direction; this is another aspect of *polarization*.

(*c*) Complete transfer of a π electron, consummating the process shown in (*c*). Two electrons now occupy one orbital (—), and although the other orbital is vacant (+) the illustration shows how the positively charged atom exerts a polarizing effect by its attraction for the electron cloud. This diagram shows the equivalent of the formula $+CH_2—\underset{\cdot\cdot}{C}H_2^-$ in figure 17.2. It is apparent that the electron *pair* now exposed to a reacting molecule is brought into position by transfer of a *single* π electron, although the phenomenon is generally referred to as the shift of a pair of π electrons.

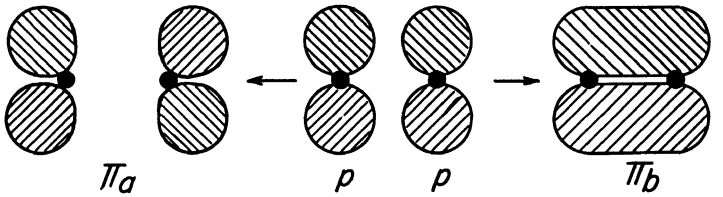


FIGURE 17.3*c*. Interaction of a pair of *p* atomic orbitals from two similar atoms, to give either antibonding (π_a) or bonding (π_b) molecular orbitals

Observe from the shading that when the *p* orbitals overlap to a *bonding* orbital, they do so "in phase," whereas in the *antibonding* orbital, the electrons are "out of phase." The nodal plane of π_b includes the nuclei of the two atoms. The nodal plane of π_a is at right angles to that of π_b.

The student is reminded that the hourglass (or dumbbell)) used to represent a *p* atomic orbital is a convention. The electron density (wave function) in each half of an orbital extends to infinity, and the spheres simply indicate the boundary surface at which it is negligibly small. The two *p* orbitals should be drawn to show that, at interatomic distances, they overlap somewhat, but this would confuse the diagrams shown elsewhere in this book; for example, in figure 18.4, where figure-8's are employed for the sake of clarity.

The slight gap between the two halves of a *p* or π orbital indicates the absence of electron density in the nodal plane.

and a negative effect (—*E*) when they attract the electrons from the rest of the molecule. In figure 17.4 the chlorine atom has a +*E* effect. An atom, such as chlorine, with unshared pairs of electrons, or a

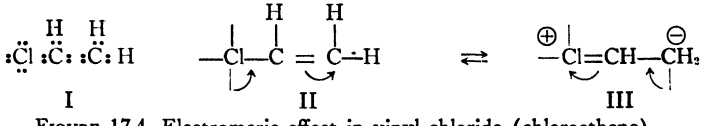


FIGURE 17.4. Electromeric effect in vinyl chloride (chloroethene).

multiple bond, such as C=C, is called an electron "source." An unsaturated atom or group, such as $=CH_2$ at the end of a molecule, is

an electron "sink." In structure II of figure 17.4, the Cl atom is an electron source, and CH_2 a sink; in structure III, these are reversed, that is, the CH_2 is a source and the Cl atom a sink. The unshared pairs of electrons on the Cl atom (see structure II) are said to be *conjugated* with the double bond in the molecule, because of the *alternating* arrangement of *unshared pair — single bond — double bond.* This will be better understood when conjugate systems are explained in section 18.1 and 18.10.

Each unshared pair of electrons on the Cl atom in structure I may be considered a *potential valence bond.* In structure II they are accordingly replaced by valence bonds. This convention with respect to unshared electron pairs and the convention with respect to indicating the positive and negative charges in the molecule, as in structure III, are described more fully in section 18.6, which the student should read at this point.

17. 4. Nucleophilic and Electrophilic Reagents. In section 8.5, which should be reviewed, the formation of a dative bond was illustrated by the following reaction:

$$H_3N: + BCl_3 \rightarrow H_3N \rightarrow BCl_3$$

In this reaction, the BCl_3 molecule is said to be *electrophilic,* which is a classical way of saying *electron-seeking.* The NH_3 molecule is electron-rich, and is willing to share the electron pair which is not actively used for bonding. An *electron donor,* such as the NH_3 molecule, is said to be *nucleophilic,* a term used to signify that such a molecule is ready to react with a molecule deficient in electrons in the sense of the octet theory (section 6.5), that is, has a tendency to fill up the quota of eight electrons in the valence shells of the atomic nucleus.

Positive ions (such as H^+) are electrophilic. Negative ions (such as $:\ddot{\underset{\cdot}{\underset{\cdot}{Cl}}}:^-$) are nucleophilic.

We can now reconsider the addition reaction to a double bond which was originally described in part *d* of section 15.2.

$$[CH_3{-}CH{=}CH_2] \rightleftarrows CH_3{-}\overset{+}{C}H{-}\overset{-}{C}H_2 \quad (\text{Propene}) \quad + \quad H:\ddot{\underset{\cdot}{\underset{\cdot}{Cl}}}:$$

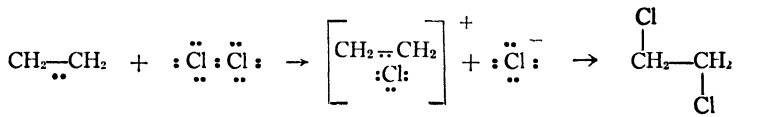
$$\rightarrow [CH_3{-}\overset{+}{C}H{-}CH_3] \quad (\text{A carbonium ion}) \quad + :\ddot{\underset{\cdot}{\underset{\cdot}{Cl}}}:^- \rightarrow CH_3{-}CHCl{-}CH_3 \quad (\text{2-Chloropropane})$$

The activation of the propene molecule, resulting in the displacement of electrons, called the electromeric effect, takes place at the instant the molecule is in collision with a polar reagent, such as hydrochloric acid. When the collision occurs, there is a distortion of the electrostatic field which aids the electron displacement.

Although the polarized form of propene is written to show that it has equal positive and negative charges (electrophilic and nucleophilic centers, respectively), the over-all behavior of the molecule is nucleophilic. It extracts the proton (H^+) from the HCl molecule to yield a reactive carbonium ion (section 24.5), which is then attacked by the nucleophilic Cl^- ion. The reaction takes place in steps. This electronic interpretation explains the rule in section 15.2 that molecules adding to double bonds usually do so with the negative half attaching itself to the carbon atom which holds the least hydrogen. This has long been known as Markownikoff's rule.

An olefin molecule like propene develops more readily a region of high electron density than does ethene, which, because of its highly symmetrical nature, is polarized with difficulty (see (*d*) under figure 17.3*b*, and see last paragraph in section 15.4). The addition of a halogen acid to ethene, however, takes place in the steps described for propene, that is, extraction of a proton and subsequent combination of the reactive carbonium ion with the negative half of the acid.

The addition of a halogen to the double bond likewise takes place in steps; a halogen molecule is in general an electrophilic reagent:



Ethene — A chloronium ion — 1,2-Dichloroethane

In the first step the π electron pair is the point of attack; it removes from the chlorine molecule a positive chloride ion $:\ddot{\underset{\cdot\cdot}{Cl}}^+$ to form a highly reactive intermediate ion which has a positive charge. In the subsequent reaction with negative halide ions which are in the reaction mixture, this intermediate yields the dichloro addition product. Presumably several intermediate reactions occur other than that shown here; for example, the positive chloronium ion may react with

a molecule of chlorine to remove a Cl^- ion (thus giving the final product) and leave Cl^+ ion in solution. This positive Cl ion would react with ethene to yield more chloronium ion. Analogous reasoning with respect to various possible reaction paths applies to the propene reaction with HCl described in the preceding paragraphs. These reactions will be referred to again in section 22.16.

In this discussion, we have examined in a general way the possible behavior of a molecule or molecular fragment with respect to its nucleophilic or electrophilic activity. In practice, these terms are applied to the *reagents* which are employed to attack a carbon compound, and the *reaction* is then also considered nucleophilic or electrophilic. The terminology is used mostly in connection with reactions in which substitution occurs for atoms or groups attached to carbon. The hydrolysis of methyl chloride, for example, is a nucleophilic reaction:

$$Na^+ \; :OH^- \; + \; \overset{\delta+}{CH_3} \; :\overset{\delta-}{Cl} \; \rightarrow \; CH_3 : OH \; + \; Na^+ \; :Cl^- \quad (S_N2 \text{ reaction})$$

The OH^- ion is nucleophilic, attacking the positive end of the polar CH_3Cl molecule, with which it shares its electrons, thus displacing the Cl^- ion. The symbol S_N2 means *substitution, nucleophilic, bimolecular.* The purpose in labeling the reaction bimolecular will be discussed in the concluding paragraphs of section 17.10 (see also sections 22.16 and 26.1).

Similarly, a substitution reaction in which the reagent is electrophilic is labeled S_E followed by a number which shows the order of the reaction. An example will be given in section 20.2. The school of chemists which introduced the terms *I* and *E* (sections 17.2 and 17.3) also projected into the literature of chemistry this S_N and S_E terminology as well as other symbols which we shall not discuss but which can be found in books devoted especially to the study of electron theory applied to organic chemistry. The use of the symbol *S* is rather unfortunate because the word *substitution* in organic chemistry (section 9.4) has in the past always been restricted to the substitution by a radical or other atom for the H atom in the C–H bond. In this newer nomenclature *S* represents replacement (displacement) of *any* atom or radical (X) in a C–X bond by another atom or radical.

17. 5. Chemical Reactivity. So far in this chapter we have pictured in a qualitative way *how* certain molecules react in accordance with the electron-valence theory. Now we shall develop, in an elementary way, the principles on which the *driving force* in a reaction can be estimated. Chemical reactivity is not an easy term to define. For example, when discussing the series of paraffin hydrocarbons, CH_4, CH_3–CH_3, CH_3–CH_2–CH_3, etc., we made the statement in section 10.7 that the smaller molecules react more rapidly than the big ones. This is not an exact statement, for by raising the temperature of a large hydrocarbon molecule, we may cause it to react faster with chlorine than a smaller molecule does at ordinary temperatures.

When speaking of the chemical reactivity of a certain substance, we therefore use relative terms, that is, we compare its behavior with that of some other substance under the same conditions. As in the preceding example, we may compare the rate at which the series of compounds reacts with a given substance (such as chlorine) under specified temperature conditions. Or conversely, we may measure the temperature to which each member of a series of compounds must be raised in order to react with a certain substance. These are only a few of many experimental methods available for measuring relative reactivities.

The physical chemists have developed a somewhat more definite measure of chemical reactivity in terms of *free energy,* which will be discussed in section 17.9. In order to prepare a background for this quantitative measurement of reactivity (that is, *why* molecules react), we must digress once more into the field of physical chemistry to review the meaning of thermochemical equations.

17. 6. Heat of Formation. In this book, we have shown how the conversion of one set of substances into another set can be expressed by means of symbols such as these:

$$CH_3—CH_3 + Cl_2 \rightarrow CH_3—CH_2Cl + HCl$$

and we have been careful to use an arrow sign to indicate the nature of the *reaction.* What we have written here cannot be called an *equation* because an essential factor has been omitted, that is, the extent of the energy or heat change.

Equations, however, can be written when the heat change is considered, as in the formation of carbon dioxide:

$$C(s) + O_2(g) = CO_2(g) + 94{,}400 \text{ cal.}$$
$$\text{or, } C(s) + O_2(g) = CO_2(g); \quad \Delta H_{298} = -94{,}400 \text{ cal.}$$

This thermochemical equation states that 1 atomic weight of carbon in the solid state (s) reacts with 1 molecular weight of gaseous oxygen (g) to yield 1 molecular weight of gaseous carbon dioxide (g) with the liberation of 94.4 kg. cal. (94,400 cal.) of heat. The symbol $\Delta H_{298} = -94.4$ kg. cal. indicates that this is the heat change at 298° K. or 25° C., the negative sign showing that heat is evolved in the reaction as read from left to right. The quantity 94.4 kg. cal. is called the *heat of formation* of carbon dioxide. The heat of formation is defined as the heat change when one mole of a substance is formed from its elements in their *standard states,* that is, their stable forms at ordinary temperature and a pressure of 1 atmosphere.

Conversely, in order to decompose 1 mole of CO_2, that is, to make the reaction go from right to left, requires the absorption of 94.4 kg. cal. This amount of heat energy is, therefore, taken to be a measure of the stability of the CO_2 molecule.

Similarly, the heat of formation of methane is given by the equation,

$$C(s) + 2\,H_2(g) = CH_4(g); \quad \Delta H_{298} = -18.1 \text{ kg. cal.}$$

And at this point we shall also insert the apparently unrelated information that the heat of atomization of carbon, *i.e.,* the heat required to vaporize it, is given by the equation,

$$C(s) = C(g); \quad \Delta H = 124.3 \text{ kg. cal.}$$

This last value will be used in some of the calculations to be given in section 18.3.

17. 7. Bond Energy. It has been found that the heat energy required to dissociate the hydrogen molecule into its atoms is given by the equation:

$$H\text{—}H = H + H; \quad \Delta H = 103.4 \text{ kg. cal.}$$

This, it will be seen, is a direct measure of the stability of the H–H single valence bond. Only in a few cases is it possible to obtain these

bond energy values directly for the single bond, but physical chemists have found that it is easy to calculate such values from the large amount of thermochemical data available for more complex compounds. The same thing is true of multiple bonds, like C=O, C=C, etc. In modern books on physical chemistry, one can find the data listed under *bond energy*. This is the heat energy required to disrupt the bond in 1 gram-mole of compound. A few values are listed in table 17.1.

TABLE 17.1 BOND ENERGIES AT 1 ATM. AND 291° K.

Nature of Bond	*Bond Energy* kg. cal./mole
H—H	103.4
H—Cl	102.7
C—C	58.6
C=C	100
C≡C	123
C—O	70
C=O*	152
C—H	87.3
O=O	118.2
C—Cl	66.5
C—F	107.0

*When the bond is present in compounds called ketones (section 30.1).

The data on which bond energies are based are obtained from thermochemical and spectroscopic methods. The reader going through the chemical literature is warned that he will find several different values for the same bond, depending on the interpretation of the original data. The values in the table were obtained from Pauling.

The reader is also warned as to the ambiguity in certain of the definitions in thermochemistry. In the equation,

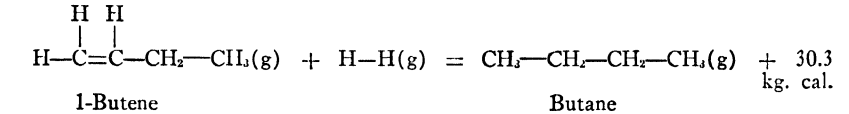
$$C(s) + 2\,H_2(g) = CH_4(g) + 18.1 \text{ kg. cal.}$$

we indicate that the elements carbon and hydrogen lose 18.1 kg. cal. of heat energy to the surroundings when they form one mole of methane. Methane, therefore, has less energy than its elements and energy must be supplied to it in order to decompose the molecule. It is called a stable molecule because of its relatively low energy content. In the chemical literature, the term heat of *formation* is often used interchangeably with heat *content* and this sometimes leads to

confusion; for example, 18.1 kg. cal. is simply the energy associated with the formation or decomposition of methane, but is not the energy in the molecule.

In the preceding table of bond energies, likewise, we do not mean that the H–H bond has an energy of 103.4 kg. cal. The actual energy content of this bond is relatively small as shown by the fact that considerable energy (103.4 kg. cal.) must be added to it in order to destroy it. The data in the table of bond energies indicate relative stabilities; a high bond energy means high heat of formation and great stability, but low actual energy content.

17. 8. Some Uses of Bond Energy Data. A comprehensive table of data, such as those in table 17.1, can be put to many uses in theoretical chemistry, of which we shall mention just two. In the first place, the data can be employed to estimate the heat change which occurs in a reaction when the information is not available in the literature. To illustrate this principle with a simple example, consider the equation for the hydrogenation of 1-butene:



The heat evolved in this hydrogenation reaction has been accurately determined, with all the substances gaseous at 1 atm. and at 355°K. (82°C.), and found to be 30.3 kg. cal./mole as indicated in the equation. If the data were not available it could be calculated from the data in Table 17.1, as follows:

Bonds broken	*Heat absorbed*
H—H	−103.4
C=C	−100
Bonds formed	*Heat evolved*
C—C	+ 58.6
2× C—H	+174.6
	Net heat evolved
	+ 29.8 kg. cal./mole

The heat of reaction, and of formation, varies to some extent with temperature. The current tendency is to record such data for measurements made uniformly at 25°C. (298°K.). Much of the data in

the handbooks are for a temperature of 18°C. (291°K.), and some data, as shown in the preceding example, are obtained at such unusual temperatures as 82°C. The variation over a range of as much as 50° is usually less than 0.1 kg. cal./mole, so that data from various sources can generally be used for approximate calculations without temperature correction.

Another application which may be mentioned briefly is the calculation of the relative electronegativities in table 8.2. With data available for the bond energy of such *normal covalent* bonds as H:H and C:C, it may be assumed that half the bond energy of each of these, when added together, should give the bond energy of C:H. From the data for H–H and C–C in table 17.1 the energy of the bond C–H calculated in this way is ½(103.4 + 58.6) or 81.0 kg. cal. The deviation from the listed value of 87.3 kg. cal. for this bond is interpreted as being due to deviation from *normal covalent* behavior. The C:H bond has partial ionic character due to the difference in the relative electronegativities of the two atoms, that is, difference in attractive power for the electron pair. By ingenious arithmetic the experts have translated such deviations into the set of values shown in table 8.2.

17. 9. Chemical Reactivity and Free Energy. In this chapter we have made frequent use of thermochemical equations, that is, equations which indicate the extent of heat changes in chemical reactions. In so doing, we showed that the stability of a molecule or of a particular bond in that molecule may be stated in terms of its heat of formation. For example, the heat of formation of methane is given by the equation,

$$C(s) + 2\,H_2(g) = CH_4(g);\ \Delta H_{298} = -18.1 \text{ kg. cal.}$$

and this heat change is a measure of the stability of the CH_4 molecule in that the equation also shows how much heat energy must be added to methane in order to decompose it.

This *thermochemical stability* should not be compared too closely with chemical reactivity, as already pointed out in section 15.10. Although the two factors are often closely related for certain compounds, there are many instances in which they are quite different. A quantitative measure of chemical reactivity is furnished by the *free energy change* in a reaction rather than by the *heat change* of

the reaction. We can introduce the reader to free energy at this point, because the technical language and equations employed are similar to those used throughout this chapter. If we make a slight change in the chemical reaction which we wrote in the preceding paragraph,

$$C(s) + 2\,H_2(g) = CH_4(g);\ \Delta F_{298} = -12.2 \text{ kg. cal.}$$

we find we have a new symbol in a familiar background. The symbol $\Delta F_{298} = -12.2$ kg. cal. indicates that the reaction between solid carbon and gaseous hydrogen to form a molecule of methane is accompanied by a decrease in free energy of 12.2 kg. cal. at 25° C. (298° K.). This heat change is equivalent to the driving force in the reaction. It is said to be a measure of the chemical *affinity* of carbon and hydrogen under these conditions.

Substances will react with each other without outside help (that is, spontaneously) only if the reaction takes place with a decrease in free energy. Some external means, such as a catalyst, may be required to start the reaction, but it then proceeds spontaneously. Methane cannot decompose spontaneously, because the preceding reaction written in reverse is:

$$CH_4(g) = C(s) + 2H_2(g);\ \Delta F_{298} = +12.2 \text{ kg. cal.}$$

The free energy change is positive and energy would have to be added to methane in order to break it up.

The *sign* of ΔF (whether + or —) indicates in which direction reaction takes place spontaneously. The *size* of ΔF gives a rough idea of the extent to which reaction takes place. When $\Delta F = 0$ the system is in equilibrium.

The free energy change (ΔF) of a reaction is important to physical organic chemists, because it is directly related to the equilibrium constant (K), which is the quantitative value of the chemical reactivity of a system. The relation between the free-energy change and the equilibrium constant of a reaction is given by

$$-\Delta F = RT \times 2.303 \log K \qquad (17.1)$$

The following example shows how the free-energy change for the methane decomposition (just described) can be calculated from the equilibrium constant. When methane was heated at 400° K. at constant atmospheric pressure, the equilibrium constant was found to be

$$K_p = \frac{p_{H_2} \times p_{H_2}}{p_{CH_4}} = 2.86 \times 10^{-4} \qquad (17.2a)$$

The data show that the decomposition $CH_4 \rightarrow C + 2H_2$ proceeds at this temperature only to a very small extent (about 0.17 per cent by volume of H_2 is present in the gas). When the value of Kp from equation 17.2*a* is substituted into equation 17.1, it is found that ΔF_{400} is + 10.150 kg. cal. per mole.

For another useful illustration, the free energy of the reaction between ethene and hydrogen is shown by the equation

$$C_2H_4(g) + H_2(g) = C_2H_6\,(g);\ \Delta F_{298} = -24.1 \text{ kg. cal.}$$

and the extent of the reaction in the gas phase at constant pressure is given by the equilibrium constant

$$K_p = \frac{p_{C_2H_6}}{p_{H_2} \times p_{C_2H_4}} \qquad (17.2b)$$

By substituting the value of ΔF_{298} in equation 17.1, the value of Kp at 25°C. and 1 atmosphere pressure is found to be 5.65×10^{17}, so that the reaction is essentially complete with respect to the formation of ethane under these conditions.

The reader will observe that $-\Delta F$ for methane (its free energy of formation) is considerably smaller than the $-\Delta H$ value (its heat of formation). These two energy factors are related as follows:

$$-\Delta H = -\Delta F - T\Delta S$$

This means that in any reaction the total decrease in heat energy ($-\Delta H$) consists of a decrease in useful energy ($-\Delta F$), and a decrease in useless energy ($-T\Delta S$). T is the temperature of the reaction, and ΔS is the symbol for *entropy*, that elusive term concerning which further information can be found in texts on physical chemistry.

17. 10. Chemical Kinetics and Activation Energy. The discussion in the preceding section is based on the thermodynamics (equation 17.1) and the equilibrium constant (equation 17.2) of a typical chemical reaction. Neither of these factors is concerned with the mechanism by which the reaction takes place; they involve only the initial and final states of the system without regard to the speed or route by which the equilibrium state is reached. The study of reaction mechanisms and reaction speeds is called *chemical kinetics*.

An obviously important factor in respect to reaction velocities is the frequency with which molecules collide. Under ordinary reaction conditions and concentrations, this is a factor which is amply provided for. As an illustration of the magnitude of collision frequency,

when nitrogen is at a pressure of 1 atmosphere at 25°C., there are 2.46×10^{19} molecules per cubic centimeter and pairs of molecules are colliding at the average rate of 7.8×10^{28} times per second.

Most reactions in organic chemistry are slow. Since frequency of collision of the molecules as indicated here is tremendous, it must be concluded that very few molecular encounters lead to chemical reaction. Reactions in inorganic chemistry (if we restrict the discussion to the chemistry of ions) generally take place so fast that their speed cannot be measured readily. When Na^+ Cl^- and Ag^+ NO_3^- are mixed in equal molecular quantities in aqueous solution the reaction yields Na^+ NO_3^- and insoluble Ag^+ Cl^-. In each gram-mole there are 6.02×10^{23} particles of each species, yet they find partners, and react, practically instantaneously.

The difference between the reaction speeds in organic chemistry (molecules) and inorganic chemistry (ions) can be attributed to the difference in the degree of activation of the reacting particles. The first sentence in section 17.2 states that "molecules become more active when an electron displacement occurs." Since ions are the product of *complete* displacement of an electron pair (sections 9.6 and 10.3), an ionic "molecule" can be regarded as in a state of complete activation when dispersed in a solvent; such a molecule is Na^+ CH_3^-. The molecule CH_3Cl can be activated, as indicated in section 9.5, but CH_4, of course, is difficult to activate.

This theory of activated molecules can be placed on a quantitative basis by considering the energy values involved. To break up the ionic crystal lattice of Na^+ Cl^- shown in figure 8.1 and to disperse the ions in aqueous solution requires the expenditure of energy per gram-mole comparable to the energies listed in table 17.1. This activation energy is supplied by the phenomena accompanying solvation of the crystal and is retained as potential energy by the hydrated ions until called upon for further chemical reaction. To activate organic molecular reactions, the common means in an organic chemistry laboratory is the use of the Bunsen burner, which supplies energy in the form of heat. However, we can show from equation 13.3 that the kinetic energy of one mole of a gas is raised only to

the extent of 0.3 kg. cal. (300 cal.) if its temperature is raised 100°C. A reaction of the type

$$A\text{–}B + C\text{–}D \rightarrow A\text{–}C + B\text{–}D$$

is said to require an activation energy equivalent to 28% of the energy required to dissociate both AB and CD into their constituent atoms. Roughly, a bimolecular reaction, with an appreciable reaction speed at ordinary temperatures, requires an activation energy of about 20,000 cal. per mole. The usefulness of a Bunsen burner in the laboratory must, therefore, have some other explanation than the in-

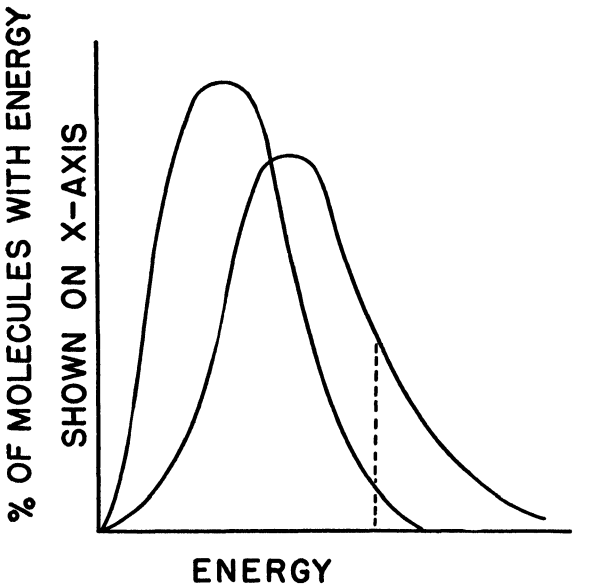


FIGURE 17.5. Typical Maxwellian distribution of energy among molecules of a gas at two temperatures (curve at right is for the higher temperature). To the right of the dotted line are the molecules having abnormally high energy (at least 10 kg. cal./mole) and capable of chemical reaction.

crease in kinetic energy (calculated previously) which it supplies; this will be discussed further in the following.

The fact that a certain organic reaction is slow means that few molecular encounters lead to chemical reaction; the fact that the reaction takes place at all, however, means that at any one time some of the molecules have the energy required for the reaction to occur.

This can be explained by the kinetic theory, according to which a series of collisions in the same direction will give any one molecule an abnormally high velocity (energy). The most probable distribution of velocities among the molecules of a substance is given by the Maxwell distribution law; this can be converted to an analogous expression for distribution of energies. In a fixed number of molecules (see figure 17.5), at any instant, the relative number of molecules with very low or very high energies is extremely small.

A slow reaction is due to lack of a sufficiently large number of molecules in the region to the right of the dotted line. The total area under each of the curves is constant (same total number of molecules), so that at higher temperatures, it will be seen, there is a considerable increase in the number of high-energy molecules. In fact, the increase is so great that at ordinary temperatures, a 10° rise in temperature doubles the speed of many reactions. This is the reason why using the Bunsen burner increases the rate of reaction (see comment above on the energy supplied by the burner).

According to modern theory, a reaction always takes place by way of the intermediate formation of an "activated complex," which can be illustrated as follows:

$$\underset{\text{Reactants}}{\text{A—B + C—D}} \rightarrow \underset{\text{Activated complex}}{\left\{\begin{matrix}\text{A—B}\\ \text{C—D}\end{matrix}\right\}} \rightarrow \underset{\text{Products}}{\text{A—C + B—D}} \qquad (17.3)$$

The energy change required to form the complex and set the stage for breaking bonds and forming new ones is called the activation

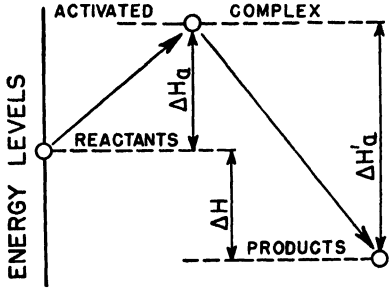


FIGURE 17.6. Energy levels in a chemical reaction. (Adapted by permission from F. Daniels, *Outlines of Physical Chemistry*, John Wiley and Sons, 1948)

energy, ΔH_a. The intermediate complex has a very short life of about 10^{-13} second. The relation between the heat of activation ΔH_a and

the heat of formation ΔH, which was discussed in section 17.6, is shown diagrammatically in figure 17.6 for an exothermic reaction, that is, one in which heat is evolved or ΔH is negative.

The heat of activation $\Delta H'_a$, shown in figure 17.6, applies to the reverse reaction; that is, to transform the products back to the reactants requires absorption of energy equivalent to the height of the line $\Delta H'_a$ before reaction takes place. ΔH is the difference between $\Delta H'_a$ and ΔH_a.

Mention may be made of the methods available for calculating ΔH and ΔH_a. They will be considered together because of the striking resemblance between the formulas used. The heat of formation (or reaction) can be found by determining the equilibrium constants K_1 and K_2 for the reaction (compare equation 17.2) at two different temperatures T_1 and T_2, and applying equation 17.4. The heat of activation is calculated similarly from the velocity constants k_1 and k_2 at two temperatures, and applying equation 17.5.

$$2.303 \log \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textit{Heat of formation} \qquad (17.4)$$

$$2.303 \log \frac{k_2}{k_1} = -\frac{\Delta H_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textit{Heat of activation} \qquad (17.5)$$

Calculation of the equilibrium constant K has already been described. The velocity constant k refers to the rate of change in the concentration of reactants or products. If the concentration of a reactant is c at time t its rate of disappearance is $-dc/dt$. For the reaction in equation 17.3, the rate equation is

$$\text{rate} = -dc/dt = kc_A^{\alpha}\ c_{CD}^{\beta} \qquad (17.6)$$

The sum of the values of the exponents ($n=\alpha+\beta$) in the rate equation is called the *order of the reaction.*

The reaction between the CH_3Cl molecule and the OH^- ion in section 9.4 is an example of a *bimolecular* reaction in organic chemistry. It would be called an S_N2 reaction according to the terminology in section 17.4. The reaction is second order, since it is first order with respect to each reactant (α and β are both 1 in equation 17.6). Frequently, a reaction as written may not be at all representative of the actual order of the reaction calculated from the rate equation.

This may lead to new discoveries regarding the mechanism of the reaction; an example will be discussed in section 26.1 in connection with the hydrolysis of compounds closely related to CH_3Cl, which actually are found to hydrolyse by a *unimolecular* mechanism, although on paper one would expect bimolecular behavior.

The electronic interpretation of the mechanism of a bimolecular reaction, that is, the formation of an intermediate activated complex (equation 17.3), is of considerable importance because it also helps to explain several related phenomena. This discussion will be found in section 22.16.

For a long time, it was thought that unimolecular reactions did not exist, but some are now known which follow the rate law

$$-dc/dt = kc^n \qquad (17.7)$$

where n is the order of the reaction. The decomposition of nitrogen pentoxide, $2N_2O_5 \rightarrow 2N_2O_4 + O_2$, is an example of a reaction in which the order n is equal to 1. In this case, the activated complex consists of only one molecule rather than two as shown in equation 17.3. For the *para*-hydrogen to *ortho*-hydrogen conversion mentioned in section 45.1, the order of the reaction is 1.5, an illustration of the fact that n in rate equations is not necessarily a whole number.

17. 11. Photochemistry. Methane (CH_4) and chlorine react slowly when mixed in diffused daylight, but, if such a mixture is prepared in a bottle which is then rolled into the sunlight, it may explode because of the rapid reaction that takes place (see last paragraph of section 10.7). This is an extreme example of the efficiency of radiation when used to supply energy of activation to a chemical reaction. One of the advantages of this method of activation is that radiation (such as visible radiation or ultraviolet radiation) permeates the reaction mixture and reaches the reacting molecules instantly, whereas raising the temperature of a reaction mixture to speed up the reaction is essentially a slow process.

In order to activate a reaction by radiation, one must select a wavelength which is absorbed by one of the molecular species. If a molecule can absorb the radiation completely, the absorbed energy is converted into heat. The excess energy in the irradiated molecule may be given up by collision with other molecules, thus increasing their kinetic energy, it may be released by collision with the walls of the

retaining vessel, or it may be used in a chemical reaction. The efficacy of the radiation is, therefore, calculated in terms of the *quantum yield* Φ as follows:

$$\Phi = \frac{\text{number of molecules reacting chemically}}{\text{number of quanta absorbed}}$$

The energy quantum was discussed in section 13.13, which should be reviewed. The quantum absorbed by an individual molecule is $\varepsilon = h\nu$. One mole of quanta is equal to $Nh\nu$ and is called an *einstein.*

The efficiency of a source of light which is to be used in a photochemical reaction is measured with an *actinometer,* such as that which employs uranyl oxalate. It has been determined that light in the wavelength range of 2540 to 4350 Å will decompose 0.57 mole of oxalic acid for each einstein absorbed, when the solution contains uranyl sulfate and oxalic acid at certain concentrations. The uranyl ion does not react chemically, but simply absorbs energy and transfers it to the oxalic acid. After a light source has been calibrated with such an actinometer, it can be used to determine the Φ value for other photochemical reactions.

17. 12. Chain Reactions. A few examples of photochemical reactions which take place at ordinary temperatures are the following:

$$2\ HI \xrightarrow{\textit{Radiation at about } 3000\ A} H_2 + I_2 \qquad \Phi = 1$$

$$H_2 + Cl_2 \xrightarrow{\textit{Radiation at about } 4000\ A} 2\ HCl \qquad \Phi = 100{,}000$$

The first reaction is very simple; each molecule that absorbs a quantum of energy decomposes without secondary reactions. The enormously great quantum yield in the second reaction can be explained on the basis that it is a *chain* reaction which takes place in these steps:

$$Cl_2 + h\nu \rightarrow 2\ Cl \qquad (a)$$
$$Cl + H_2 \rightarrow H + HCl \qquad (b)$$
$$H + Cl_2 \rightarrow Cl + HCl \qquad (c)$$

The quantum of radiation in reaction (a) causes a Cl_2 molecule to dissociate into free chlorine atoms, which are *free radicals* as discussed in section 10.3 and are in an excited state. A chlorine atom has sufficient energy of activation to react with a molecule of H_2 ac-

cording to reaction (b), which results in a free hydrogen atom. Reaction then takes place as in (c) and the cycle represented by (b) and (c) continues until the energy of the quantum absorbed in (a) is dissipated, or until the chain is broken by one of the activated molecules colliding with the walls of the reaction vessel or with a molecule of impurity.

It is obvious that a small amount of impurity will have a relatively great effect in stopping a chain reaction, especially if the chain is a long one; for example, one molecule of an impurity which absorbs the energy of a Cl_2 molecule immediately after it is activated by reaction (a) may prevent the formation of 100,000 molecules of HCl. Tetraethyllead is added to gasoline as such an *inhibitor*. The combustion in a gasoline engine is a chain reaction, which causes engine knock (section 10.8) when the reaction goes too fast, but is controllable by trace amounts of the inhibitor.

17. 13. Abnormal Addition to C=C Bond. This is a subject which depends for its explanation on most of the topics discussed in this chapter. In section 17.4, it was stated that HCl adds in accordance with Markownikoff's rule to an unsymmetrical olefinlike propene. The mechanism of the reaction, as described, is ionic; this is normal behavior and should be reviewed.

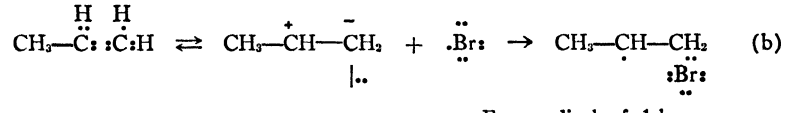
It has been found that HBr differs from HCl in that it will add normally to propene only if the reaction is conducted in the absence of certain catalysts, principally air. In the presence of oxygen (air) or in the presence of organic peroxides, HBr adds in an abnormal manner:

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H{-}Br \;\nearrow\; CH_3{-}CHBr{-}CH_3 \text{ (Normal "Markownikoff addition")}$$
2-Bromopropane

$$\underset{\text{Propene}}{CH_3{-}CH{=}CH_2} + H{-}Br \;\searrow\; CH_3{-}CH_2{-}CH_2Br \text{ (Abnormal "peroxide addition")}$$
1-Bromopropane

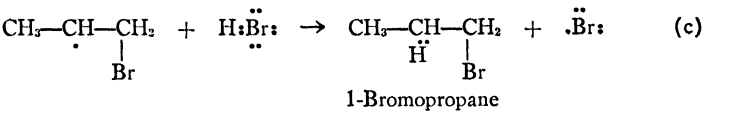
The mechanism of the abnormal addition to propene has been thoroughly studied and is believed to be a free-radical chain reaction, which may be assumed to take place in the following steps:

$$H{:}\ddot{\underset{\cdot\cdot}{Br}}{:} + {:}\ddot{\underset{\cdot\cdot}{O}}{:}\ddot{\underset{\cdot\cdot}{O}}{:} \longrightarrow \underbrace{{:}\ddot{\underset{\cdot\cdot}{O}}{:}\ddot{\underset{\cdot\cdot}{O}}{:}\,H \;+\; \ddot{\underset{\cdot\cdot}{Br}}{:}}_{\text{These are free radicals}} \qquad \text{(a)}$$



(b)

Free radical of 1-bromopropane



(c)

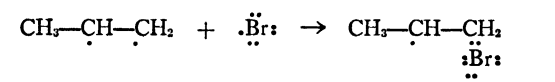
1-Bromopropane

When a molecule of oxygen (or of an organic peroxide) sets free a bromine atom in reaction (a), the activation energy introduced initiates a reaction chain. The chain is propagated by the excited bromine atoms as indicated by the cycle of reactions (b) and (c); free bromine atoms are used up in (b) and are born again in (c). The chain persists until the energy introduced by the molecule of oxygen is exhausted, and it can be nearly completely prevented by inhibitors which react with organic peroxides or with bromine atoms. An example of such an inhibitor is diphenylamine (section 33.2).

In (a) it is assumed that the presence of propene causes a molecule of oxygen to decompose the HBr molecule to form bromine atoms. Now, it was shown in section 17.4 that the negative chloride *ion* attacks the middle carbon atom of propene because of its positive charge; it is probable that the free bromine *atom* attacks the terminal carbon atom because of the high electron density at that point. In so doing, it "uncouples" an electron from one of the electron pairs of the original double bond (the π electrons discussed in section 17.3) and the result of the interaction is a free radical as indicated in (b). This organic free radical is capable, like oxygen, of decomposing HBr into free bromine atoms, as shown in (c). When the free bromine atom in reaction (b) attacks the propene molecule, the action may be regarded as one in which the unpaired electron on bromine couples with that π electron which is of opposite spin; the other π electron is then repelled to another point in the molecule.

If the student will read section 26.4 at this point, he will find that the propene molecule can also be written as a *diradical,* a *dot-dot* structure similar to that of the oxygen molecule shown in reaction

(a). Using such a structure we can write an equation to replace reaction (b), thus,



(b′)

which on paper, at least, looks more reasonable than reaction (b).

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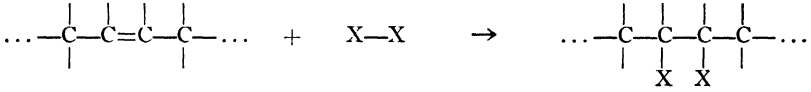
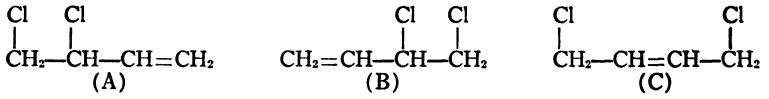
18. FROM PARTIAL VALENCE TO RESONANCE

18. 1. The 1,4-Addition Reaction. The trouble with many of the rules in chemistry is that they cannot always be trusted. Perhaps that is what makes them so interesting. The principal rule we hoped the reader would carry with him from chapter 15 is the one regarding compounds containing $-\overset{|}{C}=\overset{|}{C}-$ groups. It was explained that such compounds add on other molecules, and that addition takes place across the double bond:



After reading these pages, it will be evident that there is an exception to this rule which is almost as important as the rule itself.

An important structure in organic chemistry is 1,3–butadiene, $CH_2=CH-CH=CH_2$, which has double bonds at the first and third carbon atoms as indicated in its name. One of its derivatives has a methyl group on carbon atom 2; its name is isoprene and it is of so much importance in nature that we shall devote an entire chapter to it (chapter 37). Now 1,3–butadiene does not behave normally in reactions with certain substances. If we added one molecule of chlorine to 1,3–butadiene we should expect it to add on across *either one* of the double bonds, as shown in (A) or (B):



Instead, the product obtained is largely that shown in (C).

This has been found to be a common occurrence among compounds of a certain type in which there is an alternate series of double bonds and single bonds in the chain:

$$\ldots\text{—}CH_2\text{—}CH{=}CH\text{—}\underset{1}{CH}{=}\underset{2}{CH}\text{—}\underset{3}{CH}{=}\underset{4}{CH}\text{—}CH_2\text{—}\ldots$$

In such cases, when only one molecule is added to the compound this molecule usually adds on to a large degree across the carbon atoms labeled 1 and 4, and a new double bond then appears between 2 and 3. This is what happens when Cl_2 is added to 1,3-butadiene.

The alternate double and single bond arrangement is important enough to have been given a special name. It is called a *conjugate*

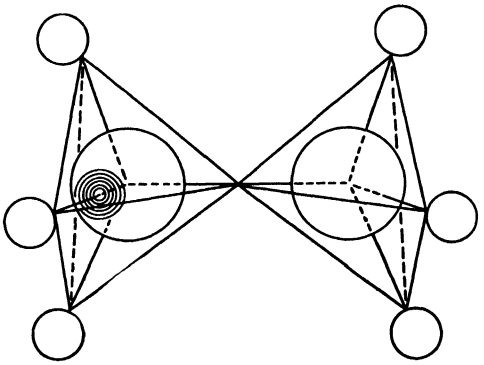


FIGURE 18.1. Single bond between carbon atoms, as in ethane, $H_3C—CH_3$.

system, and the addition reaction to such a system is generally called 1, 4 addition.

18. 2. Partial Valence. Toward the close of the last century, Thiele showed that addition to double bonds can be explained by a theory which he called the theory of partial valence. The carbon atom (according to the theory) is supposed to be spherical, with valence force radiating from the center in straight lines. Although this valence

force is assumed to be distributed over the surface of the atom as indicated by the shaded area in figure 18.1, the directional effect is equivalent to four valence bonds radiating to the corners of a regular tetrahedron. When the carbon atom is linked to four identical atoms, as in CH_4, there is an even utilization of the valence force on the surface of the sphere.

Figure 18.2, however, shows that, according to the Thiele theory, the valence force of a bond like that designated A is not completely utilized when carbon atoms are linked by a double bond. Valence forces radiate from the atomic center in straight lines, but from elementary physics we know that a force can be resolved into several component forces by the parallelogram method, as illustrated in the figure. Thiele assumed that only the component B takes an active part in linking the carbon atoms in ethene, with some valence force left over designated by C.

Thiele, accordingly, explained the chemistry of ethene by writing the formula as $CH_2{:}{:}CH_2$, using dotted lines to indicate the fact that the carbon atoms have some residual valence force left over, and the dotted lines were called "partial valence bonds." That was his way of expressing the nature of the reactivity of carbon atoms when they

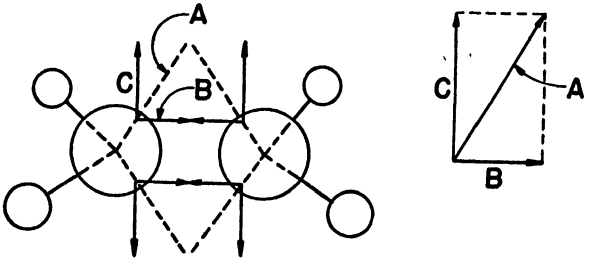
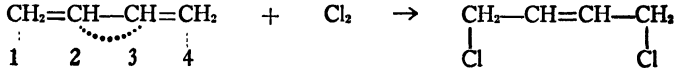


FIGURE 18.2. Double bond between carbon atoms, as in ethene $H_2C{:}{:}CH_2$.

are linked by more than one bond. The addition reaction is then written as follows:

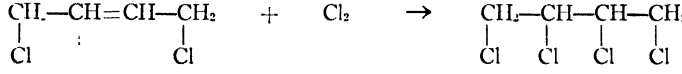
$$CH_2{:}{:}CH_2 + Cl_2 \rightarrow \begin{matrix} CH_2 & CH_2 \\ | & | \\ Cl & Cl \end{matrix}$$

One of the best uses of the partial valence theory has been its application to conjugate systems. This is the way the theory explains the behavior of 1,3–butadiene:



It is assumed that the neighboring valences marked 2 and 3 react on each other to form a loose bond, leaving 1 and 4 open as the only reactive centers in the molecule. Then, after 1, 4 addition has taken place, a normal double bond is formed between 2 and 3.

If another chlorine molecule is added to the dichloro product, the addition takes place in the customary manner:



To the expert, the theory of partial valence is now merely a "matter of historical interest," but the theory still offers to the novice a good elementary picture of the mechanism by which addition takes place to compounds, like butadiene, which contain conjugate systems.

For a more modern explanation of the nature of the conjugate system, we must discuss the phenomenon of resonance. This however, requires a brief study of a few thermochemical equations of the kind described in section 17.6, which should now be reviewed.

18. 3. Calculation of Heat of Formation of Methane, $\begin{matrix} & H & \\ & | & \\ H-&C&-H \\ & | & \\ & H & \end{matrix}$.

We should be able to arrive at the heat of formation of methane by summing up the energy of the four C—H bonds in methane as given in table 17.1, namely, $4\times87.3=349.2$ kg. cal. This should be identical with the experimental value of the heat of formation of CH_4 which is $\Delta H = -18.1$ kg. cal., but before we can compare the two figures, we must recalculate the second value on the basis of the heat of formation from the *atoms,* that is, C(g) + 4H(g), rather than from solid carbon and molecular hydrogen, C(s) + $2H_2$(g). The

calculation is easy to follow as shown below, using only data (in equations 1, 2, and 4) which can be found in section 17.6 and in table 17.1:

Equation						
1.	$C(s)$	+	$2H_2(g)=CH_4(g)$			+ 18.1
2.	$C(s)$		$=C(g)$			— 124.3
3. (1. minus 2.)			$2H_2(g)=CH_4(g)$	—	$C(g)$	+ 142.4
3. (rearranged)	$C(g)$	+	$2H_2(g)=CH_4(g)$			+ 142.4
4.			$2H_2(g)=4H(g)$			— 206.8
5. (3. minus 4.)	$C(g)$	+	$4H(g)=CH_4(g)$			+ 349.2 kg. cal.

The result obtained is thus found to be in complete agreement with the theoretical value obtained by adding the energies of the four C–H bonds, as stated before.

18. 4. Calculation of Heat of Formation of Carbon Dioxide, CO_2 or O=C=O. This calculation should also give agreement between the experimental value and the theoretical value obtained by adding up the bond energies, *but it fails to do so.* The sum of the bond energies is twice the value of the C=O bond shown in table 17.1, that is, $2 \times 152 = 304$ kg. cal. The experimental value is given in the literature for the reaction,

$$C(s) + O_2(g) = CO_2(g); \Delta H = -94.4 \text{ kg. cal.}$$

We can recalculate this to the *atom* basis just as we did for methane, as follows:

Equation						
1.	$C(s)$	+	$O_2(g)=CO_2(g)$			+ 94.4
2.	$C(s)$		$=C(g)$			— 124.3
3. (1. minus 2.)			$O_2(g)=CO_2(g)$	—	$C(g)$	+ 218.7
3. (rearranged)	$C(g)$	+	$O_2(g)=CO_2(g)$			+ 218.7
4.			$O_2(g)=2O(g)$			— 118.2
5. (3. minus 4.)	$C(g)$	+	$2O(g)=CO_2(g)$			+ 336.9 kg. cal.

For the CO_2 molecule we thus find a discrepancy between the experimental heat of formation of the molecule, 336.9 kg. cal., and the theoretical heat of formation calculated on the basis of two C=O bonds, which is 304 kg. cal. The reason for this difference of 32.9 kg. cal. is explained in the following.

18. 5. Resonance. It has been found that for molecules like methane, $H-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-H$, and ammonia, $H-\overset{H}{\overset{|}{N}}-H$, we always get satisfactory agreement between the experimental heat of formation and the theoretical value obtained by adding up the separate bond energies of the normal valence bonds.

When the experimental and theoretical heats of formation do not agree, we find that the molecule does not have a *definite* structure. The carbon dioxide molecule illustrates this phenomenon; it has an *indefinite* structure, by which is meant that several different valence bond structures can be written for it. The more important of these structures are:

$$\underset{(b)}{O\text{—}C\equiv O^{-+}} \qquad \underset{(a)}{O=C=O} \qquad \underset{(c)}{O^{+-}\equiv C\text{—}O}$$

The implications of these formulas can be made much clearer by using the tetrahedral models for CO_2 as shown in figure 18.3, where (*a*), (*b*), and (*c*) correspond to the three valence bond formulas.

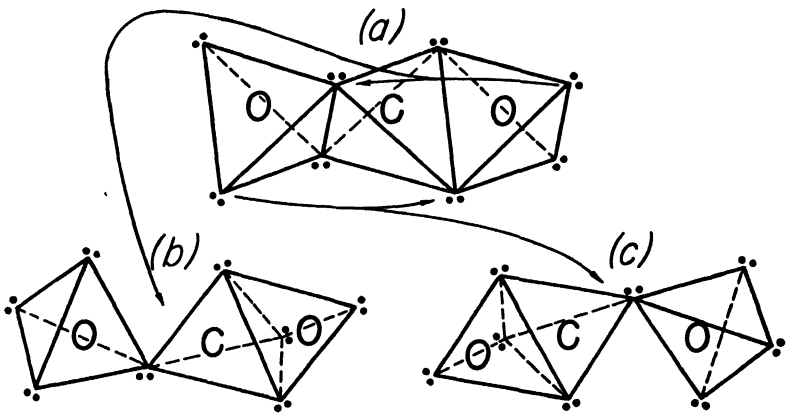


FIGURE 18.3. Mechanical explanation of resonance of carbon dioxide.

Figure 18.3 shows how it is possible to write structures for CO_2 in which one of the O=C bonds changes to the O≡C bond simply by

rotation of the oxygen atom on its edge-to-edge union with carbon to form a face-to-face union (see section 14.1 for these terms). This can be followed readily by means of the arrow signs. The change can take place through either of the C=O bonds as shown and it consists simply of transfer of electrons from one part of the molecule to another, *the relative positions of the atoms with respect to each other remaining unchanged.* The shift of electrons causes a displacement of electric charge which we represent by the structures $^{-}O\text{–}C{\equiv}O^{+}$ and $^{+}O{\equiv}C\text{–}O^{-}$. These are polar molecules, but opposite in effect, and necessarily cancel each other to give the CO_2 molecule the zero dipole moment listed in table 8.1. We shall refer again to this electron shift in section 18.6.

From these remarks on the carbon dioxide molecule, it will be evident that it ought to exhibit *average* properties which satisfy the requirements of several plausible valence-bond structures. This is

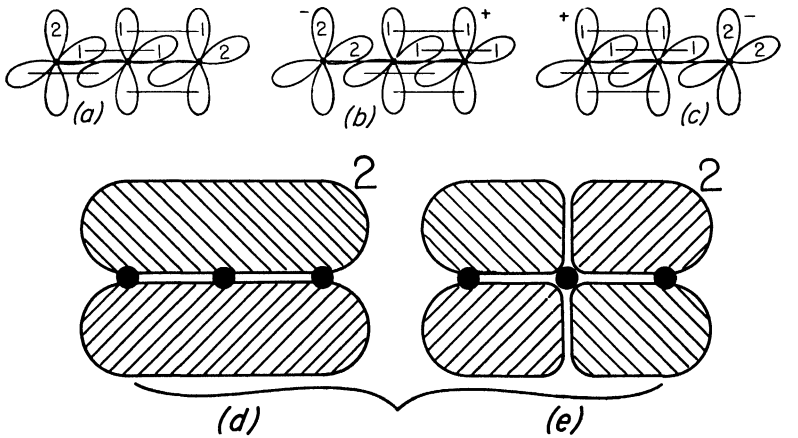


FIGURE 18.4. Resonance of carbon dioxide (O=C=O) according to the theory of molecular orbitals. The numbers indicate how many electrons are present in a given orbital. Overlapping of the *p* orbitals is represented by tie-lines.
Structures (*a*), (*b*), and (*c*) correspond to those in figure 18.3. More electron pairs are shown in figure 18.3 because the *s* electron pairs are included in that figure.
(See comments under figure 17.3*c*).

found to be the case, not only for carbon dioxide, but also for many other compounds. The phenomenon is called resonance.

The fundamental properties by which resonance of a molecule can be recognized (energy, bond length, etc.) will be discussed later

in section 18.8. We shall now continue to examine the resonance phenomenon pictorially, using the molecular orbital approach as shown in figure 18.4. The carbon-atom valences in CO_2 have the digonal symmetry mentioned in section 15.1*a*, and, when the carbon atom is linked to two other atoms, the orbitals in the valence shell hybridize (table 7.1) to *sp*, *sp*, *p*, and *p* orbitals. The molecule can then be constructed on the basis of the following electron distribution:

$$\begin{matrix}(s)\\(p)\,.\,\ddot{\mathbf{O}}\,.\,(p)\\(p)\end{matrix} \qquad \begin{matrix}(p)\\(sp)\,.\,\dot{\mathbf{C}}\,.\,(sp)\\(p)\end{matrix} \qquad \begin{matrix}(s)\\(p)\,.\,\ddot{\mathbf{O}}\,.\,(p)\\(p)\end{matrix}$$

Normal bonds of the *sigma* type result by overlapping of *p* and *sp* orbitals and yield the outline structure O–C–O, which is shown in figure 18.4 (*a*). The carbon atom still has two *p* atomic orbitals, each with one electron. Each of the oxygen atoms has a filled *s* orbital (spherical) which is omitted from the diagrams. One of the hourglass-shaped *p* orbitals on each oxygen atom has only one electron, but the other *p* orbital has two electrons. The single electrons in the *p* atomic orbitals pair off by overlapping of their orbitals to give molecular *pi* orbitals exactly as illustrated in figure 15.3 (*e*) and (*f*). It will be observed that the π orbitals in figure 18.4(*a*) have a common center line through OCO, but the nodal plane of the π orbital on the right is perpendicular to the plane of the paper, whereas the nodal plane of the π orbital on the left is the plane of the paper. The structure in figure 18.4 (*a*) can be written O⩧C⩧O, where the dots are two pairs of the π electrons which were described in section 17.3 as having considerable mobility.

We have not yet referred to the *p* orbitals that contain two electrons. Structure (*b*) in figure 18.4 is possible through shift of an electron from the pair in the *p* orbital of the oxygen atom on the right of structure (*a*). The oxygen atom on the right, having lost an electron, is marked with a positive charge, and the oxygen atom on the left, having acquired an electron, is labeled with a negative charge. The formula can be written $^{-}$O–C⩧O^{+}, analogous to that of ethyne in figure 15.4 and section 15.1*b*.

Structure (*c*) in figure 18.4 is the same as (*b*) except that it is reversed, namely, $^{+}$O⩧C–O^{-}.

From this discussion, it would appear that the resonance phenomenon is an equilibrium state in which the various possible electronic structures of a single molecule take part. The two or more electronic structures that can be written for a molecule are often called *electromers* (section 17.3). It is of interest to note that, if an equilibrium state existed among various structures, each structure would necessarily have the very short life cycle of 10^{-13} second, the rate of oscillation of an electron.

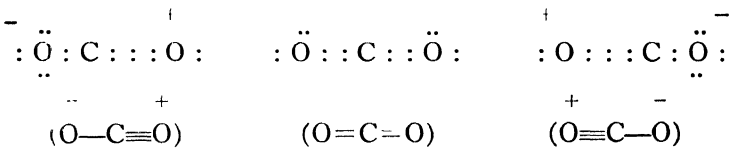
Authorities on this subject consider a molecule which shows the resonance phenomenon to be an average molecule; it is a single structure with the average properties of all the possible structures. For this reason, resonance is often called *mesomerism,* from the Greek word *mesos,* meaning intermediate. This is better explained on the basis of the molecular orbitals in figure 18.4 than with the tetrahedral atoms in figure 18.3. Consider structure (*a*) in figure 18.4, which shows three *p* atomic orbitals (vertical on the printed page) in the optimum state to permit overlapping. Although they are drawn flat in the plane of the page, they should be visualized as neighboring hourglasses. Four electrons are distributed among these three orbitals. When they overlap, they create π orbitals shown in (*d*) and (*e*). The orbital in (*d*) contains two of the electrons and the orbital in (*e*) contains the other pair. The orbital in (*d*) has a nodal plane at right angles to the page and is a *bonding* orbital as explained in the text under figure 17.3*b*. The structure in (*e*) shows an orbital which has two nodal planes at right angles to each other; one of the electrons is the bonding type (π_b) and the other is *antibonding* (π_a). The π_a nodal plane can be displaced, as explained in paragraph (*d*) under figure 17.3*b,* providing a path to and fro through the molecule for a mobile electron.

The stable state of the CO_2 molecule is represented by the orbitals in figure 18.4 (*d*) and (*e*). The term *resonance* implies that the electrons in the molecular orbitals are mobile, and the structure of the molecule is such that *the electrons may encompass more nuclei than the normal two.* In the case of CO_2 the π electrons are not restricted to two nuclei but encompass three, and may appear at either end of the molecule. In the case of benzene (section 19.7), the π electrons normally assigned to a pair of nuclei will be found to en-

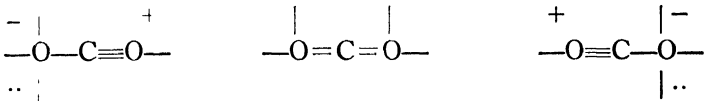
compass six. According to the resonance theory, there is no oscillation between structures (*a*), (*b*) and (*c*). This will be discussed again at the close of the chapter.

18. 6. Electric Charge on Structures in Resonance. The + and − signs used in writing the formulas of structures in resonance should not lead the reader to assume that they are to be classed with ionic compounds. They belong to the polar covalent compounds in which transfer of a single electron produces an excess of one negative charge in that part of the molecule to which it has moved, leaving an equivalent positive charge of one. As explained in section 17.3, this movement of an electron is equivalent to the *apparent* shift of an electron *pair* in formulas as usually written. In chemical shorthand, the polarity of the molecule is indicated thus, $^{+}O{\equiv}C{-}O^{-}$.

A clearer method of chemical shorthand is to write the "resonating" structures according to the electronic procedure in which each pair of electrons constitutes a valence bond, thus:

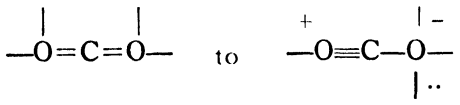


Since each electron pair is either an actual or a potential valence bond, another shorthand method is to write

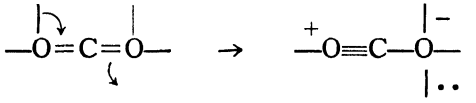


This last method is the best one for the reader to master because it is frequently used in modern literature. The valence bonds indicate either electron pairs actually shared between atoms or unshared electron pairs, that is, potential valence bonds, and an electron pair is shown on that atom to which the final shift has been made.

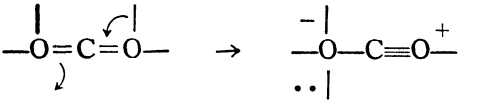
As usually written, the change from



looks as if the bonds flip-flop through the molecule, thus

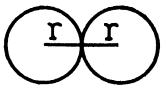


or,



and, as a matter of fact, this is the usual mental picture when writing the various electronic configurations of a molecule. The final effect is that a pair of electrons makes its appearance in a different part of the molecule in the form of a new potential valence bond. This will be illustrated in some detail in section 21.5.

18. 7. Bond Length and Atomic Radius. The distances between the atoms in normal covalent molecules have been quite accurately measured for many valence bonds by a number of methods which include X-ray study of crystals, and electron-diffraction and spectroscopic study of gaseous molecules. For example, it has been found that the bond distance in C–C is close to 1.54 A in a large variety of carbon compounds (A is the Angstrom unit, or 10^{-8} cm., a distance first used in section 8.3 and table 13.2). For the corresponding double bond C=C, the distance between the atomic centers is 1.33 A and for the triple bond, C≡C, it is 1.20 A. Similarly for the oxygen bond O=O, the distance is 1.10 A.

Now it has been demonstrated that one-half the distance between the atoms in a valence bond may be taken as the effective *atomic radius,*  , where r is the radius. Therefore, if we simply add up the atomic radii of two atoms we can determine the bond length between them. By adding the atomic radius for carbon in C=C, and oxygen in O=O, we can find the bond length for C=O. This is 1.33/2 + 1.10/2 = 1.22 A, using the data which we have just cited.

18. 8. Criteria of Resonance. It was just shown that the *theoretical* distance between the atoms in the double bond C=O in the mo-

lecule of CO_2 is 1.22 A. When *experimentally* determined, however, this distance is found to be 1.15 A. The reason for this shortened bond can be found in figure 18.3, where it is seen that the average distance between atomic centers is necessarily decreased because of the shorter bonds in the polarized structures. This is even more apparent from figure 18.4, where it was explained that the *p* orbitals in structure (*a*) will overlap to give structures (*d*) and (*e*). Coalescence of these orbitals readily explains the shortened bond distances between the atoms.

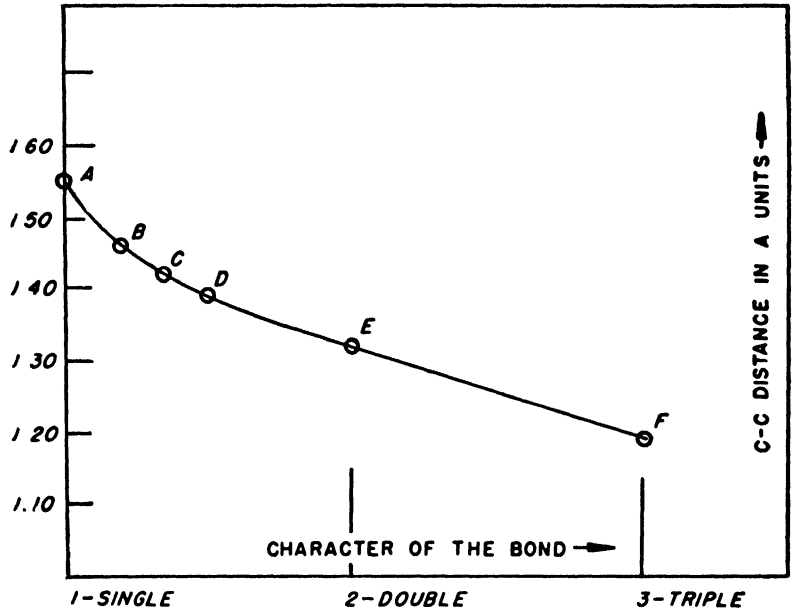
Shortened bond length is one of the two important criteria of resonance. When two or more equivalent structures can be written for a compound, it is found that the bonds are shorter than those calculated for the "normal" structure. In the case of carbon dioxide, the over-all length of the molecule is much shorter than that corresponding to the structure O=C=O as it is usually written.

The second important criterion of resonance is increased stability. A compound for which resonance structures can be written is always more stable than we would expect it to be on the basis of the structure which we normally assign to it. It was stated in section 18.4 that the CO_2 molecule has a measured heat of formation of 336.9 kg. cal., which is more than 10 per cent higher than the value of 304 kg. cal. which it ought to have on the basis of the structure O=C=O. The difference between the actual heat of formation of the molecule and the theoretical value calculated from the bond energies is called the *resonance energy* (32.9 kg. cal. in the case of CO_2). This resonance energy indicates the extent of stabilization given to the molecule by the various structures which are said to be in resonance.

A compound will have resonance energy if the various electronic structures which we can write for it have similiar energy contents. For example, we showed that the theoretical stability of the O=C=O structure corresponds to a heat of formation of 304 kg. cal. (the sum of two C=O bonds) and similarly it can be shown that the stability of the $^{-}O-C{\equiv}O^{+}$ and $^{+}O{\equiv}C-O^{-}$ structures is equivalent to a heat of formation of 285 kg. cal. (75 for the C–O bond, and about 210 for the C≡O bond, which is not accurately known, but is probably close to the heat of formation of carbon monoxide from its atoms). The structure of greater stability, that is, lower energy content, will have

the greater effect on the properties of the molecule. If the preceding calculations are correct, the properties of CO_2 are due almost equally to the three structures we have written for it. The resonance effect is maximum (that is, *complete*) when the several electronic structures are of *equal* energy content (see benzene, section 19.3).

These observations on resonance energy are in accord with fundamental laws of bodies in motion, namely, (1) a body adjusts its



A - Ethane, $H_3C—CH_3$
B - Butadiene (section 18.9)
C - Graphite (section 19.6)
D - Benzene (section 19.3)
E - Ethene, $H_2C=CH_2$
F - Ethyne, $HC\equiv CH$

FIGURE 18.5. Relation between character of the bond and distance between carbon atoms.

motion so as to reach a minimum energy level, and (2) greater freedom of motion results in a lower energy level. The hydrogen molecule in figure 7.3 illustrates these laws. As shown in table 17.1, energy of 103 kg. cal. must be added to the H:H molecule to break it down to the two H atoms. That much energy was given up by the two atoms when they combined to form the molecule; when the elec-

trons became partners, they (1) developed a system of lower energy content, and (2) each obtained greater freedom of motion by encompassing two nuclei instead of only one.

Similarly, in the carbon dioxide molecule of figure 18.4 (*d*) and (*e*) the resonance energy is the energy liberated as a result of greater freedom of motion of the electrons, which can encompass three nuclei instead of the two indicated in figure 18.4 (a) before overlapping of orbitals takes place.

18. 9. Calculation of Resonance Effects from Bond Lengths. The result of resonance, as we have just seen for O=C=O, is that a bond which does not behave definitely as a single or double bond, but assumes some intermediate character, will also show an intermediate length. The extent to which this shortening of the bond takes place can be measured, as we have just shown, and a considerable amount of data is now available for the distance between carbon atoms in many types of compounds. Some representative data are shown in figure 18.5. In this figure, a smooth curve has been drawn through the data for ethane ($H_3C–CH_3$), ethene ($H_2C=CH_2$), and ethyne ($HC\equiv CH$), which can be taken as standards, that is, the carbon-carbon distances in these molecules are not affected by the presence of disturbing factors which often affect the distance in more complex molecules.

When data for compounds which have been shown to be in resonance are plotted on this same scale, they fall on the curve as indicated. This is quite interesting, for it enables us to determine quantitatively the extent to which resonance affects a compound. For example, in 1,3-butadiene, $CH_2=CH–CH=CH_2$, the length of the normally single bond between the second and third carbon atoms has been found to be 1.46 Å, and from the position of this point on the curve it can be estimated that it has about 18 per cent of double bond character because of resonance. The resonance effects in this compound are, therefore, relatively small.

In figure 18.6 are shown models which conform with the best present information as to the distances between the nuclei of the atoms and the valence angles between the atoms. The models are constructed on a scale of 100,000,000 to 1, so that 1 cm. in the model represents 1 Angstrom unit in the actual molecule. An Angstrom unit is

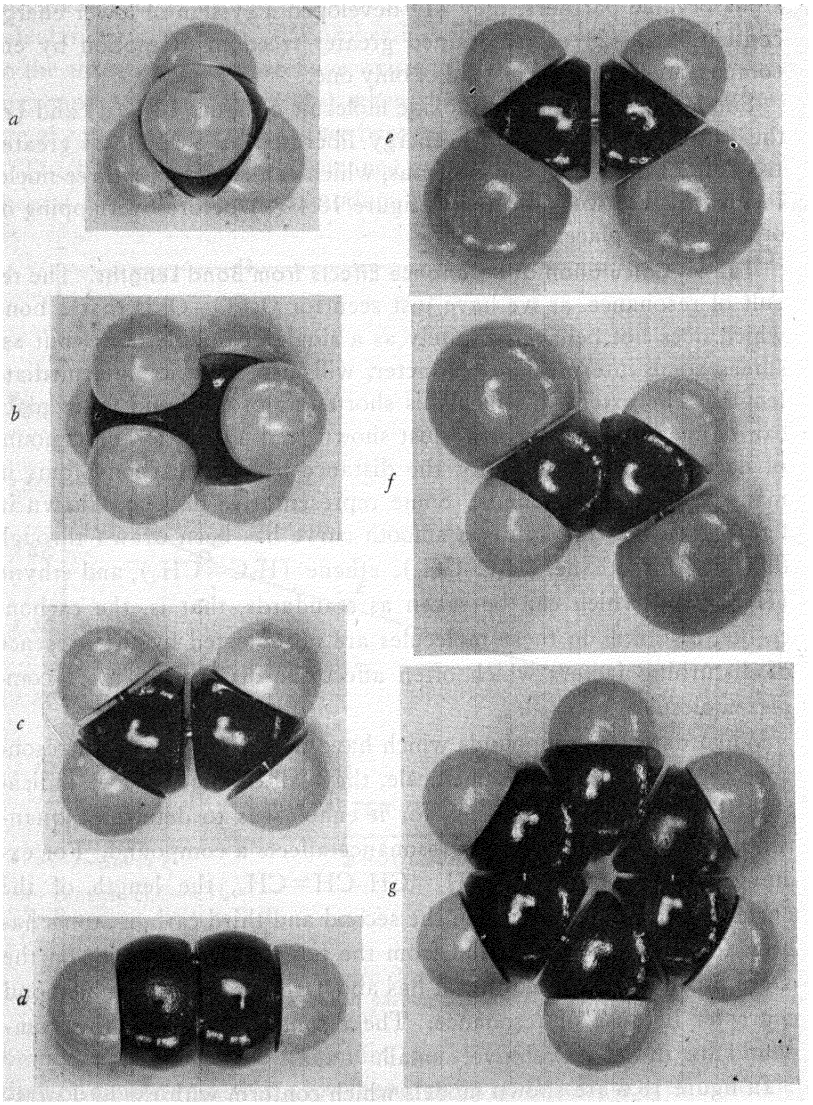


FIGURE 18.6. Fisher-Hirschfelder molecular models.

a. Methane (figure 12.1.)
b. Ethane (section 9.7.)
c. Ethene (figure 15.1.)
d. Ethyne (section 14.2.)
e. cis-Dichloroethene (section 35.3*b*.)
f. trans-Dichloroethene (section 35.3*b*.)
g. Benzene (section 19.2.)

equal to 0.000,000,01 cm. A more complex molecule of this type is shown in figure 46.4.

These molecules, consisting of atoms linked by electron-pair bonds, should be compared with the molecule of silver bromide (figure 8.2), which consists of ions linked by electrostatic attraction.

18. 10. Conjugate Systems. In the discussion of butadiene, we have returned to our starting point in this chapter, namely, the conjugated system. We discussed resonance in considerable detail, because it will be used in later chapters to explain important phenomena, such as the structure of benzene (section 21.5), all of which are concerned with conjugated systems of single and double bonds, $-X=X-X=X-X-X-$, where X stands for atoms like C, N, O, etc.

In butadiene, the single bond between carbon atoms 2 and 3 has a small amount of double bond character. This is experimental fact, showing that resonance takes place to a small extent. In order to picture the possible resonance structures derived from the "normal" formula, we can flip-flop the valence bonds to give the *polarized* structures shown in figure 18.7. The explanation of 1,4 addition to

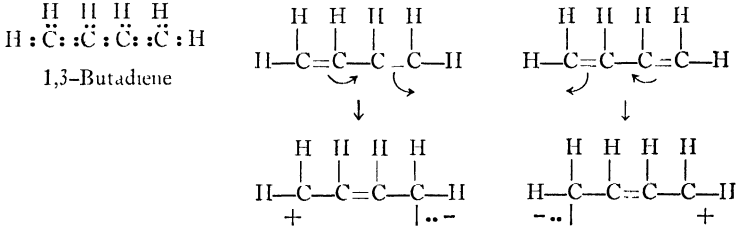
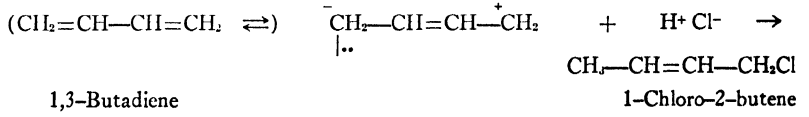


FIGURE 18.7. Flip-flop procedure for working out polarized structures of butadiene.

butadiene follows the same argument already used in sections 17.3 and 17.4, which should be reviewed. The polarized structures are electron donors, and promote attack by an electrophilic reagent (such as H^+) at one end of the conjugate system. This leaves the other end of the molecule open to add on the other fragment of the reagent, and a stable double bond appears in the 2,3 position:



It should be observed that 1,4-pentadiene (see section 18.11), in which the double bonds are not conjugated through *one* single bond, cannot have its valence bonds flip-flopped.

This discussion of the resonance of butadiene will be concluded by referring briefly to the pictorial representation of the molecule

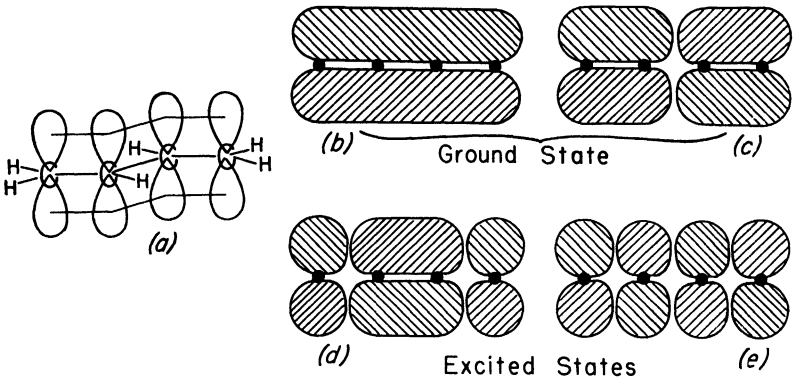


FIGURE 18.8 Resonance of 1,3-butadiene according to the theory of molecular orbitals. The *p* atomic orbitals on the carbon atoms in (*a*) should be visualized as hourglasses rather than as flat figure-8's. Overlapping of *p* atomic orbitals is represented by tie-lines.

(*a*) The nuclei of all the C and H atoms are in one plane at right angles to the page and to the *p* orbitals.

(*b*) Two π_b electrons are in this molecular orbital.

(*c*) Two electrons at slightly higher energy level are in this molecular orbital, which has two nodal planes. One electron is bonding (π_b) and the other antibonding (π_a) (review part (*d*) under figure 17.3*b*).

(*d*) An excited structure, with one electron in each of the π_a orbitals, and two still in the π_b orbital.

(*e*) An excited structure, with one electron in each of the three π_a orbitals, and one remaining in the π_b orbital.

(See comments under figure 17.3*c*.)

according to the method of molecular orbitals. In figure 18.8 (*a*) the normal bonds between the atoms are of the *sigma* type, built up from sp^2 hybrid atomic orbitals of the carbon atom, just as shown for ethene in section 17.3 and figure 17.3*b*. On each of the four carbon atoms, there is left one *p* atomic orbital; they can yield a system of lower energy if they overlap. In seeking this lower energy level, the molecule becomes planar, that is, the H atoms and C atoms are in a plane which is also the nodal plane of the *p* orbitals and is perpen-

dicular to the printed page. The p orbitals are then in neighboring positions (because they are at right angles to the nodal plane) and can coalesce as in figure 18.8 (b). Although the molecule is planar (flat), it does zigzag; however, the planar nature of the molecule permits mobility of the π electrons in the π orbitals of figure 18.8 (b) and (c), where four electrons encompass four nuclei. This is a more stable arrangement than that in which the electrons are isolated on individual atoms.

The ground state of butadiene is the resultant of the orbitals represented by (b) and (c). If the molecule is excited by absorption of light, the higher (excited) energy levels are represented by the orbitals in (d) and (e).

18. 11. Resonance and Heat of Hydrogenation. The discussion of the heat of hydrogenation of 1-butene should now be reviewed in section 17.8, where it was shown that addition of hydrogen to the double bond is accompanied by evolution of 30.3 kg. cal. of heat when 1 mole of each reagent is used. Experiment has shown that this is the usual extent of the heat change when a double bond in a compound like butene is hydrogenated. If there are two double bonds in the molecule, the heat evolved on hydrogenation should be twice as great, or 60.6 kg. cal. per mole, but it has been found that if the double bonds are conjugated, the rule is not followed. This is illustrated by the following compounds:

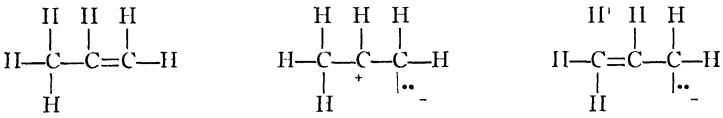
$CH_2=CH—CH=CH_2$ Heat of hydrogenation to butane = 57.1 kg. cal.
1,3-Butadiene

$CH_2=CH—CH_2—CH=CH_2$ Heat of hydrogenation to pentane = 60.8 kg. cal
1,4-Pentadiene

The heat of hydrogenation of 1,3-butadiene is 3.5 kg. cal. lower than one would expect it to be. This is a quantitative measure of the increased stability of the molecule due to its conjugated system (alternating double and single bonds) with the resultant resonance possibilities. Since there are no resonance forms for 1,4-pentadiene, it gives the expected heat of hydrogenation.

18. 12. Hyperconjugation, or No-bond Resonance. There is still another way of writing an electromeric or resonance structure for

certain molecules. This can be illustrated with propene (sections 17.4 and 17.13), as follows:



Normal form A resonance structure A "no-bond" resonance structure

The theory of no-bond resonance is needed largely to explain the results of dipole-moment measurements on certain compounds. The essential feature is that some molecules tend to lose a hydrogen ion which remains within bonding distance, as shown by the formula for propene, the electron pair which formerly bound the proton now making itself evident elsewhere in the molecule to give the molecule polar characteristics. The phenomenon is also known as *hyperconjugation*, and will be referred to later (section 21.7).

18. 13. Partial Ionic Character. If the student will now review sections 17.2 and 17.3, he may find that he is somewhat confused by the overlapping in the ideas expressed in those places and the ideas presented in this chapter on the resonance theory. In chapter 17 it was shown that a molecule in its normal state may be polarized by an inductive effect, and that in certain types of molecules the polarization may be due to an electromeric shift as the result of approach of an attacking reagent molecule. The electromeric structures are identical in all respects with those postulated in the resonance theory, except for the factor of "actuality." The resonance theory simply states that a molecule may behave as if it had a hypothetical average of all the theoretical structures we can write for it on paper, whereas electromeric forms are definite structures which we believe are actually present at the instant of reaction with other molecules.

Electromeric forms are written with double arrows ⇄ connecting them, to show that one structure can be changed into the other by the external conditions. A resonance hybrid is perhaps most clearly visualized in the benzene molecule, which is a hybrid of two Kekulé structures (section 19.3). Such a phenomenon is represented by writing the theoretical structures side by side, or by connecting them with a double-headed arrow ◂ —▸.

Even though we do not regard resonance structures as forms that can be isolated, if plausible valence-bond configurations can be written which show *polarization* of the molecule, it means that the molecule has what may be considered "partial ionic character." Separation of charge brings about a lower stability, that is, greater reactivity. Polarized structures were written in section 18.10 for the 1,3-butadiene molecule, whose properties are reasonably well accounted for by the resonance theory. One of the polarized *resonance* structures of 1,3-butadiene shown in section 18.10 was regarded as an *electromeric* form in the chemical reaction which was described.

SUGGESTED READING

See references at the end of chapters 7 and 17.

19. THE BENZENE RING

19. 1. Introduction. At the time when Michael Faraday, the famous English scientist, was preoccupied with the problem of liquefying gases, a new illuminating gas industry had arisen in London. The Portable Gas Company was distilling inflammable gases from whale and cod oil, and compressing the gases in portable vessels which could then be employed in private dwellings for lighting purposes.

In 1825, Faraday investigated the liquid in some of these vessels and separated from it a new compound containing hydrogen and carbon. Its composition (in modern symbols) he found to be C_6H_6, and it had a melting point of 5° C. and boiling point of 80° C. The chemical industry holds this substance in such high esteem that 100 years later a celebration was held, and many essays extolled the virtues of both the compound and its discoverer.

In 1834, a chemist obtained the same compound from a plant substance called *gum benzoin,* and accordingly C_6H_6 was named *benzin.* In 1837, still another chemist proposed the name *phene,* from the Greek word *phainein,* meaning bring to light, because the substance was first found in gas used for lighting purposes. Neither of these names has been adopted. At present the compound C_6H_6 is known as *benzol* in most European countries, and as either *benzene* or benzol in America. However, many compounds derived from benzene are

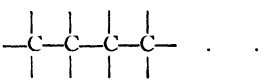
named as derivatives of *phene,* examples of which are phenol, phenacetin, thiophene, etc.

In 1845, the presence of benzene in coal tar was discovered. Coal tar is the black, oily mixture which separates from the gases generated in the distillation of coal for lighting purposes. Coal tar varies considerably in composition, but benzene is always one of its most important ingredients, and is obtained from the tar by a fractional distillation.

It was soon observed that benzene, C_6H_6, shows a distinct fatherly relationship to an enormous number of compounds that were being isolated in nature, or being prepared in the laboratory, like the famous coal-tar dyes. But just when it seemed that chemistry was in a position to grow by leaps and bounds, chemists realized that they were trying to advance in the dark without a guiding star; outside of its composition, C_6H_6, the nature of benzene was still a complete mystery. Anyone who has read the first portions of this book can understand the difficulties in working with a substance without a knowledge of its outline structure.

In 1865, a satisfactory formula for benzene was invented, and that date marks the beginning of modern progress in organic chemistry.

If the reader will review the last 100 pages quite rapidly, he will notice that their most prominent feature is a chain of carbon atoms,



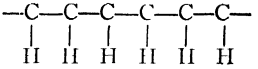
We have been describing these chains so glibly that perhaps the impression has been gained that such structures go back to the earliest days of chemistry. That is far from the truth. It required much speculation, from 1803 to 1858, before chemists were able to visualize the valence force of an atom in the form of a straight-line bond, as it is given in the preceding formula. That great step forward was made by a Scot, named Couper.

However, it was the German chemist, August Kekulé, who most clearly saw the carbon atom with its valence of four as we see it today, and as we have described it in this book in our structural formulas. It really is not at all strange that Kekulé should have been the one to start us off in the role of chemical architects. His father

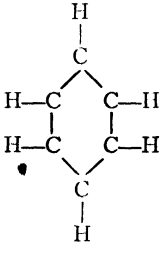
had intended August to be an architect when he grew up, but the result was more gratifying to the chemical industry than to the housing corporations.

Kekulé became a builder of *chemical* structures, and showed how carbon atoms can unite with themselves to form chains. This phenomenon was described in chapter 10 on carbon chains, and we have already seen how fruitful the idea has been in the preparation of large families of compounds. The carbon chain was invented in 1858, but Kekulé cannot claim all the credit for the invention because other men had furnished him with many clues. Eight years later, Kekulé not only invented the carbon ring but also the double bond, and for that he is one of the immortals in chemistry.

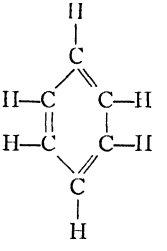
This crowning achievement of Kekulé came about as a result of his ability as a dreamer as well as laboratory worker. He said "Let us dream, gentlemen; perhaps we shall find the truth." Accordingly, when progress in chemistry struck a snag, because nobody could find a satisfactory formula for C_6H_6, Kekulé put on his nightcap, dreamed about six carbon atoms arranged in a chain like a group of dancing imps,



and then saw the imps at the ends of the chain join hands in a ring dance, as in formula A:



(A)



(B)

When he awoke, Kekulé realized that this ring might truly be the structure of benzene, except for the valence of carbon, which must necessarily be four to agree with chemical experience. It was a simple step, then, to the assumption that the bonds are alternately double

bonds and single bonds as in formula B, which satisfies all the valence requirements for a compound of the composition C_6H_6.

This is how we got our carbon-ring systems described in chapters 11 and 12, and the double bonds of chapter 14, as well as a good formula for benzene.

19. 2. The Benzene Ring. Benzene is a famous compound not only because of its importance in the chemical industry, but also because of its unique chemical properties. In order to understand the queer behavior of benzene, we must compare its properties with those we have a right to expect from its formula. We shall, therefore, take up some of the important characteristics of the substance from the point of view of the rules we have laid down in our study of architecture of carbon compounds.

In the Kekulé formula for benzene, we have the following building units, and we should also have the corresponding properties to go with them:

1. A six-membered ring, which, we know from experience, is one of the most stable of ring structures (section 12.7).

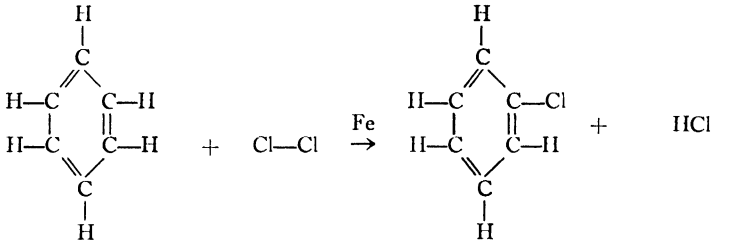
2. The C–H bond, which is quite stable, but can be altered by substitution reactions in which the H atom is replaced by such substituents as Cl and Br (section 10.1).

3. The C–C bond, which we have learned is very firm indeed (section 10.1), and the C=C bond, remarkable for its chemical reactivity as shown by its ability to add other molecules and its sensitivity to oxidizing agents (section 15.2).

As shown in the following discussion, the first two of these principles describe the properties of benzene very nicely, but the third does not apply so well:

1. Benzene is very stable toward most reagents. Many benzene derivatives can be decomposed, benzene itself being a final product, but if the decomposition is carried further to simpler molecules all the characteristic benzene properties are lost with the breaking of the ring.

2. Benzene resembles the paraffin hydrocarbons in that its H atoms are replaced directly by halogen atoms:



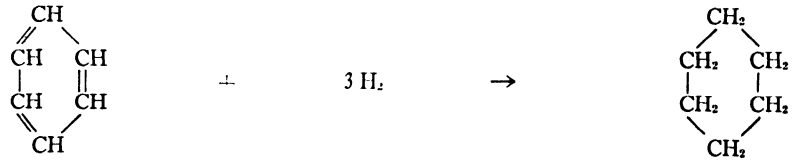
Chlorobenzene

This substitution reaction takes place quite rapidly at ordinary temperatures, when small amounts of iron are added as a catalyst. Later, (section 20.2) this substitution reaction will be described in detail and it will be shown that the procedure used for introducing a halogen atom into the ring is quite different from that employed for chain compounds. Under the proper conditions, all six hydrogen atoms can be replaced by halogen.

3. The unique properties of benzene are probably due to the nature of the valence bonds which link the carbon atoms in the ring.

Benzene is so very stable that it would seem almost certain that the ring consists of nothing but C–C bonds. It was explained in section 15.4 that the C=C bond in a compound can easily be detected by two color reactions; first, when it is oxidized by a solution of potassium permanganate, and second, when it adds a molecule of bromine by treatment with bromine in a suitable solvent. Benzene reacts with neither of these reagents, so that it appears that if there are any double bonds in benzene they are not behaving the way we should expect.

However, the fact that there *are* double bonds in benzene is indicated by a few addition reactions. Under certain conditions it will add three molecules of hydrogen,

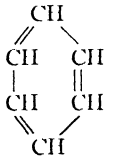


Benzene

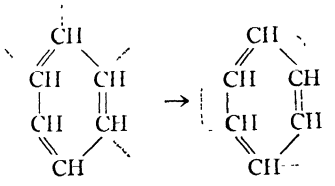
Hexahydrobenzene
Cyclohexane

which suggests the presence of three double bonds. Similarly, it will add three molecules of chlorine to yield $C_6H_6Cl_6$, an insecticide known as *666* which is chemically benzene hexachloride or hexachlorocyclohexane.

We see then that the C=C bond in benzene is unusual, because it goes through addition reactions only with great reluctance and is not susceptible to oxidation. In order to explain this state of things, many chemists have offered formulas which they thought were more satisfactory than that of Kekulé. Most chemists turned to the Thiele variation of the Kekulé formula:



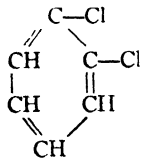
Kekulé formula

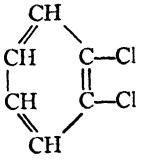


Thiele formula

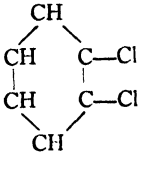
According to the Thiele partial valence theory (section 18.2), the activity of a double bond is due to residual or partial valences as suggested by the dotted lines. It seemed probable that, in benzene, all the partial valence bonds unite to form a satisfied ring, with practically no valence force left over for addition reactions. This Thiele formula gave a simple explanation of the reluctance of benzene to act like other compounds containing double bonds. Also, it offered one of the simplest explanations of the following problem, which is the chief drawback of the Kekulé formula.

When two adjacent H atoms of benzene are replaced by chlorine, the Kekulé formula would lead us to expect two different compounds to be formed, in which the Cl atoms are across a single bond in one case and across a double bond in the other:





Kekulé

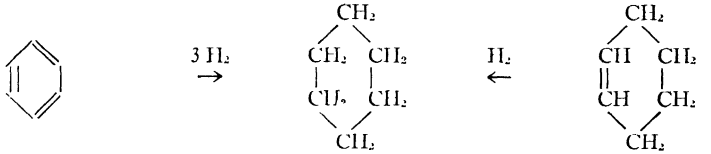


Thiele

Actually, only one such dichlorobenzene has ever been isolated, which agrees with the symmetrical nature of benzene as expressed in the Thiele modification of the Kekulé formula.

19. 3. Resonance of Benzene. At present, the unusual properties of benzene are rather clearly explained by the resonance theory. When the theoretical heat of formation of benzene is calculated from the sum of the bond energies (6 C–H + 3 C–C + 3 C=C), by the method described in section 18.3 for methane, it is found to be 39 kg. cal./mole less than the experimentally determined heat of formation. This is a criterion of resonance (section 18.8), that is, a greater actual stability than we would expect from its normal structure.

A more accurate estimate of the resonance energy of benzene is obtained from heat-of-hydrogenation measurements (compare section 18.11) on benzene and on cyclohexene:



Heat of hydrogenation = 49.8 Kg. cal.

Heat of hydrogenation = 28.6 Kg. cal.

One would expect the heat of hydrogenation of benzene to be 3 × 28.6 or 85.8 kg. cal. per mole, instead of the observed value of 49.8 kg. cal. The difference 85.8 — 49.8 = 36 kg. cal. is the measure of the increased stability of the benzene structure due to its resonance possibilities.

The observed value for the carbon-carbon distance in benzene is 1.39 Å, which is exactly half-way between single-bond and double-bond character in figure 18.5. It, therefore, fulfills the second requirement for resonance, that is, a shortened bond length.

Five or six electronic structures can be written for benzene, but only two are important and are the two possible Kekulé structures:

These have identical energy contents and, therefore, enter into complete resonance, with the corresponding increase in stability. Since the actual state of the molecule of benzene is intermediate between these structures, it explains why only one dichlorobenzene can exist of the type shown in the last paragraph of the preceding section. This will be even more apparent when the structure of benzene is described according to the molecular orbital theory in section 19.6.

Chemists have found it useful to represent the molecule of benzene simply by a hexagon (usually referred to as a ring),

in which each corner stands for a C–H group. Sometimes, to call attention to some particular H atoms in the ring, they are indicated as shown in the last of these diagrams.

The benzene ring is a shorthand symbol, indicating only the cyclic and symmetrical structure of benzene. Thus we eliminate all controversies as to the way the carbon atoms are connected in the cycle. The question will be raised again in section 36.3, however, when we describe five-membered rings which have so-called "aromatic" properties.

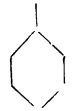
19. 4. Hydrocarbons Containing the Benzene Ring. A large number of hydrocarbons derived from benzene are known. Many of these are found in coal tar and in resins, balsams, or other plant substances.

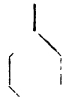
Because many of the benzene derivatives first prepared were found to have a pleasant odor, they came to be known as the "aromatic" compounds. The term is still used to differentiate these compounds from the compounds described earlier in this book.

The nature of the benzene hydrocarbons is shown by the formulas of some representative members of the series given in table 19.1. The student should examine these formulas rapidly at first, just to get acquainted with the new type of architecture being described. Then the names should be studied from the following points of view:

Many compounds have a *common* name, often acquired from the nature of their source; for example, toluene is so-called because it

was discovered among the distillation products of balsam of Tolu. It can also be named *systematically* as derived from benzene (*i. e.*, methylbenzene), or as derived from a chain hydrocarbon (*i.e.*, phenylmethane).

The radical C_6H_5–, which is a benzene ring  with one H atom missing, is called *phenyl,* from the obsolete name for benzene, which is phene. This radical has a valence of one, just like the methyl radical, CH_3–, and the ethyl radical, CH_3–CH_2–.

19. 5. Nucleus and Side Chain. Benzene is such a stable unit that chemists like to consider it as the principal part of a compound when it is found combined with other radicals. For example, ethyl benzene  is looked on more as a derivative of benzene than of ethane, so it is more often called ethylbenzene than phenylethane.

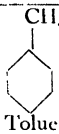
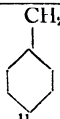
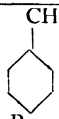
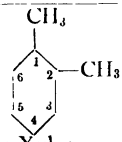
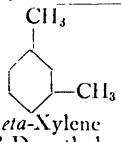
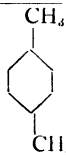
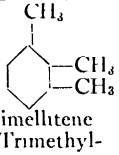
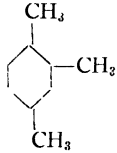
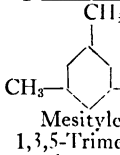
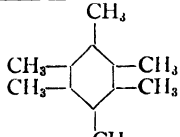
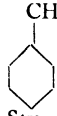
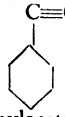
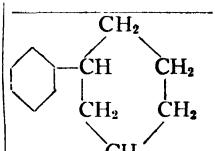
In a compound like this one, the benzene ring is called the *nucleus,* while the chain of carbon atoms attached to the nucleus is called the *side chain.*

The side chain can have any of the various forms we have already studied, and to illustrate this fact, we have included examples of these various types in table 19.1. The side chain can be of the *open* type, in which the carbon atoms are joined by single bonds ($-CH_2-CH_3$), by double bonds ($-CH=CH_2$), or by triple bonds ($-C\equiv CH$). This side chain can also be of the *closed* type, as shown by the last compound in the table, phenylcyclohexane.

In every case, the benzene hydrocarbons have two sets of properties — the properties of the nucleus as given in this chapter and the properties of the side chain as given in preceding chapters. Each set of properties, of course, will be affected by the presence of the opposing type of structure in the molecule. The nucleus is generally more stable (less reactive) than the side chain, as we shall learn more definitely in later chapters.

TABLE 19.1. HYDROCARBONS CONTAINING THE BENZENE RING

With the exception of the last three compounds, these hydrocarbons belong to the *benzene series* of hydrocarbons. The general formula of the family is C_nH_{2n-6}.

 Benzene (Phene) C_6H_6 b.p. 80°C	 Toluene Methylbenzene Phenylmethane C_7H_8 C_6H_5–CH_3 b p. 110°C	 Ethylbenzene Phenylethane C_8H_{10} C_6H_5—C_2H_5 b p 134°C.	 Propylbenzene Phenylpropane C_9H_{12} C_6H_5—C_3H_7 b.p. 157°C
 *ortho*-Xylene 1,2-Dimethyl-benzene C_8H_{10} *o*-$C_6H_4(CH_3)_2$ b.p. 144°C.	 *meta*-Xylene 1,3-Dimethyl-benzene C_8H_{10} *m*-$C_6H_4(CH_3)_2$ b p. 139°C	 *para*-Xylene 1, 4-Dimethyl-benzene C_8H_{10} *p*-$C_6H_4(CH_3)_2$ b.p. 138°C.	Note. The three xylenes are isomers of ethyl benzene.
 Hemimellitene 1,2,3-Trimethyl-benzene *vicinal*-Trimethyl-benzene C_9H_{12} *vic*-$C_6H_3(CH_3)_3$ b p 175°C.	 pseudo-Cumene 1,2,4-Trimethyl-benzene *unsymmetrical*-Trimethylbenzene C_9H_{12} *unsym*-$C_6H_3(CH_3)_3$ b.p. 169°C.	 Mesitylene 1,3,5-Trimethyl-benzene *symmetrical*-Trimethylbenzene C_9H_{12} *sym*-$C_6H_3(CH_3)_3$ b p. 165°C.	Note. The three trimethylbenzenes are isomers of propylbenzene.
 Mellitene Hexamethyl-benzene $C_{12}H_{18}$ $C_6(CH_3)_6$ m.p. 164°C.	 Styrene Phenylethene C_8H_8 C_6H_5—CH=CH_2 b.p. 144°C.	 Phenylacetylene Phenylethyne C_8H_6 C_6H_5—C≡CH b.p. 142°C.	 Phenylcyclohexane $C_{12}H_{16}$ b.p. 237°C.

19. 6. Graphite and Diamond. We have just stated that the nucleus and the side chain differ considerably in chemical properties. We also find that there is a marked difference when we examine their probable physical structures. This difference is best shown by contrasting the structures of graphite and diamond, which are apparently related to each other in much the same way as the benzene compounds are related to the chain compounds.

Carbon occurs in nature in two forms. One is the cheap variety known as graphite and sometimes used as a lubricant. The other is the expensive variety known as diamond and quite often worn as jewelry. These two kinds of carbon have been thoroughly studied by X-ray methods and their structures are shown in figures 19.1 and 19.2.

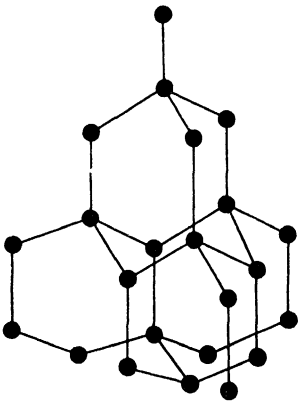


FIGURE 19.1. Arrangement of carbon atoms in diamond

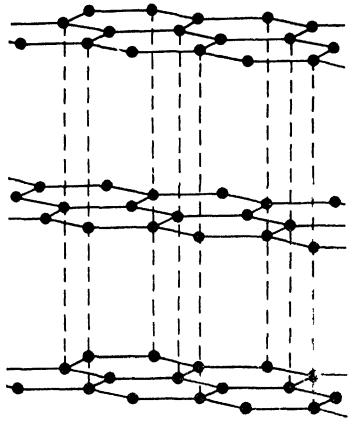


FIGURE 19.2. Arrangement of carbon atoms in graphite.

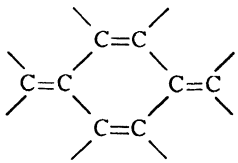
A diamond crystal is a giant molecule. It consists of an interlacing network of the tetrahedral carbon atoms described in detail in chapter 12. Each carbon atom is linked to four others, and the angle between the valence bonds is the theoretical 110°, which generally means great stability (section 12.6). The distance between any two atoms is 1.54 A units.

The chain (and closed-chain) compounds are built on the diamond principle. In the model for diamond, the reader will recognize the

zigzag chains mentioned in section 12.3 and the crumpled rings described in section 12.7.

Benzene derivatives are apparently built on the graphite principle. The benzene ring is flat, and atoms attached to the ring are in the same plane as the ring. In the graphite molecule, there is a network of plane rings to form a continuous sheet. Each sheet is a giant molecule, whereas in diamond the whole crystal is a giant molecule. The angle between valence bonds in graphite is 120°, and each carbon atom is linked to three others. The sheet molecules are 3.4 Å units apart, and they are, therefore, too far apart to be bound by covalent bonds, but are held together by weak molecular forces which permit slippage. This accounts for the lubricating properties of graphite. The reason for the electrical conductivity of graphite will be mentioned in section 19.7.

In figure 19.2, only three valence bonds are shown on each carbon atom. The position of the fourth valence bond will be described shortly in section 19.7, but one of the reasonable explanations is based on resonance structures similar to those of the benzene ring shown in section 19.3. One of these structures is the following:



Each ring consists of six linkages, of which two are C=C bonds. The ring, therefore, has 33⅓ per cent double-bond character, instead of the 50 per cent double-bond character found for benzene with its three double bonds in six linkages. The distance between carbon atoms in the graphite ring is 1.42 Å. The relation between extent of double-bond character and C–C distance is shown graphically in figure 18.5.

19. 7. Molecular-Orbital Representation of Benzene. The flat benzene ring is pictured in figure 19.3 (*a*), where the valence angles are 120°, just as in the graphite rings shown in figure 19.2. The reason for the flatness was discussed in connection with figure 15.3 (which should be reviewed), where it was shown that σ-type molecular or-

bitals are formed in a plane surface when the carbon atom is linked with three other atoms.

The residual p electron on each carbon atom is shown in figure 19.3 (b) in atomic orbitals perpendicular to the ring. The coalescence

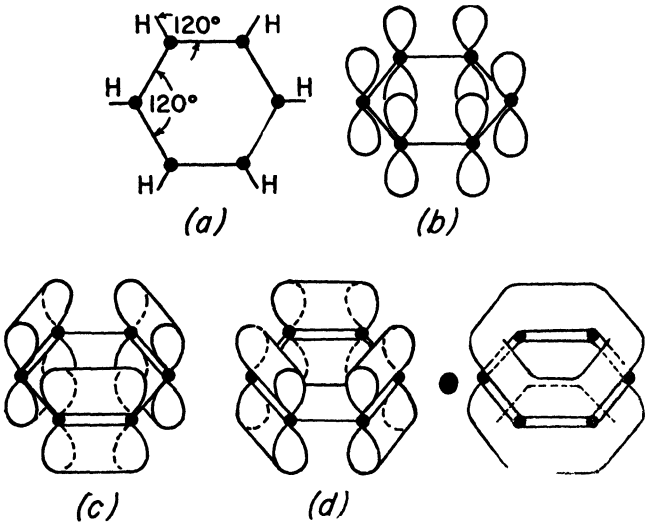


FIGURE 19.3. Structure of benzene on the basis of molecular-orbital theory.
(a) Three of the four valence bonds on each carbon atom are σ-type, and are all in the same plane. The valence angles are 120°. The molecular-orbital nature of the C—C and C—H bonds was described in figure 15.3.
(b) One p electron is left on each carbon atom. The H atoms are not shown.
(c) and (d) Overlapping of adjacent p atomic orbitals to form three π molecular orbitals. The two arrangements correspond to the two Kekulé structures in section 19.3.
(e) The resultant π molecular orbital in benzene offers a continuous path for the six π electrons. It should be remembered that an electron occupies both portions of an orbital.
(See comments under figure 17.3c.)

of adjacent p atomic orbitals to form molecular π orbitals follows the reasoning applied to butadiene in section 18.11 and figure 18.8. Instead of the four π electrons on four carbon atoms, we now have six π electrons on six carbon atoms and these mobile electrons can travel a continuous circular path. The closed orbital should be visualized as two concentric doughnuts.

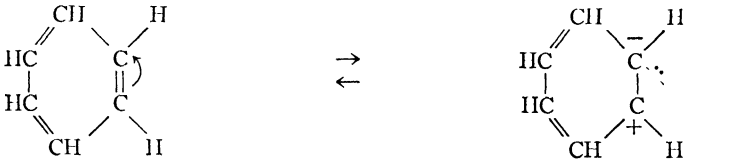
An orbital in the ground state of benzene may have all the π electrons in phase, or the phases may be reversed on alternate carbon atoms. In other words, all six of the π electrons may be the bonding type (π_b), or three of them may be antibonding (π_a). These terms should be reviewed in connection with figure 18.8 and earlier discussions. The wave motions of the π electrons around the ring have been calculated by the methods of wave mechanics.

Under the influence of a magnetic field perpendicular to the plane of the benzene ring, the π electrons flow preferentially in one direction. This results in diamagnetism (section 26.4). The flat graphite-sheet molecules have π electron characteristics similar to those of benzene, and the electrical conductivity of graphite (a metallic property) is due to the mobility of the π electrons when the two ends of a molecule are subjected to a difference in electrical potential.

20. NUCLEAR REACTIONS

20. 1. Introduction. Since the invention of the atomic bomb, in 1945, most laymen became acquainted with the meaning of the nucleus of an atom, which was described in this book in figure 4.1. The study of this entity is now called *nucleonics*. Chemists, for a long time, have been concerned with a much larger nucleus, that is, the ring structure of benzene. In this chapter, we shall describe the behavior of this nucleus, especially where it behaves differently from the chain (and closed-chain) compounds studied in the earlier chapters.

When interpreted on the electronic basis, nuclear reactions are mainly *ionic* reactions. The formation of a polarized molecular structure of benzene resembles the mechanism described in section 17.2 for ethene, and in section 17.4 for propene, which should be reviewed:



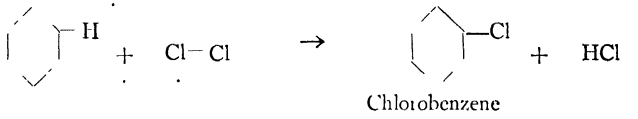
Benzene

An electromer of benzene

This polarized modification of benzene is an electromer and may also be considered as one of the less important resonance structures (section 19.3). A double bond in benzene, just as in ethene, can act as an electron source, that is, it is capable of acting as a donor of a pair of π electrons. This explains why benzene readily undergoes *sub-*

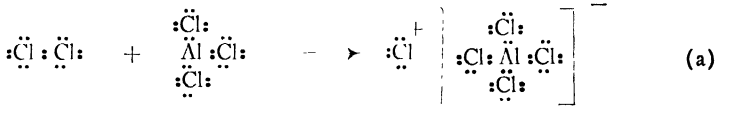
stitution reactions when attacked by electrophilic (electron-seeking) reagents, as described in the following pages.

20. 2. Halogenation of the Nucleus. The chlorination of benzene can be written simply as



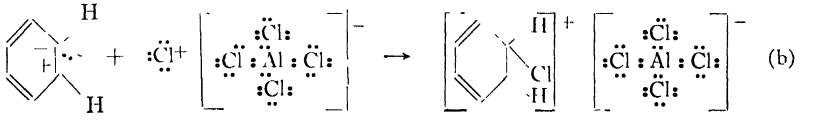
Chlorobenzene

but the reaction is not so simple. To chlorinate most hydrocarbons of the benzene series, certain catalysts must be employed and the reaction generally must be conducted in the absence of light. The catalyst is an electron-deficient substance of the type represented by boron trichloride (section 8.5). A commonly used catalyst is aluminum chloride,



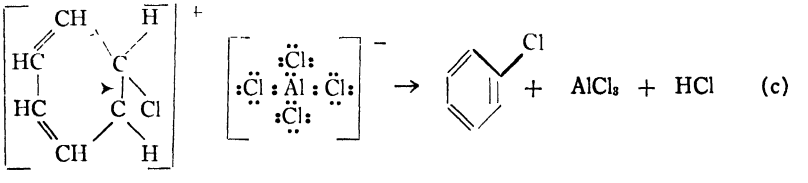
(a)

which forms an intermediate complex containing the Al in a negative ion, leaving a positively charged chloride ion. The Cl^+ ion is electron deficient, it attacks the benzene molecule, promotes formation of the polarized form, and attaches itself to the electron pair:



(b)

The complex produced in reaction (b) then decomposes according to reaction (c):



(c)

The student should closely examine the product in reaction (b) to make sure he understands why the complex ion containing the benzene ring is positively charged. It should also be observed that the catalyst is regenerated in reaction (c), to be used over again in (a).

In the terminology of the concluding paragraphs of section 17.4, the replacement of a hydrogen atom in the benzene ring by another atom or radical is typically S_E2, that is, *substitution, electrophilic, bimolecular.*

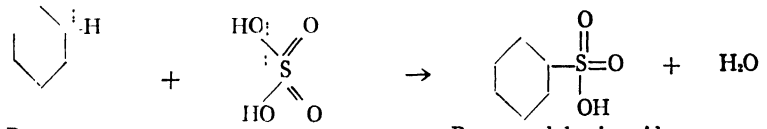
As already stated, the tendency of benzene to undergo ionic reactions is similar to that of olefin hydrocarbons, that is, hydrocarbons containing double bonds (section 17.2). The paraffin hydrocarbons react mainly by a free radical mechanism. It has been stated (section 17.11) that the reaction between methane (CH_4) and chlorine to give chloromethane (CH_3Cl) takes place with explosive violence in direct sunlight. This is a characteristic chain reaction, which was explained in section 17.12 as a reaction due to free radicals. In this case, the free radicals are chlorine atoms; in other words, whereas chlorination of benzene takes place through Cl^+ ions, chlorination of methane takes place through Cl atoms:

$$\begin{array}{rcl} Cl{:}Cl & \rightarrow & Cl\cdot + \cdot Cl \quad (a) \\ \cdot Cl + CH_4 & \rightarrow & HCl + \cdot CH_3 \quad (b) \\ \cdot CH_3 + Cl{:}Cl & \rightarrow & CH_3Cl + \cdot Cl \quad (c) \end{array}$$

In these equations, only the electron-pair bond in the chlorine molecule is shown, for the sake of simplicity, and it will be recalled that the odd electron characterizes a free radical (section 10.3). The reaction is initiated by (a), and the chain is kept going by (b) and (c).

It was further explained in section 17.12 that photochemical reactions are free-radical reactions; it is, therefore, understandable why chlorination of paraffin hydrocarbons is best accomplished in the light (high temperature is also helpful). The student should refer to section 25.5 in which the chlorination of toluene is discussed. This compound consists of a nucleus (ionic behavior) and a paraffin side chain (free radical behavior).

20. 3. Sulphonation. When the benzene hydrocarbons are treated with concentrated sulphuric acid, characteristic compounds are formed known as sulphonic acids. The reaction is ordinarily written as:



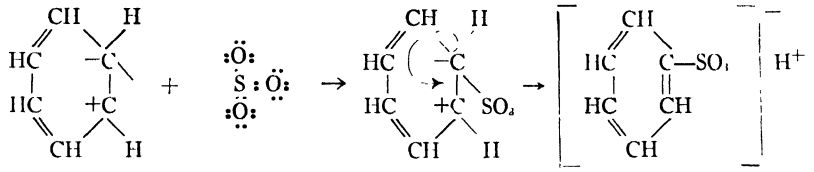
Benzene Benzenesulphonic acid

This process is called *sulphonation.* Benzene itself can not be sulphonated as readily as most compounds of the benzene series, but the reaction can be speeded up by using sulphuric acid containing dissolved sulphur trioxide, that is, fuming sulphuric acid. In fact, it is now believed that SO_3 is the active reagent.

Most of the sulphonic acids are water-soluble solids and are strong acids in solution. The structure of the sulphonic acids must not be confused with that of the sulphates. In the sulphonic acids, a carbon atom of a hydrocarbon radical is united directly with the S atom in a C–S union which is very stable, and a complete –OH group in $HO–SO_2–OH$ is replaced, whereas in the sulphates (section 34.3), only the H atom is replaced.

Sulphonic acids of the paraffin hydrocarbons, like methanesulphonic acid, $CH_3–SO_2–OH$, can be made but usually by indirect methods; the straight-chain hydrocarbons are not easily sulphonated. When olefins are treated with concentrated sulphuric acid, addition takes place as described in section 15.5.

The electronic interpretation of the sulphonation reaction follows the principles already developed in the preceding section, since SO_3 is an electrophilic reagent:

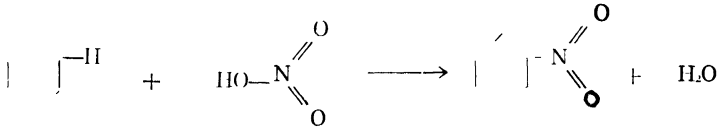


Benzene Sulphur trioxide Intermediate complex Benzenesulphonic acid

When the intermediate complex breaks down, the positive charge in the ring is neutralized by the shift of a valence bond as shown (which means an electromeric shift of an electron pair). This leaves a proton

(H^+) free. The structure of benzenesulphonic acid is written in this reaction in the ionized form; it can also be written with the hydrogen attached to an oxygen in the SO_3 group, as in the introduction to this section. For more information on the electronic structure of sulphur compounds, see section 34.3.

20. 4. Nitration. Concentrated nitric acid, like concentrated sulphuric acid, acts on benzene hydrocarbons to give products in which the OH group of the acid is replaced:



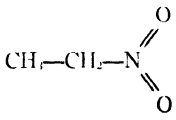
Nitrobenzene

These products are called *nitro* compounds, and the process is known as nitration or nitronation. A carbon atom in the ring is directly bound to the nitrogen, in a C–N union which is very stable.

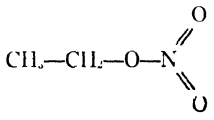
The introduction of $-NO_2$ groups into benzene hydrocarbons can generally be accomplished quite easily with concentrated nitric acid at ordinary temperatures. Nitration of open-chain hydrocarbons, however, is more difficult and must be carried out with more dilute acid at temperatures above 100° C., the temperature being a more important factor than the concentration. In some cases, as in the manufacture of nitroethane, $C_2H_5NO_2$, better results are obtained by nitrating in the vapor phase. The chain hydrocarbons most readily nitrated are those of tertiary structure (section 26.1). In the olefin series, the action of nitric acid generally causes decomposition of the compound.

The nitro compounds derived from the benzene hydrocarbons are yellow liquids or solids, with a great many practical uses. They are especially useful in the dye and explosives industries. The nitro compounds of the paraffin series are colorless liquids and are useful as solvents. This is discussed further in section 33.15.

The structure of the *nitro* compounds must not be confused with that of the *nitrates;* the nitrates, it will be remembered, are formed when only the acid H atom of the nitric acid molecule is replaced:

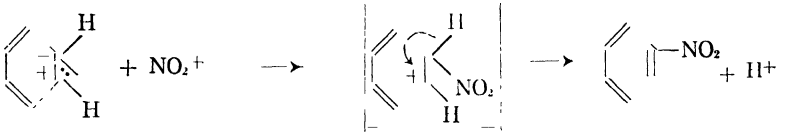


Nitroethane



Ethyl nitrate

The actual mechanism of nitration is not certain, but a plausible theory assumes that it is analogous to halogenation and sulphonation. The attack on the benzene ring is probably made by the electrophilic ion NO_2^+, which is present as a result of the dissociation $HO{-}NO_2 \rightleftarrows HO^- + NO_2^+$. For brevity, the benzene structure is shown in outline only, but the reader can fill in the details by referring to the preceding reactions in this chapter. The H^+ ion among the products reacts with OH^- ions that are present to form H_2O.



Benzene Nitro ion Intermediate complex Nitrobenzene

The nitro group will be used repeatedly in this book as a representative radical which has multiple bonds in its structure and is affected by resonance. We shall, therefore, discuss resonance of the group in some detail. Although the $-NO_2$ group is generally written out as $O{=}\underset{|}{N}{=}O$ in order to show the nitrogen atom with its maximum valence of five, the electronic conception of this group presents quite a different picture. The oxygen atom has six valence electrons ($:\ddot{O}:$) and the nitrogen atom has five such electrons ($\cdot\dot{\underset{\cdot\cdot}{N}}\cdot$); the pairing of these electrons in the formation of valence bonds in a molecule of $C_6H_5NO_2$ can be diagrammed as in figure 20.1. It will be seen that only one N=O double bond, that is, an edge-to-edge union, can be assigned to the nitro group, and that the other link between nitrogen

and oxygen must be a dative bond O←N (section 8.5) in which both electrons of the electron pair originate from the N atom.

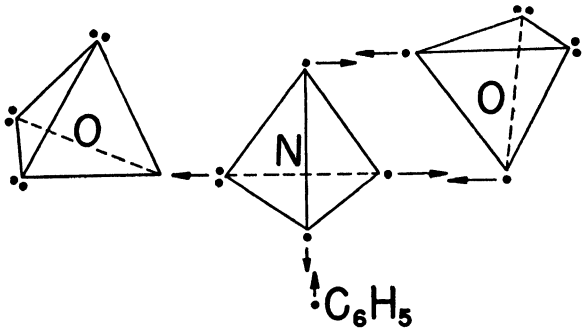


FIGURE 20.1. Electron-sharing in the nitro group.

It is possible, of course, to reverse these bonds, that is, form a normal O=N bond with the oxygen atom at the left and a dative N→O bond with the oxygen atom on the right. We then have the two structures shown in figure 20.2, which are in resonance.

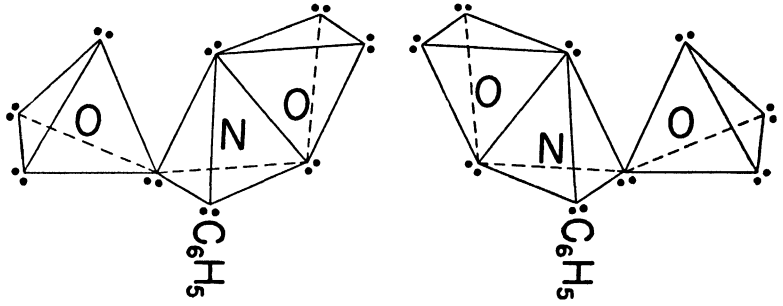


FIGURE 20.2. Resonance structures of the nitro group.

The two equal and opposite structures which we have written for nitrobenzene can be more simply represented by the following electronic formulas:

Inspection of the two possible structures for the NO_2 group indicates that each nitrogen-oxygen bond has an *average* character inter-

mediate between a single bond and a double bond. Since the properties of nitro compounds show that the NO_2 group is highly symmetrical, we can stress the great symmetry of the nitro group and remove the appearance of unbalance which the two resonance structures suggest, by writing the NO_2 group as follows, $-O-\underset{|}{N}-O-$ a dotted bond representing half a normal bond, and the unshared electron pairs indicated as in section 17.3. It is more convenient, however, to picture the two resonance structures as follows and to keep in mind that the actual structure is an intermediate one:

I II

Nitrobenzene

A third possible structure, but one that probably contributes relatively little to the resonance, is shown in figure 20.3, where we have

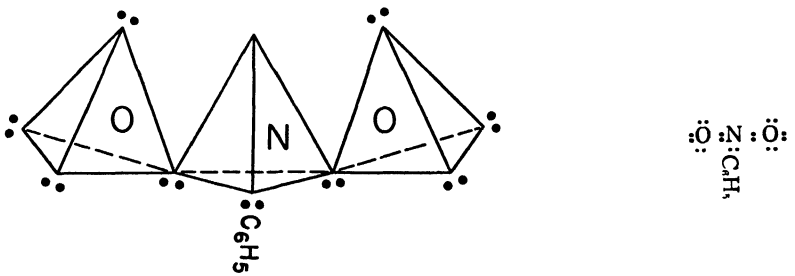
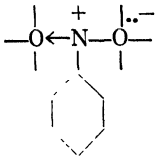
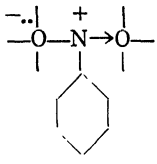


FIGURE 20.3. A third possible resonance structure (probably unimportant) of the nitro group

a structure which, in addition to the dative bond, is dependent on displacement of charge away from the N atom. This can take place in either direction as indicated by formulas III and IV.



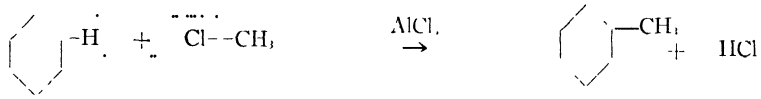
III



IV

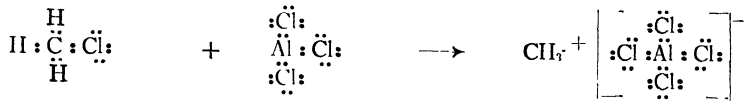
Nitrobenzene

20. 5. Friedel-Crafts Synthesis. This is a method by which the benzene ring can be coupled with many open-chain or closed-chain structures, provided they contain a halogen atom:



Benzene Chloromethane Toluene

This illustration shows how side chains can be hooked to the nucleus to form members of the benzene series of hydrocarbons. It is a substitution reaction, by which an H atom in the ring is replaced, and the mechanism is exactly the same as that described in section 20.2 for replacement of an H atom by a Cl atom. One of the best catalysts is $AlCl_3$, which forms an intermediate complex with the reagent:

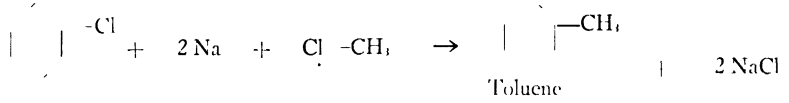


The attack on the benzene ring by the electrophilic methyl ion is similar to that of the Cl^+ ion as described in section 20.2. This is a highly important reaction in organic chemistry, and will be referred to again when *alkylation* is defined (section 24.6).

20. 6. Oxidation. When benzene hydrocarbons containing side chains are oxidized, the nucleus, due to its greater stability, is usually left untouched, but the side chain is oxidized completely. The end product is an acid; since we shall not study acids for some time, an illustrative example will not be given here but can be found in table 31.2.

20. 7. Preparation of Benzene Hydrocarbons. Most of the compounds we are considering in this chapter occur in large quantities in nature or as by-products in the chemical industries, and consequently are seldom prepared synthetically except for special purposes. A few brief paragraphs on the synthetic preparation of these compounds, however, will give us a better understanding of their relative position in chemistry.

One of the general methods for preparing benzene hydrocarbons is exactly the same as the method we have used at various times for other classes of hydrocarbons (see especially sections 10.1 and 10.2):



When applied to the preparation of the open-chain compounds, we called this operation the Wurtz synthesis. When the method is used for the preparation of benzene derivatives it is called the Fittig reaction. Fittig was the first to show that benzene can be coupled with other radicals in this way.

A second general method, and one that is perhaps of even greater usefulness to the synthetic chemist, is the Friedel–Crafts reaction, which we have already described. In this process, an open-chain radical can be directly inserted into the ring, in place of an H atom. It is not necessary, as in the Fittig reaction, to begin the synthesis by first placing a Cl atom in the ring. By means of the Friedel–Crafts synthesis it is possible to introduce six CH_3 groups into the ring, to form hexamethylbenzene (see table 19.1).

Soon after the nature of benzene compounds was discovered, it was recognized that the chemistry of benzene is quite different from that of the chain compounds. Its properties are so different that it was even thought that the benzene ring cannot be synthesized from a chain of carbon atoms. Several methods of preparation of benzene ring compounds from straight-chain compounds have been developed, however, and one such method will be found mentioned in section 30.5*d*. Another, and much more direct method, is to pass a straight-chain compound of six or more carbon atoms at 450 to 700°C. over a special catalyst:

$CH_3—(CH_2)_5—CH_3 \rightarrow C_6H_5—CH_3 + 4\,H_2$

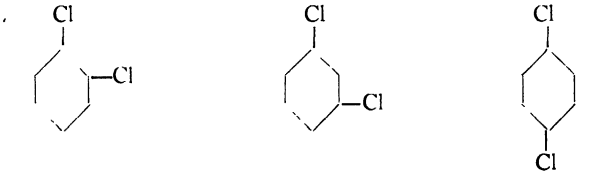
Heptane (table 10.2) Toluene (table 19.1)

*

21. THE GEOGRAPHY OF THE BENZENE RING

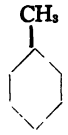
21. 1. How to Name Compounds Derived from Benzene. The benzene ring is a hexagon, and at each of its six corners there is an H atom which can be replaced by other elements or radicals.

Suppose we were to replace two of these hydrogen atoms at the corners of the hexagon, forming dichlorobenzene, $C_6H_4Cl_2$. The problem before us is this — which of the six hydrogen atoms are replaced? The enterprising reader will take out paper and pencil and figure out three possibilities:

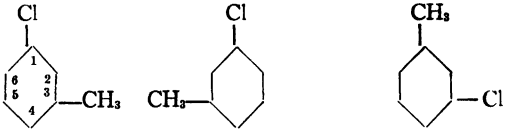


Either one, two, or all three of these substances are possible, and it is our task in this chapter to find out how the organic chemist knows which one of them he is dealing with, and how he can tell them apart.

Before going into this little question in geography, let us first discuss the nomenclature of benzene derivatives. When the compound is a substitution product, obtained by replacing the H atoms in the ring by other elements or groups, the number system is always a safe one to use:



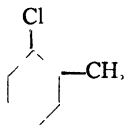
Methylbenzene
(Toluene)



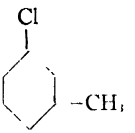
1-Chloro-3-methylbenzene
(The same compound written three ways)

If there is only one substituent in the ring, as in methylbenzene, no number is necessary because all six positions in the ring are equivalent. When there are two or more substituents in the ring, the number system tells us definitely where they are. The 1 position is assigned on an alphabetical basis, as explained in section 11.3.

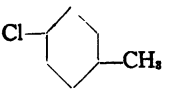
In the case of the *di*substitution compounds, such as those in the preceding illustration, it is a more general practice to locate the radicals or side chains by means of the prefixes *ortho* (o-), *meta* (m-), and *para* (p-):



o-Chloromethylbenzene



m-Chloromethylbenzene



p-Chloromethylbenzene

The prefix *para* is common in the English language, meaning opposite, as in the word paradox. The para positions in the benzene ring are those opposite each other. The prefix *ortho* is also very common, and is usually emloyed to indicate a regular, direct (or orthodox) course. In the benzene ring the ortho positions are those at the ends of a direct valence bond. The prefix *meta* means between and the meta position in the ring is that between the ortho and the para. This system of nomenclature using prefixes derived from corresponding Greek words is important because it is used extensively.

When there are three substituent elements or radicals in the ring, there is still another system for locating their positions without using numbers. This is illustrated by the formulas of the three trimethylbenzenes given in table 19.1. This method of nomenclature, however, is not widely used.

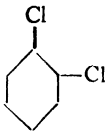
Finally, the reader should review the method of nomenclature in section 19.4 where it was shown that benzene derivatives can often be named as substitution products of chain compounds, using the name *phenyl* for the radical C_6H_5–.

The addition products of benzene are named in the customary manner by simply adding together the names of the reacting substances, as in the following example:

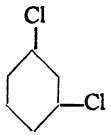
C_6H_6	+	$3Cl_2$	→	$C_6H_6Cl_6$
Benzene		Chlorine		Benzene hexachloride

21. 2. How to Locate the Positions of Radicals in the Ring. When only one element or only one radical replaces an H atom in the benzene ring, the resulting compound exists in only one form. No isomers have ever been prepared of a monosubstitution product like chlorobenzene, . For this reason we say that all six positions in the ring are equivalent, and, therefore, it does not matter where we write the Cl atom in the ring.

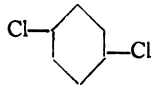
In the case of disubstitution products, we have already found there are three possibilities. For example, if we start with chlorobenzene, the compound of the preceding paragraph, and insert a second Cl atom in the ring by whatever method, the following compounds will result:



o-Dichlorobenzene
1,2-Dichlorobenzene
m.p. —17.6°C.



m-Dichlorobenzene
1,3-Dichlorobenzene
m.p. —24.8°C.

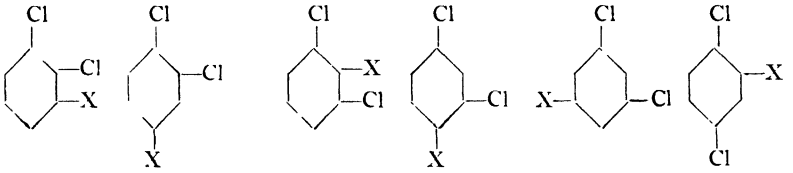


p-Dichlorobenzene
1,4-Dichlorobenzene
m.p. +52°C.

The chemists who boldly state that the ortho compound is the one which has a melting point of —17.6°C., must have had some proof that the two Cl atoms in that particular compound are really in the ortho position. Similarly, methods must have been available by which one could tell where the two Cl atoms are situated in each of the other two compounds.

The process of finding out where in the ring the substituting elements or radicals are situated is called *orientation.* A simple orientation method for the disubstituted compounds has been developed by Körner. This is often spoken of as Körner's 2-3-1 method.

The Körner orientation method consists in the introduction of a *third* element or radical into the ring. For instance, if all three of the *di*chlorobenzenes are put through a series of reactions by which trichlorobenzenes are made we obtain the following compounds. The third Cl atom in each ring is represented by an X:



From the dichlorobenzene which melts at —17.6° C.

From the dichlorobenzene which melts at —24.8° C.

From the dichlorobenzene which melts at +52°C.

To understand this more easily, the reader should copy these formulas and satisfy himself that no other products are possible. It will then be clear that ortho, meta, and para *di*substitution compounds respectively result in 2, 3, and 1 *tri*substitution compounds.

If we start, then, with a dichlorobenzene from which we can prepare two different trichlorobenzenes we know definitely that the original dichlorobenzene is the ortho compound. If we should determine the melting point of this dichlorobenzene we would also find that it melts at —17.6° C. In this way it can be found that the *m*-compound is the one melting at —24.8° C., and that the *p*- compound melts at + 52° C.

21. 3. Reference Compounds. Naturally, when somebody has already gone through the Körner procedure to definitely locate the two Cl atoms in the dichlorobenzenes, it is not necessary for anyone else to repeat it. All we need to do, when we have a sample of Cl–C_6H_4–Cl and when we do not know whether the Cl atoms are in *o*-, *m*-, or *p*- position, is to find the melting point of the compound. Then, by looking in the tables of the textbooks of organic chemistry, we can find out which one it is from its melting point.

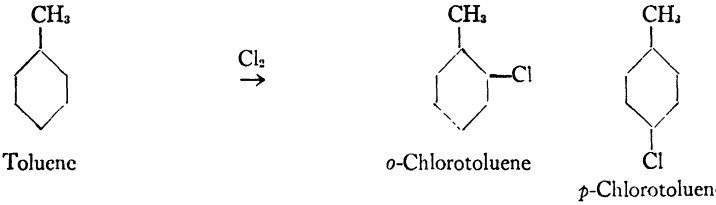
It is also possible to use the three dichlorobenzenes as reference compounds for determining the structure of other disubstitution compounds. For example, suppose we are the first persons to have made a sample of dinitrobenzene, NO_2–C_6H_4–NO_2 and we do not know the positions of the two NO_2 groups in the ring. By a roundabout process, it is possible to convert NO_2–C_6H_4–NO_2 into Cl–C_6H_4–Cl and from the melting point of this compound, we can tell where the Cl atoms are situated. If the product happens to be the *p*-dichlorobenzene, we feel certain that the original compound was *p*-dinitrobenzene:

Data on reference compounds of many types are part of the stock equipment of the synthetic chemist. In order to find out the structure of an unknown substance he tries to convert it by as direct a route as possible to a reference compound of known structure and known constants. Sometimes an element or radical may wander from one position in the compound to another position during the transformation. That makes the game more interesting. This action is beyond our scope and will not be discussed here.

21. 4. How Radicals Can Be Directed to Certain Positions in the Ring. After reading the preceding sections of this chapter, the student may be led to think that every time the organic chemist prepares a benzene derivative with more than one substituent in the ring, it will be very difficult to find out where the entering element or radical has entered the ring.

As a matter of fact, the expert chemist usually knows where the second substituting element or radical is about to enter the ring, even before he starts the experiment. After many thousands of benzene compounds had been prepared, it was found that the second radical inserted into the ring takes up a position which depends on the nature of the first radical originally present in the ring. First let us give some examples, and then we can generalize.

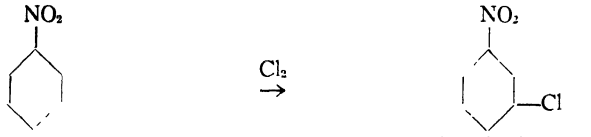
When toluene is chlorinated under such conditions that the Cl atom enters the nucleus, but does not enter the side chain, the compounds formed have the following structures:



Toluene *o*-Chlorotoluene *p*-Chlorotoluene

The Cl atom, as indicated, enters the *o*- and *p*- positions, the relative amounts of the two compounds formed depending on the conditions of the experiment. In fact, it does not matter what groups we insert into the toluene molecule; they will all go mainly into the *o*- and *p*- positions.

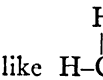
However, if we start with nitrobenzene, and insert a second element or radical,

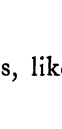


m-Chloronitrobenzene

it will go into the ring mainly in the *m*- position.

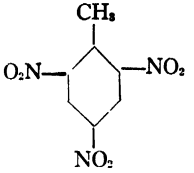
It has been found that the *position* of the second substituent in the ring depends on the *nature* of the first.

1. *Ortho and Para Substitution.* If the first substituent in a ring is an element like Cl, or a group in which there are only single bonds, like  and –OH, the second substituent is directed mainly to the *o*- and *p*- positions.

2. *Meta Substitution.* If the first substituent in a ring is a group in which there are double or triple bonds, like  and –C≡N, the second substituent is directed mainly to the *m*- position.

These are known as the *rules for substitution in the benzene ring.* Like all good rules, these rules have their exceptions, but we shall not consider the exceptions in this elementary book.

Let us finish this topic with the high explosive, T.N.T., the chemical name of which is trinitrotoluene, or 1-methyl-2,4,6-trinitrobenzene.



This is made by direct nitration of toluene in several steps, using strong nitric acid. The nitro ($-NO_2$) groups enter the molecule in accordance with the preceding rules, that is, ortho and para to the CH_3- group, and meta to each other.

21. 5. Resonance and Rules for Substitution. The theory of resonance which we explained in some detail in section 18.5 offers a highly

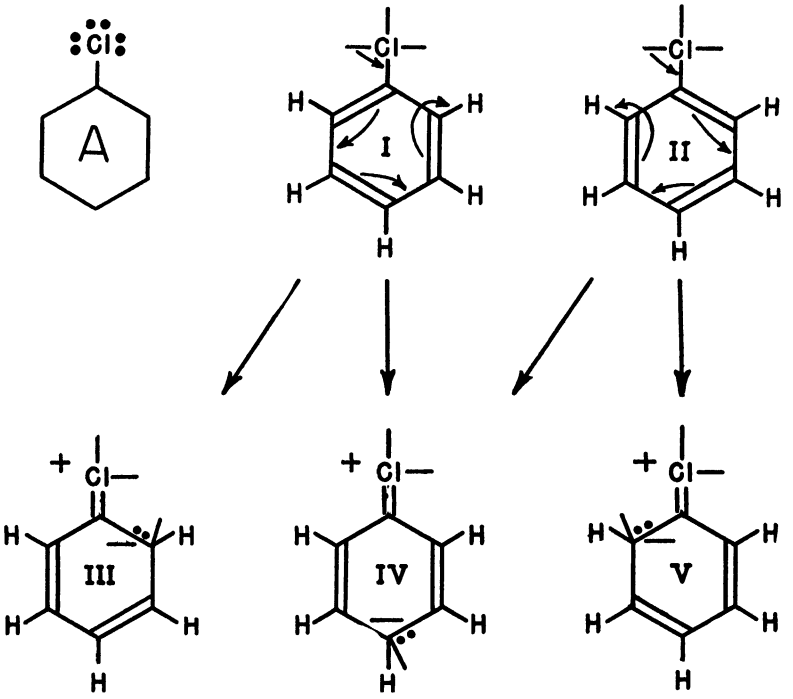


FIGURE 21.1. Resonance structures of chlorobenzene.

satisfactory explanation for the rules of substitution in the benzene ring. Consider first the molecule of chlorobenzene in figure 21.1.

Structure A is written in such a way as to emphasize the fact that the atom attached to the ring contains *unshared* pairs of electrons. In structures I and II the same molecule is shown in the two electronic configurations corresponding to the two resonance structures for benzene (section 19.3). The Cl atom is shown with the unshared electron pairs (potential valence bonds) as lines.

From structures I and II, we can construct three other resonance structures, marked III, IV, and V, by flip-flopping the valence bonds starting at the Cl atom, as suggested in section 18.6. Structure III is arrived at by shifting the bonds in a nearly complete cycle, the terminus being indicated by the electron pair at an *ortho* carbon atom which now has a negative charge. The atom from which the shift started acquires a positive charge. Similarly, from structure II, we can arrive at V.

From both I and II we can construct structure IV simply by stopping the shift at the *para* carbon atom in the ring, and conferring a negative charge or potential valence bond on that atom. It is not possible by this system to write any structure in which the ***meta*** position acquires a negative charge.

As explained in the last chapter, the introduction of nitro groups and sulphonic acid groups, etc., into the ring takes place because they are electrophilic (electron-seeking) reagents. They react with benzene when it becomes polarized and presents an electron pair to the attacking reagent. Since the presence of a Cl atom in the ring predisposes the ring to a condition in which the electron pair tends to appear at *o*- or *p*- positions, the Cl atom causes *o*- and *p*- substitution. Orientation to these positions takes place only when the atom already linked to the ring contains an unshared electron pair, as in $-\ddot{\text{C}}\text{l}:$ and $-\ddot{\text{O}}:\text{H}$. The five structures shown for chlorobenzene are in resonance; the true state of the molecule is an average of all the structures, the arrow signs having no significance other than to help explain the theory.

Now consider the molecule of nitrobenzene in figure 21.2. Resonance of the $-NO_2$ group was described in figure 20.2 but, for the sake of simplicity, we shall use only one of the structures, structure B, where it is seen that the atom directly linked to the ring does not contain unshared pairs of electrons. This group, moreover, contains a

highly electron-attracting element, oxygen, and also contains a double bond conjugated (section 18.10) with the benzene ring. Structures VI and VII are the resonance Kekulé structures, as explained before and from them, we can construct a number of other resonance structures, principally those shown in VIII, IX, and X.

The nitrobenzene molecule differs from the chlorobenzene molecule in that we cannot start the flip-flop shifting of bonds from the

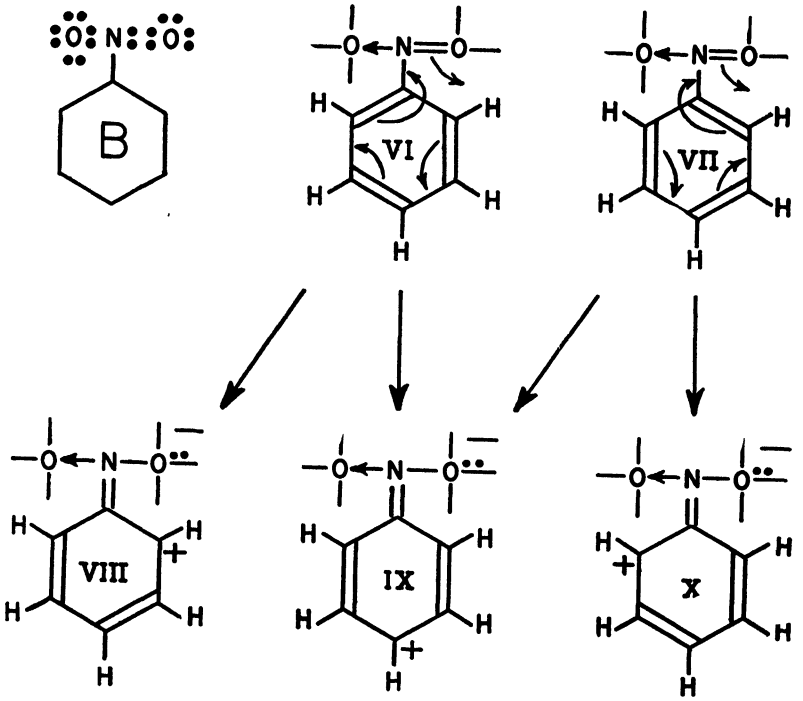


FIGURE 21.2. Resonance structures of nitrobenzene.

$-NO_2$ group into the ring. We can, however, start this operation from a point *in* the ring as shown for the change from structure VI to structure VIII, and from structure VII to structure X. From either VI or VII we can also work out structure IX, by starting at the lowest double bond pictured.

In structures VIII, IX, and X, the reader should observe that the transfer of electrons is away from the ring, leaving positive charges on the *ortho* and *para* carbon atoms; as all these structures are in resonance, the average state of the molecule is one in which the *o*- and *p*- positions are positively charged. In other words, the *meta* positions are more negative and that is where substitution will most likely take place.

When the atom directly attached to the ring has no unshared electron pairs, is in a group containing an electronegative element, and is in a group containing double or triple bonds conjugated with the ring it will, therefore, orient other substituents into the *meta* position.

Finally, it is of interest to observe that atoms or groups which tend to induce *o*- and *p*- substitution also tend to activate the ring; the substitution is more easily accomplished than with benzene itself. This is ascribed to the transfer of electrons from the side chain to the ring. Substitution into the *m*- position, however, is more sluggish presumably because of transfer of charge away from the ring to an electronegative element in the side chain.

21. 6. Dipole Moments of Benzene Derivatives. In section 8.4, we gave a brief discussion of the meaning of dipole moment and of the great value of dipole-moment data in working out the structures of compounds. The dipole moment is a measure of the electron displacement; thus a compound AB may be represented by A : B normally, or it may be represented by A :B under certain other conditions. This displacement effect is not only one of *size,* but also one of *direction.*

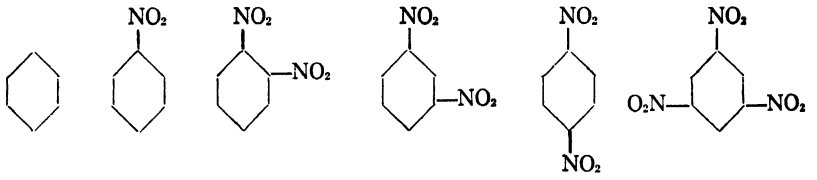
The simple *p*- compounds in the benzene series have zero dipole moments. That is what one would expect from symmetrical compounds like Cl– –Cl, for the dipole moments Cl←C and C→Cl cancel each other. They are in opposite directions and the benzene ring is flat.

The *o*- and *m*- compounds are not symmetrical and, therefore, have high dipole moments as shown by the data in table 21.1.

The $-NO_2$ group is electronegative; it tends to attract electrons. In nitrobenzene, $C_6H_5-NO_2$, the displacement of the electron pair is toward the $-NO_2$ group, thus $C_6H_5^+ :NO_2^-$, leaving the phenyl

group positive. In toluene, C_6H_5–CH_3, however, the phenyl group is electronegative, the displacement of the electron pair being toward

TABLE 21.1. DIPOLE MOMENTS OF NITROBENZENES



Dipole moment in Debye units					
0	3.8	6.0	3.8	0	0

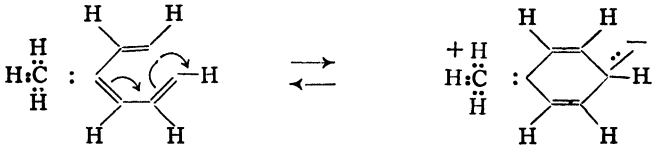
the phenyl group, $C_6H_5{:}^- CH_3^+$. The dipole moments of some groups and atoms attached to the benzene ring are as follows:

	NO_2	OH	Cl	H	CH_3
Dipole moment (Debyes)	–3.9	–1.7	–1.5	0	+0.4

The plus or minus sign indicates whether the group is negative or positive with respect to the benzene nucleus.

21. 7. Substitution in Toluene. Examination of the structure of toluene will show that orientation of a second group introduced into the ring is not well covered by the rules given in section 21.5. Those rules are based on the theory of *electromeric* shift of an electron pair to other parts of the molecule. The process shown in figure 21.1 for example, depends on the presence of a "potential" valence bond which is conjugated with the ring, but there is no conjugation possible in toluene.

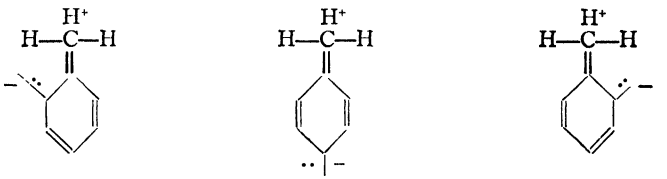
The *o*- and *p*- substitution in toluene is explained by the *inductive* shift, which was defined in section 17.2 as a simple displacement of the electron pair. This displacement in the toluene molecule was described in the last paragraph of section 21.6 as one which leaves the CH_3– group positive with respect to the ring, which then becomes more negative. This is referred to as electron release by the CH_3– group; the group is also said to be electron-repelling when attached to the phenyl group. The effect of the electron release to the ring can be pictured as follows:



Toluene A polarized form of toluene

These illustrations show how polarization through the inductive effect will lead to *p*- substitution. By following the scheme in figure 21.1, corresponding structures leading to *o*- substitution can be written. It should be understood that polarization of toluene is brought about by attack of an electrophilic reagent.

The dipole moment of toluene referred to in section 21.6 has also been explained as a result of hyperconjugation, or no-bond resonance, the phenomenon described in section 18.12. On the basis of this theory, structures of the following type may be written:



Since each of the three H atoms in the CH_3– group of toluene can enter into such no-bond resonance, nine such structures can be written. All tend to throw increased electron density into the ring.

SUGGESTED READING

See references at the end of chapter 17.

22. STEREOCHEMISTRY AND ISOMERISM

22. 1. Introduction. In chapter 12 we showed how a large part of our chemistry would be confusing if we persisted in thinking of molecules simply as flat figures no thicker than the ink on this page. We found that to understand the molecule we must examine it as something with a definite shape. As usual, "the Greeks had a word for it," and in this book we have called the study of the shapes of molecules *morphology,* as in the title for chapter 12. This term is familiar to biologists, who use it when dealing with the classification of plants and animals according to form and structure.

The scholars who put organic chemistry on its feet in 1860 to 1890 knew so much Greek they could not help using it in chemical literature. They introduced the term *stereo*chemistry to designate the branch of chemistry devoted to the shapes of molecules. The word *stereos* in Greek means solid, but to the modern mind it connotes space. For example, our unit of space is the *stere,* or one cubic meter. According to a standard dictionary, stereochemistry is the "chemistry dealing with the arrangements of the parts of a molecule in space."

A stereoscope, it will be recalled, is an instrument for viewing special kinds of picture post cards; it is capable of transforming a flat landscape into a scene in which the cows and the farmer's daughter are substantial objects rather than flat wallpaper sketches.

In stereochemistry, likewise, we put on our stereoptical spectacles, and instead of looking at the flat carbon atom $-\overset{|}{\underset{|}{C}}-$ in which the valence bonds point north, east, south, and west, we see the bonds occupy space in the shape of a regular tetrahedron, as shown in section 12.2.

In our first chapter on morphology, we found that the carbon chain takes on a much different appearance when we examine it from this space point of view, and as a result of this different way of looking at the molecule, we learned why it is that carbon atoms can form ring structures as well as chain structures (section 12.3). In the earlier chapter, it sufficed to indicate the general shapes of the molecules built from carbon atoms. In this chapter, our attention will be focused more directly on various parts of the molecule. It is necessary to know the spatial arrangement of the atoms in order to understand the several types of isomerism to be discussed in this chapter.

22. 2. Simple Isomers. In section 10.5, we defined isomers as compounds with the same composition and same molecular weight, but different properties. To illustrate the meaning of isomerism, we described two different compounds of the same composition, C_3H_7Cl, but with different properties, and we showed that the difference between them is due to the position of the Cl atom in the molecule:

$$\begin{array}{c} CH_3—CH—CH_3 \\ \quad\quad | \\ \quad\quad Cl \end{array} \qquad\qquad CH_3—CH_2—CH_2Cl$$

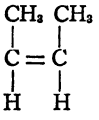
As we have already pointed out, the word *isomer* is another term descended from the Greeks.

In the case of simple isomers, like those in the preceding paragraph, it is not necessary to examine the shapes of the two molecules to see that they are different. We do not have to build any models of these molecules to see that they will behave differently, for it is apparent even in these flat formulas. The variations between simple isomers are due to a distinctly different arrangement of the atoms in the molecule, evident in a *plane* diagram.

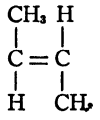
22. 3. Geometric Isomers. The isomers we shall consider in this section cannot be explained as easily as the simple isomers that were just described. Even so, after we know more about them, we shall

find that a flat formula on paper usually suffices to indicate the nature of the isomerism.

For our illustration we shall go back to the chapter on olefins, the compounds containing C=C bonds, and pick out from table 16.1 the compound 2-butene, $CH_3–CH=CH–CH_3$. This looks like the formula for a single substance of the composition C_4H_8. There are, however, two chain compounds of this composition, and their structures are written as follows:

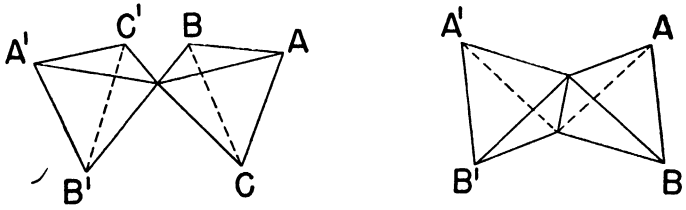


cis-2-Butene



trans-2-Butene

In order to explain the existence of these two isomers, we must picture once again (in figure 22.1) the structure of a double bond as the organic chemist looks at it, as compared with the structure of a single bond.



Single bond Double bond

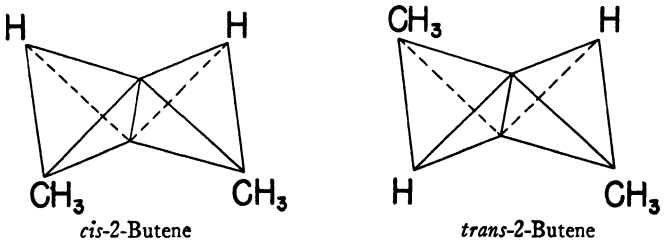
FIGURE 22.1. Comparison of single bond and double bond.

In section 13.11 it was explained that there is a barrier to free rotation about a single bond, which has been measured for certain molecules. The energy to overcome for free rotation is so small, however, that isomeric forms have never been isolated. The chemist imagines a single bond as normally allowing free rotation.

In the double bond, however, we see that the groups are permanently fixed in position because the double bond prevents free rotation. In the process of formation of the molecule, if A and A′ happen to be placed on the *same side* of the double bond they must stay where they are; moreover, the compound thus formed is distinctly

different from one in which A and A′ are on *opposite sides* of the double bond. This is illustrated by *cis*-butene and *trans*-butene in figure 22.2.

This phenomenon due to a double bond in the molecule is known as geometric isomerism and also as *cis, trans* isomerism, to distinguish it from the simple isomerism discussed in the preceding section. *Cis*



cis-2-Butene *trans*-2-Butene

FIGURE 22.2. Geometric isomers of 2-butene.

is a Latin prefix meaning on this side, and *trans* is the corresponding prefix which means on the other side. The two geometric isomers of butene are not much different in properties, and are not very important. The reader will find more noteworthy examples of this kind of isomerism in the index of this book, under *isomers*.

It is also of interest to study the methods by which we can determine whether the chemically important groups are on the same side of the double bond, or on opposite sides. Although we do not have the space in this book to discuss the methods of distinguishing *cis* and *trans* isomers, a brief note on the problem will be found in section 35.3*b*.

From the description of geometric isomers, it is evident that we cannot understand the governing principles unless we make space models of the molecules. The phenomenon is explained on the assumption that the same groups occupy different space positions in the two isomers and that these positions are fixed. Since it depends purely on an arrangement in space, the phenomenon of geometric isomerism is also called stereoisomerism. Geometric isomers are also known as *stereo* isomers.

Although space models are necessary to explain geometric isomers, if we have once become familiar with such isomers, we do not need to make space models every time we wish to write about them. All we need to indicate is that the double bond tends to fix the positions of other atoms or groups in the molecule:

22. 4. Mirror-Image Isomers. This is the third, and last, of the various kinds of isomerism to be described in this chapter. It all de-

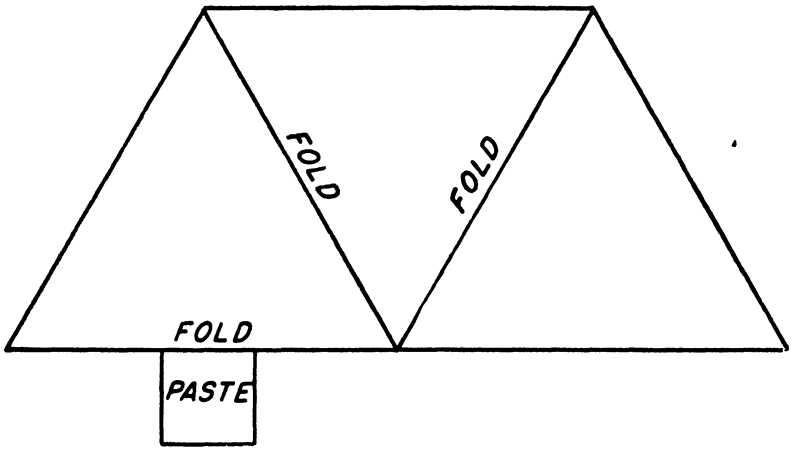


FIGURE 22.3. Design for making tetrahedral models. Cut a sheet of stiff paper this shape and fold as indicated. A little paste on the flap will hold the model together.

pends on a simple bit of solid geometry, as we can easily discover by examining a tetrahedron. If we make a tetrahedral model, as described under figure 22.3. and place four different things at the corners, it will be found that two different arrangements are possible. These arrangements are I and II of figure 22.4. Anyone reading about this phenomenon for the first time will at once say to himself that this is silly and that these two molecules are the same. However, a few minutes spent in trying to superpose one of these models on the

other (as illustrated by model III), will convince any skeptic that they are decidedly different.

The most curious thing about these models is that they are mirror images of each other. This relationship is more clearly expressed

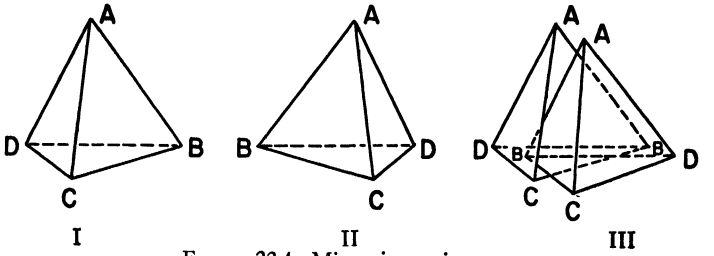


FIGURE 22.4. Mirror-image isomers.

by the models shown in figure 22.5, which may be compared to a man standing in front of a mirror. If the man adjusts his necktie with the right hand his reflection in the mirror does the same thing with

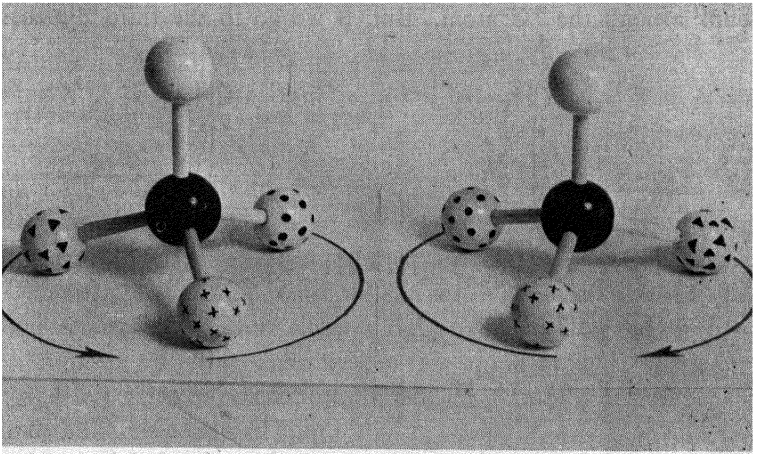
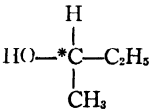


FIGURE 22.5. Models of mirror-image isomers.

the left hand. Figure 22.5 shows an opposite arrangement of the same groups around the central carbon atoms, but we shall explain presently that the two molecules have a certain opposite physical

effect, just like the right-handed man and his left-handed image. That is the reason for the arrows in figure 22.5.

Now let us see how this bit of geometry applies to the chemistry of carbon compounds. The carbon atom, we have agreed, behaves as if its four valences were directed to the corners of a regular tetrahedron. If, then, we attach *four different* elements or groups to the four valences of the carbon atom, we can arrange them in two different ways as just described for the models in figure 22.5. As an illustration of this, suppose we examine the structure of 2-butanol, the formula of which is $CH_3–CH_2–*CH(OH)–CH_3$. The carbon atom in this compound indicated by an asterisk (*) has four different elements or groups attached to it, namely, –H, –OH, $–CH_3$, and $–CH_2–CH_3$. Writing the formula in the usual flat way, like this,



gives no indication at all that there are two ways of arranging the groups around the *C atom. But, if we go to the third dimension

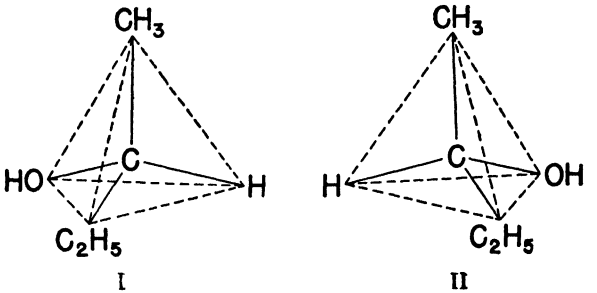


FIGURE 22.6. Mirror-image isomers of 2-butanol.

and arrange the groups in space, we get the pair of right-hand and left-hand molecules shown in figure 22.6.

Chemists call these mirror-image molecules *enantiomorphs,* the Greek word meaning opposite in shape. Since the isomerism of these pairs of molecules can be explained only on the basis of a different

space arrangement of the same groups, we also call them *stereo*-isomers, but it is not as satisfactory a name as enantiomorphs.

22. 5. Optical Isomers. Up to this point we have simply called to the attention of the reader the fact that certain substances can exist in two forms which are mirror images of each other. This state of affairs comes about when a compound contains a carbon atom to which *four different* elements or groups are attached.

The next step in our remarks should be, of course, a proof of all these statements about isomeric molecules that seem to be so much more at home in a looking glass than in a chemist's beaker.

In preceding chapters, when simpler isomers were described, it was usually sufficient to indicate that they had different melting points

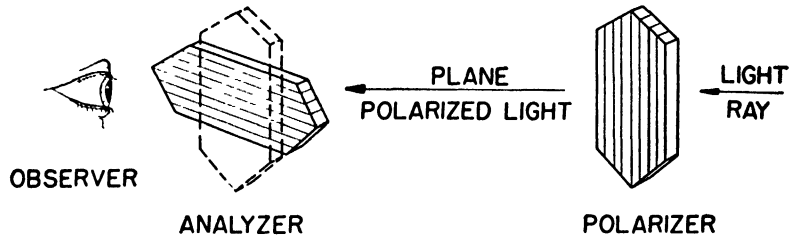


FIGURE 22.7. An elementary illustration of the formation and detection of plane-polarized light. It is explained further in section 22.15.

or boiling points and were, therefore, different substances. The mirror-image isomers, however, have the same boiling point, same melting point, same density — in fact, all their properties are alike except one.

The only physical difference we can discover between mirror-image isomers is that they have either a right-hand or left-hand effect on a certain property of light. Because of this action on light, mirror-image isomers are generally called *optical* isomers; optics is the science dealing with the properties of light.

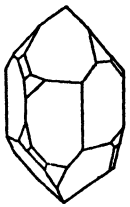
Before we explain more definitely why mirror-image isomers are also called optical isomers, we must first recall the phenomenon in optics called polarized light. Certain crystalline substances, such as tourmaline, when placed in the path of a ray of light will cut out all vibrations except those in one plane, as indicated in figure 22.7. The

light which issues past this substance is called plane-polarized light, and the crystal causing the polarization is known as the polarizer.

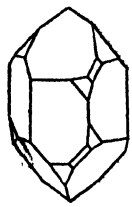
If a second piece of tourmaline, called the analyzer, is placed so that its axis is at right angles to that of the polarizer as indicated in the diagram, this plane polarized light is intercepted and the light is completely blocked out. If the analyzer is rotated into the position indicated by the dotted lines, so that its axis is parallel to that of the polarizer, the light is able to pass through it and the observer sees the crystal illuminated.

Assume that the analyzer is in the dotted position in figure 22.7, and is illuminated. If now we place a quartz plate between the polarizer and the analyzer the light will be blotted out. Then, on rotating the analyzer, at some point the light will go through again.

This shows that the quartz plate rotates the plane-polarized light, and that by rotating the analyzer until it is illuminated we can measure the rotating effect of the quartz plate. The rotation is usually expressed in degrees, that is, a certain thickness of quartz may have a rotating effect of 30°, and a slightly thicker sample may rotate the light 45°, and so on. The laboratory instrument known as the polar-



Left-handed quartz crystal



Right-handed quartz crystal

FIGURE 22.8. Quartz crystals. These are mirror images (or enantiomorphs, in Greek). A section of quartz 1 mm. thick, cut perpendicular to the principal axis of a quartz crystal, rotates the plane of yellow (D line of the spectrum) light through an angle of 22°.

iscope or polarimeter is based on this principle, and is used to measure the light-rotating activity of various substances (section 40.4).

All this was known shortly after the year 1800, and it was also common knowledge at that time that certain samples of quartz rotate plane polarized light to the left and others rotate it to the right. This,

the crystallographers showed, is because some quartz crystals are right-handed and others are left-handed. In other words, there are two kinds of quartz crystals, identical in every respect except that they are not superposable but are mirror images (figure 22.8). They also knew that certain organic compounds like sugar, tartaric acid, camphor, etc., when in solution, are able to rotate polarized light.

All these substances affecting polarized light are said to be optically active, and since some substances even in solution are optically active, it is clear that the phenomenon can be caused by *molecules* as well as by *crystals*.

In 1848, Pasteur's work on tartaric acids showed that the structure of the molecule itself, just like the structure of quartz crystals, may give rise to right-hand and left-hand effects. Then the world had to wait another 25 years until 1874 for the invention of the tetrahedral carbon atom, which explained how it is possible to obtain two mirror-image isomers if there are four different groups attached to it, as we demonstrated earlier in the chapter. The tartaric acids, which played such an important role in the explanation of optical activity, are described briefly in section 32.7.

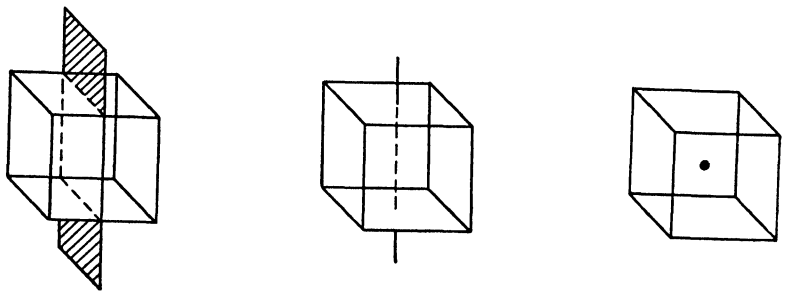


FIGURE 22.9. Illustrations of the meaning of symmetry.

22. 6. Symmetry of Crystals and Molecules. The phenomenon of optical activity is associated with the symmetry of substances, and is shown by all crystals or molecules which have no plane, axis, or center of symmetry. Let us recall what these terms mean before we proceed. A cube has a high order of symmetry, and is a good model for an elementary explanation as shown in figure 22.9.

When a plane can be drawn through a crystal in such a way as to cut it into two halves that are mirror images of each other, the crystal is said to have a plane of symmetry. If a line, or axis, can be drawn through a crystal, so that when the crystal is rotated about this axis it presents the same face to an observer several times in a revolution, it is said to have an axis of symmetry. The cube presents the same face, or the same edge, four times in one revolution about its axis of symmetry. A crystal has a center of symmetry when its faces are arranged in pairs, as they are in the cube.

22. 7. Asymmetric Crystals and Molecules. If we apply these principles of symmetry to the quartz crystals pictured on one of the pre-

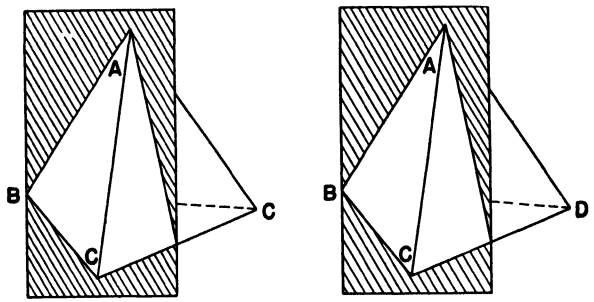
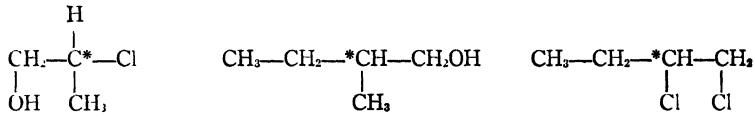


FIGURE 22.10. A plane of symmetry can be drawn through a molecule in which only three different groups are at the corners of the tetrahedron, but not when there are four different groups.

ceding pages, it will be found that they have a very low order of symmetry. They have no principal plane of symmetry and no center of symmetry; such a substance is said to be *asymmetric*, which is simply a way of saying not symmetrical. It should not be inferred that the crystal of quartz has no symmetry whatever, for it may have several minor planes (or axes) of symmetry. What is meant is that the crystal lacks symmetry in that two forms are possible which are not superposable, but are mirror images.

If we apply the principles of symmetry to the molecule of 2-butanol (figure 22.6), we find that it is really devoid of all symmetry. It, therefore, occurs in the form of two mirror-image isomers which are optically active in solution, that is, they rotate plane polarized light either to the right or to the left. The reader should study figure 22.10.

Mirror-image isomers are due to lack of symmetry of the molecule as a whole. Chemists, however, usually state that mirror-image isomers are produced when a molecule contains an asymmetric carbon atom. By an *asymmetric carbon atom* we mean one that has four different elements or radicals attached to it. In the following examples the asymmetric carbon atoms are indicated by (*). Each of these molecules can exist in two mirror-image forms.



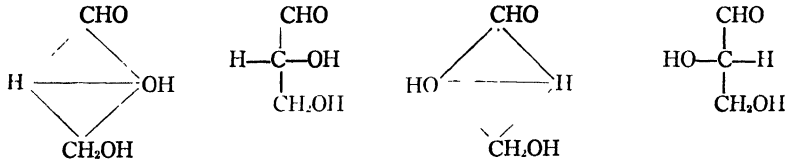
22. 8. Dextro and Levo Compounds. It will be shown later (section 22.13) that optical isomers often exhibit important differences in biological behavior. However, all their physical properties are the same, but one. Pairs of optical isomers have identical melting points, boiling points, surface tensions, etc. They differ in but one physical property, and that is in their *directional* effect on light. Since their only physical difference is in their action on polarized light, we may logically name them on that basis. We now approach the problem of the relation between the structure of the molecule and the direction in which it will rotate the plane of plane-polarized light.

22. 8a. Rotational Nomenclature. The form producing a right-hand rotation is called a *dextro* compound; the opposite form is then a *levo* compound. Although these isomers have *opposite* effects on light, the *amount* of rotation is the same. That is, if one rotates the light 30° to the right, under the same conditions the other rotates it 30° to the left. The compounds pictured in figure 22.6 are *dextro*-2-butanol and *levo*-2-butanol, but we make no attempt as yet to indicate whether the *dextro* molecule is model I or model II.

22. 8b. Configurational Family. As the result of considerable discussion, it has been decided to name optical isomers on the basis of family relationships. Let us say there is a right-handed Smith and a left-handed Smith, and that each has sons, grandsons, great-grandsons, etc. A descendant of R. H. Smith may be left-handed, but we find that that is a minor consideration compared with the fact that he belongs to the family of R. H. Smith rather than to that of L. H.

Smith. However, we can designate him in such a way as to bring out both factors; thus, RH(*levo*)-Smith shows he is left-handed although descended from a right-handed patriarch.

In a similar fashion, the experts in this field of chemistry have designated a few simple asymmetric compounds as progenitors of a Dee series and an Ell series of compounds. The structures of a pair of these compounds are shown in figure 22.11. These are called *projection* formulas, and are discussed in detail in sections 39.3 and 39.5. The asymmetric carbon atom is drawn as a regular tetrahedron, with a *vertical edge* resting *in the plane* of the paper. The chemical



D(*dextro*)-*Glyceraldehyde*
Head of the Dee family

L(*levo*)-Glyceraldehyde
Head of the Ell family

FIGURE 22.11. The reference compounds for determining D or L configuration of optically active compounds.

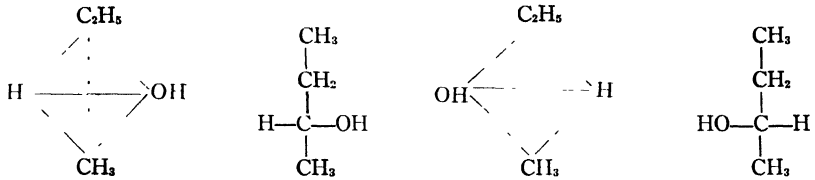
nature of the compound pictured need not concern us in this chapter, but it should be emphasized that the CHO group (the principal functional group) in this molecule is always at the top. The ruling is made that the molecule with OH on the right is a Dee compound and is labeled with the prefix D-. It happens that this compound is *dextro*-rotatory in aqueous solution, and that the Ell compound (L-) is *levo*-rotatory.

If the reader will turn to figure 39.6, he will find that the important series of compounds called α-amino acids is considered to stem from D-serine and from L-serine. These, in turn, can be shown to be descended from the respective Dee and Ell compounds pictured in figure 22.11, the *reference standards*. L-Serine is a *levo* compound in neutral aqueous solution, but it is *dextro* if the solution is made acid. This indicates why more attention is paid to the *configurational family* than to the *direction of rotation*.

Another illustration of the lesser importance of rotational direction will be found in the discussion of lactic acid (section 32.7) where it

is shown that the D-lactic acid configurationally descended from the Dee compound in figure 22.11 is *levo* in aqueous solution under the same conditions as the ancestral compound in figure 22.11 is *dextro.*

We return now to compounds already mentioned in this chapter. To determine the configuration of compounds I and II pictured in figure 22.6, we must obey the conventions and employ projection formulas. This is done in figure 22.12, where the D and L family



D(*levo*)-2-Butanol
(Model I of figure 22.6)

L(*dextro*)-2-Butanol
(Model II of figure 22 6)

FIGURE 22.12. Assignment of the 2-butanols to Dee and Ell families.

assignments are based on proofs in the chemical literature as to their relations to the reference standards in figure 22.11. The D compound is *levo* with respect to light, although it belongs to the right-handed family.

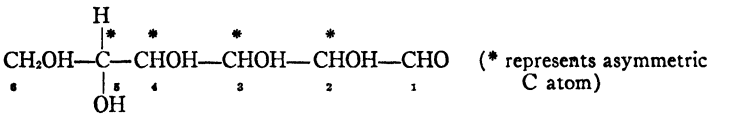
The student will obtain a better understanding of the procedure by which the configurational family is determined if he reviews, at this point, the subject of reference compounds in section 21.3. In that discussion, we showed how chemists can locate the position of a group in the benzene ring by converting the compound being investigated by as direct a route as possible into a compound of which the structure is known. Similarly, among optical isomers, we do not necessarily convert all compounds to the family heads in figure 22.11 in order to find out to which family they belong. In the course of time, the D and L configurations of many compounds have been determined, and these, in turn, can serve as reference standards. As an example, the compounds in figure 22.12 can now serve as standards; a compound which can be directly prepared from the D-2-butanol, or converted to it, is a Dee compound regardless of its rotational direction. An illustration of the use of such a reference compound is the following reaction:

$$\underset{\text{3-Buten-2-ol}}{CH_3—CHOH—CH=CH_2} + H_2 \longrightarrow \underset{\text{2-Butanol}}{CH_3—CHOH—CH_2—CH_3}$$

The butenol has an asymmetric C atom and can be prepared in Dee and Ell forms. Their configurations (using projection formulas as in figure 22.12) are known from their relation to the butanols and other related compounds. The compound which hydrogenates to L-2-butanol is necessarily an L compound, regardless of its rotational direction (which happens to be *dextro*).

In performing an experiment of this kind, the experimenter must be careful that the groups in a series of reactions retain their relative positions in the molecule (see the Walden inversion, discussed in section 32.15). Reference compounds used extensively for determination of configuration are malic acid (section 32.15), lactic acid, glyceric acid, and tartaric acid (section 32.7), all of which are believed to be thoroughly established as regards their relationships to the family heads in figure 22.11.

22. 8c. Compounds with More than One Asymmetric C Atom. The first asymmetric carbon atom in a family of compounds controls the nomenclature of all of its descendants. For example, in figure 22.11, the head of the Dee family has one asymmetric C atom (with –OH to the right of the observer and –CHO at the top). The chain can be lengthened by reactions which introduce more asymmetric C atoms, thus,



but no matter what the effect of the succeeding asymmetric C atoms may be with respect to direction of rotation, these longer molecules are all Dee compounds if the original asymmetric C atom (in this illustration, C atom 5) is a Dee asymmetric atom. This is discussed fully in the study of sugars (sections 39.3 to 39.5).

22. 9. Racemic Mixture. When an asymmetric compound is made in the laboratory, the product is usually optically inactive. In the course of its preparation, by the laws of probability, equal amounts of both isomers are formed and these neutralize each other. The product may crystallize either as a mechanical mixture or as a loose double compound. It is known as the DL-compound, which indicates that it is a 50–50 combination of the D- and L- forms. The mixture of the D- and L- forms is also known as a racemic mixture or racemic

compound. The name racemic is derived from the Latin word *racemus,* meaning a bunch of grapes. The first racemic substance (a double compound of D- and L-tartaric acid) was isolated from grapes, and was known originally by the trivial name racemic acid.

The possible varieties of a compound with an asymmetric carbon atom, therefore, are the D and L modifications and the DL mixture. If we refer back to our example of 2-butanol in figure 22.12, there are these three possibilities: D-2-butanol, L-2-butanol, and DL-2-butanol.

Like butanol, illustrated in figure 22.12, the butanediol shown in figure 22.13 can be prepared in D and L forms which are actively active. The fact that the *levo* isomer in figure 22.13 belongs to the D series was proved by relating it to other compounds of known configuration. The butanediol also forms a racemic mixture, which is inactive to polarized light; it is written DL-2,3-butanediol.

22. 10. Meso Compounds. The butanediol in figure 22.13 is different from the butanol of figure 22.12 in that it can exist not only as the inactive racemic mixture but also as a simple compound which is optically inactive, known as the *meso* compound.

The new factor to explain in figure 22.13 is the *meso* modification, which does not affect plane polarized light. This type of isomer is

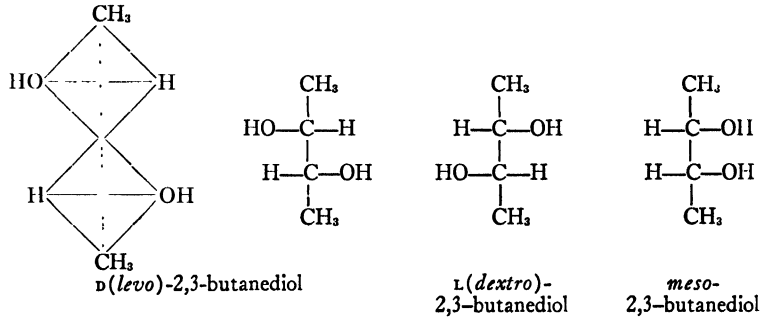


FIGURE 22.13. Assignment of 2,3-butanediols to Dee and Ell families.

possible because of the potentially greater symmetry of this molecule than of the others we have studied. The molecule in figure 22.11 shows a lower degree of symmetry because one end is –CHO and the other is $-CH_2OH$. In figure 22.13, however, both ends are the same.

If a horizontal plane is passed through the *meso* structure in figure 22.13, between the second and third carbon atoms, the two halves will be seen to be mirror images. One of these two carbon atoms is *dextro* and the other is *levo*; they effectively neutralize each other, rendering the molecule inert to polarized light. We should stress again the importance of the way in which we observe the molecules. In figure 22.11 this is simplified, because we always put the CHO

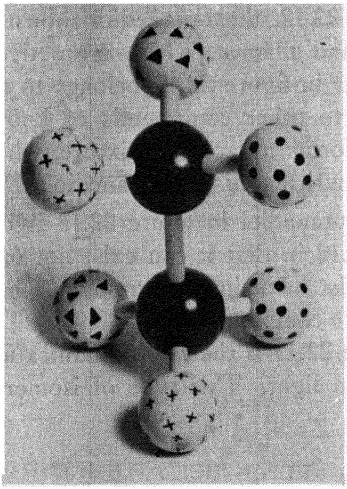


FIGURE 22.14. A meso molecule. (Optically inactive)

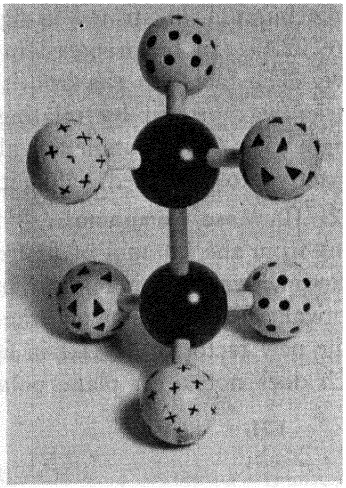


FIGURE 22.15. A D- or L-molecule. (Optically active)

at the top when the tetrahedra are drawn according to rule. In figure 22.13, however, both ends are the same, so that in order to prove that the D compound contains two asymmetric C atoms which are similar (*levo*) we must look at the molecule from each end. This is explained further in the discussion which follows.

The model shown in figure 22.14 was built by combining the two carbon atoms of figure 22.5. These two carbon atoms are of opposite rotational effect; therefore, if we link them into the same molecule through their vertical valence bonds (after removing the unmarked balls shown in figure 22.5) they neutralize each other to yield an optically inactive compound.

The fact that the two carbon atoms in figure 22.14 are of opposite rotational effect can be seen by viewing the molecule from both ends. From the top, the direction is counterclockwise when reading in the order *crosses, polka dots,* and *triangles.* From the bottom, however, the direction is clockwise for the same order of markings. It is obvious that the carbon atoms in figure 22.14 can be rotated into such a position that one-half of the molecule will be the mirror image of the other half.

The reader will be helped in visualizing this phenomenon if he places his hands together, palms touching, and then imagines light passing through his hands by entering through the back of the left hand or through the back of the right hand. It is apparent that after the light has passed through one hand it meets the other hand with opposite directional effects.

The model in figure 22.14, as we stated before, was built by linking each of the carbon atoms in figure 22.5; these carbon atoms have *opposite* rotational effects. We can also construct a model using two carbon atoms of the *same* kind, as shown by the model in figure 22.15. Each of these carbon atoms represents a clockwise directional effect when reading the attached balls in the order *crosses, polka dots,* and *triangles* (looking at the molecule from each end). The model in figure 22.15, therefore, represents an optically active modification, that is, it is either a D- or L- form.

Tartaric acid (section 32.7) has a structure exactly equivalent to that in figure 22.13, with an acid group (–COOH) replacing the $-CH_3$ groups. Some data on the possible isomers of tartaric acid will be given shortly in this chapter (section 22.12).

In the discussion of figures 22.14 and 22.15, we commented on the rotational effect of the groups when viewed from a reference point (that is, from each end of the molecule). Another way of looking at the molecule is illustrated in figures 22.16 and 22.17, where the groups are arranged around the carbon atoms in the same order as in the corresponding figures 22.14 and 22.15. Using the group marked X as the reference point, the arrows show the rotational effect on plane-polarized light of YZ around X.

In figures 22.14 and 22.15, the carbon atoms are "staggered" in the zigzag fashion described in figure 13.7. In other words, the X

groups in figures 22.16 and 22.17 should be as far apart as possible, but we have twisted the carbon atoms into such a position as to make it easier to follow the argument of a fixed reference point.

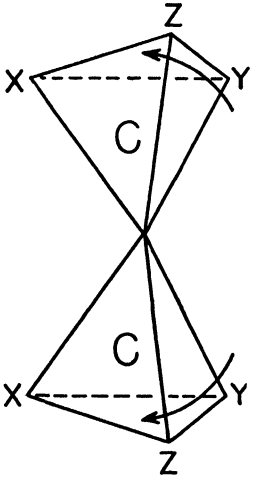


FIGURE 22.16. A meso molecule.

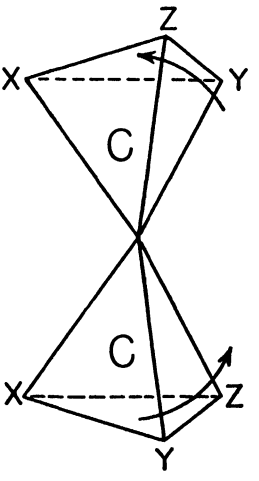


FIGURE 22.17. An optically active molecule.

22. 11. Externally and Internally Compensated Compounds. In a *meso* compound, there is no optical activity, and the molecule is said to be *internally* compensated because the neutralizing effect arises from the presence of two opposite kinds of atoms *in the same molecule.* In a *racemic* compound there is likewise no optical activity, but the substance is said to be *externally* compensated because the neutralization is brought about *by two different molecules.*

It is easy to tell the difference between racemic compounds and meso compounds. Since the racemic substance is a mixture of the D- and L- forms it can be separated into its two components by methods explained in section 22.13. The meso compound, being one single substance, cannot be separated.

22. 12. Diastereoisomers. We have now seen that there are compounds which are isomeric in that they have the same composition, and also contain asymmetric carbon atoms, but are not mirror images. The example of such isomerism in this chapter is a D- compound

and its isomeric but optically inactive *meso* compound. Later, in section 39.4, when discussing the more complex substances we shall find that compounds may be optically active as well as isomeric, yet not be mirror images. Since they are not mirror images, they do not have the same properties. Such compounds are called *diastereoisomers,* which may be briefly defined as compounds which are isomeric and contain asymmetric carbon atoms, but are not mirror images, and, therefore, have different properties. They are mentioned at this point in order to clarify the subject to be discussed in section 22.13 that follows.

The tartaric acids (section 32.7) have the same general configuration as the models shown in figure 22.13, with respect to their asymmetric carbon atoms. The difference in properties between D- or L-tartaric acid and the diastereoisomeric *meso*-tartaric acid is shown by the data in table 22.1.

TABLE 22.1. A FEW PROPERTIES OF THE TARTARIC ACIDS

	Melting Point, °C	*Specific Rotation at 20°C*
L(*dextro*)-Tartaric acid	170	+12°
D(*levo*)-Tartaric acid	170	−12°
DL-Tartaric acid	206	0°
meso-Tartaric acid	140	0°

22. 13. Resolution of Optical Isomers. Resolution of optical isomers means "how optical isomers can be separated." Optical isomers, as we have so often remarked, have the same solubility, same melting point, same boiling point, etc. One of the usual means of separating two substances (like sugar and salt) by making use of their different solubilities in water cannot, therefore, be used to separate a D- compound from its L- isomer.

There are, however, three well-known methods for separating the D- and L- varieties in a racemic compound, and all of them were originally developed by Pasteur in his famous work on the tartaric acids.

In the first place, if we crystallize the racemic substance, the D- and L- isomers will sometimes separate and crystallize in their respective mirror-image forms. One shape corresponds to the D- compound, and the other is the L- compound (compare the diagrams of the quartz crystals in figure 22.8). These crystals can be separated

mechanically by picking them out one by one with tweezers, but, of course, the process is a tedious one.

Secondly, certain molds and bacteria show a preference for either the D- or the L- isomers in a racemic mixture for metabolic use. The other isomer will be left practically untouched. It is a queer fact of nature, not clearly understood, that certain organisms should manifest this preference for a right-hand or a left-hand molecule. The opposite effect is also known; right-hand and left-hand molecules have different activities on certain organisms. For example, adrenaline (section 44.2) is used in medicine as a powerful stimulant. It is optically active, and the *levo* compound is more than ten times as effective as the *dextro* isomer.

Lastly, Pasteur found that D- and L- isomers in a racemic mixture can sometimes be separated by reacting them with another optically active substance. If we can combine them, for example, with a substance like L-adrenaline, they are then no longer mirror images and will have different properties. The D- form combined with L-adrenaline may have a different solubility from the L- form combined with L-adrenaline, and in this way the two can be separated.

This principle is difficult to make clear to a beginner in the study of optical isomers. The following outline may help:

D-compound + inactive substance L-compound + inactive substance	Internal nature of the products is not different from that of the original substances. They are still mirror images.
D-compound + L-compound L-compound + L-compound	These products cannot possibly be mirror images. They are diastereoisomers, which can be separated because they have different physical properties.

A popular illustration of this last principle is to imagine two golfers of equal ability, one of them right-handed (D-) and the other left-handed (L-). If they are both given left-handed (L-) golf clubs they instantly become unequal.

22. 14. Optical Isomers and Asymmetric Carbon Atoms. In this chapter, we have shown that mirror-image isomers cannot be superimposed one on the other. This is because they have no axis, or plane, or center of symmetry — that is, the *molecules* are asymmetric. In the simple examples of mirror-image isomers which we have de-

scribed, we also pointed out that in each case the molecule contains a carbon atom to which four different groups are attached. Such *carbon atoms* we called asymmetric.

In the past, unfortunately, the idea became prevalent that a carbon atom to which four different groups are attached is essential to the formation of mirror-image isomers. This is not true. Molecules can be asymmetric without containing such carbon atoms. A relatively simple example is found among certain derivatives of allene (propadiene), a hydrocarbon with the formula $CH_2=C=CH_2$. If the H atoms are replaced by X and Y groups, mirror-image isomers are possible, as shown in figure 22.18, and have been prepared in the laboratory. The student should refer back to the structure of ethene shown in figure 15.1.

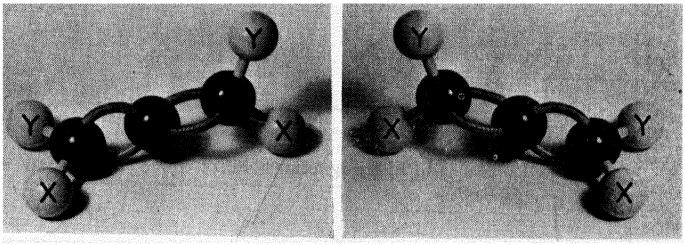


FIGURE 22.18. Enantiomorphic forms of certain allene derivatives.

The only requirement for a compound to be able to exist in the form of right-hand and left-hand isomers is that it must lack certain forms of symmetry. Whether or not the molecule also contains an asymmetric carbon is of less importance. Thus, in figure 22.18, it will be seen that there are no carbon atoms in the molecule which conform to the strict definition of "an atom to which four different atoms or groups are attached."

Later, we shall describe compounds in which asymmetry is due to nitrogen atoms (section 33.7), to sulphur atoms (section 34.5), and to the phenomenon of steric hindrance (section 32.10). The student may at this time also refer to the Walden inversion (section 32.15).

22. 15. The Nature of Plane-Polarized Light. The trouble with light is that apparently only mathematicians are capable of seeing through it and using it in a predictable manner. Until recently, few attempts have been made to render light polarization intelligible to nonmathematical chemists. The explanation of plane-polarized light in the text which accompanies figure 22.7 is designed to give only an elementary physical picture of the phenomenon, in its application to optical activity of asymmetric compounds. In this section, the phenomenon is described once more, but as an electrical phenomenon associated with the electronic structure of the molecule.

The reader is probably familiar with the fact that a wire carrying an *electric* current induces a *magnetic* field at right angles to it. This is illustrated in figure 22.19, where the wire passes perpendicularly through a sheet of paper on which iron filings, when tapped, show the magnetic lines of force. Similarly, a ray of light is composed of

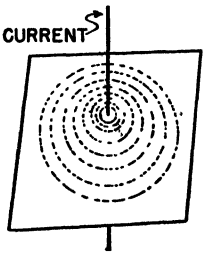


FIGURE 22.19. Magnetic field of force around an electric current.

an electric vector and a magnetic vector at right angles to each other. Both vectors, in turn, are at right angles to the direction of travel of the light, as illustrated in figure 22.20. Light travels by a series of pulsations, the intensity alternately rising to a maximum and falling to zero. The wavelength is the distance between two corresponding points on the sine curve in figure 22.20 and is divided into 360°. The vibration frequency is the number of wavelengths passing a given point per second.

It is now understood that a molecule is an electrical structure, in which the fields set up by the positive and negative charges are often not concentric (section 8.1) and result in a polar molecule as shown in figure 22.21. Even when the positive and negative fields are concentric, and the molecule is consequently nonpolar, a solvent

or other environment with the proper dielectric properties will tend to polarize the molecule to the dipole form in figure 22.21. This dipole has a characteristic vibration frequency, as discussed in section 13.14, and is analogous to the system shown in figure 22.19 in that the electric field around the molecule can be resolved into an electric vector (in the direction of the dipole) and a magnetic vector at right angles to it. In a sphere of unit intensity around the dipole, the lines of equal magnetic force are lines of latitude, with the maximum at the equator and zero at the poles (where the electric vector is also zero).

The interaction of the magnetic vector of light and the magnetic vector of a molecule is so small that it can be generally disregarded, and the entire effect of light is usually attributed to the electric vector. The electric field (figure 22.20) is vibrating and will affect the atomic

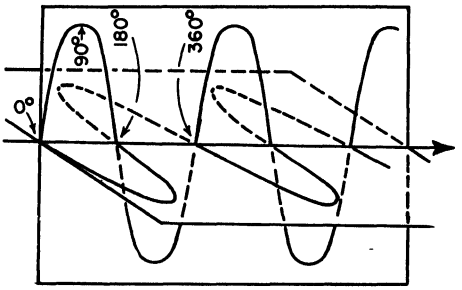


FIGURE 22.20. Magnetic and electric vectors of a light ray are perpendicular to each other and to the direction of travel.

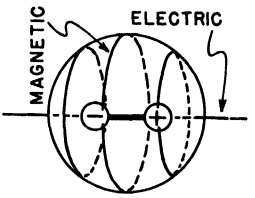


FIGURE 22.21. Magnetic field and electric field of a polar molecule.

vibrations in the molecule through induction. If the frequency of the light is exactly the same as that in the molecule, the energy of the light will be completely absorbed and the spectrum of the substance, if photographed, will show an absorption band at that frequency (section 13.14). If the frequency of the light is different, the molecule will re-emit scattered light of a new frequency with diminished energy, that is, the light ray will be slowed down if it is not absorbed. This is the origin of *refraction* of light.

The student is now asked to disregard the fact that light is associated with a magnetic component as shown in figure 22.20, and is asked instead to think of the light ray in that figure as the electric

component resolved into two vectors. (The resolution of a force by the parallelogram method into two perpendicular vectors was illustrated in figure 18.2.) When light is passed through certain crystals, one of the vectors is slowed down more than the other. By such means, it is possible to separate a light ray into its two components, and an optical system which does this is said to exhibit double refraction. This is the principle used in the Nicol prism, which should be studied further in a textbook on physics. The phenomenon does not take place along the optical axis of a crystal, nor does it occur in the highly symmetrical cubic crystal shown in figure 22.9.

The two electric vectors of a light ray are shown in figure 22.22 with the wave in the horizontal plane retarded by the medium in

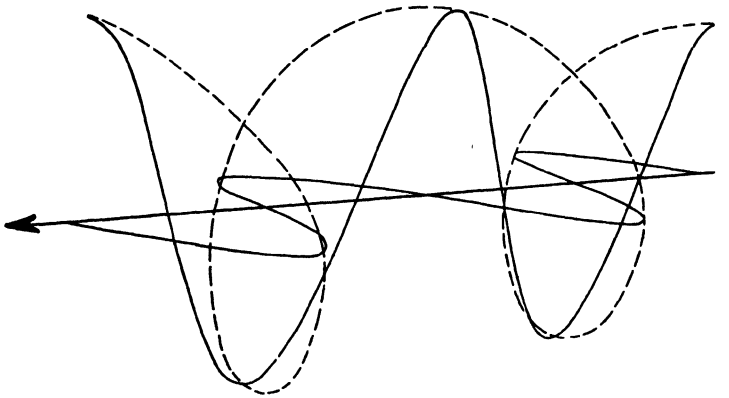


FIGURE 22.22. The two perpendicular vectors are 90° out of phase due to unequal rates of travel in a medium which is not uniform in all directions. The wave becomes circularly polarized (broken curve), the resultant being obtained by adding the two vectors [adapted from C. R. Noller, *J. Chem. Education*, **24**, 600 (1947)].

which the light travels, so that it is 90° out of phase (refer to figure 22.20) with that in the vertical plane. The resultant of these two plane waves is a spiral which represents circularly polarized light. When looking toward the source of light, the diagram in figure 22.22 illustrates a left-handed spiral. If the wave in the horizontal plane is 90° out of phase in the opposite direction, the spiral will be right-handed. *In the direction of propagation of the light,* the spiral in figure 22.22 represents right-handed circularly polarized light.

Plane-polarized light is a mixture of *dextro* and *levo* circularly polarized waves. This is illustrated by figure 22.23. The two horizontal vectors cancel each other, being in phase but opposite in direction, whereas the two vertical vectors reinforce each other. The net result is a plane polarized wave with increased amplitude. The rotation of the plane of polarization of this plane-polarized light is ascribed to the fact that one of the circularly polarized components is slowed down more than the other by certain asymmetric ("screwy") crystals or molecules. The result is a spiral similar to that in figure 22.22.

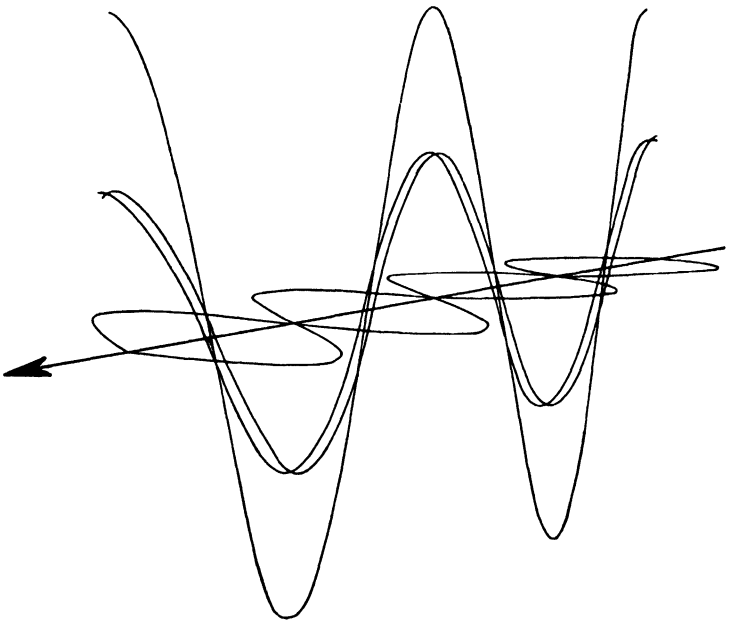


FIGURE 22.23. Plane-polarized light is the combination of *dextro* and *levo* circularly polarized light [adapted from C. R. Noller, *J. Chem. Education*, **24**, 600 (1947)].

22. 16. Stereochemistry and Reaction Mechanisms. In section 17.10 it was explained that molecules go through chemical reactions only after they have become activated, and equation 17.3 shows how reactions in which two molecules take part (bimolecular reactions) pass through a transition phase in which an activated complex is

formed. The subject matter presented in section 17.10 can be made more understandable by study of figure 22.24, which postulates a mechanism for the S_N2 reaction between CH_3Cl and the OH^- ion which was described in the closing paragraphs of section 17.4.

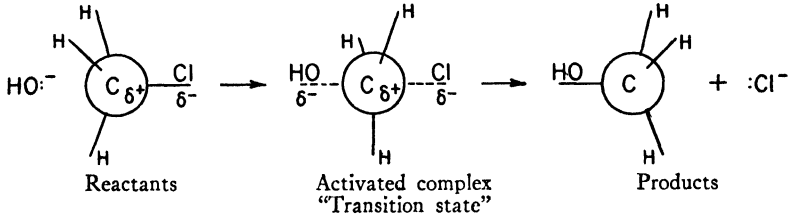


FIGURE 22 24. Bimolecular reaction between CH_3Cl and OH^- ion.

The negative OH^- ion will approach the polarized CH_3Cl molecule "from the rear" because of attraction by the positive end of the molecule and repulsion by the negative end. Theoretical calculations have shown that the transition state which requires the smallest activation energy (see section 17.10) is one in which the OH^- ion, carbon atom, and Cl^- ion are in the same straight line. The activated complex is in a state in which three atoms (or groups) attached to carbon are in one plane, perpendicular to the line in which the positively charged carbon atom is for a brief instant attached to two negative groups or atoms.

In the final stable state there is an *inversion of configuration* of the groups and atoms around the carbon atom; the phenomenon is exactly like reversal of an umbrella in a wind. In the final state there is once more a tetrahedral arrangement around the central carbon atom, but the product (CH_3OH) has the mirror-image arrangement of that in the reactant (CH_3Cl). If the four groups distributed around the carbon atom were different, that is, if the carbon atom were asymmetric, there would be an inversion of optical activity; a member of a Dee family would change over to one of an Ell family, or vice versa. This is known as *Walden inversion* and will be commented on further in section 32.15.

All bimolecular nucleophilic reactions (S_N2) take place with inversion, regardless of whether or not a change in optical activity is

associated with the reaction. Unimolecular reactions (S_N1) generally lead to racemization; in other words, even if the reactant is optically active, the product will be a mixture (generally in equal amounts) of the mirror-image isomers. To explain this, we shall refer to the hydrolysis of *tert*-butyl chloride described in section 26.1, and draw

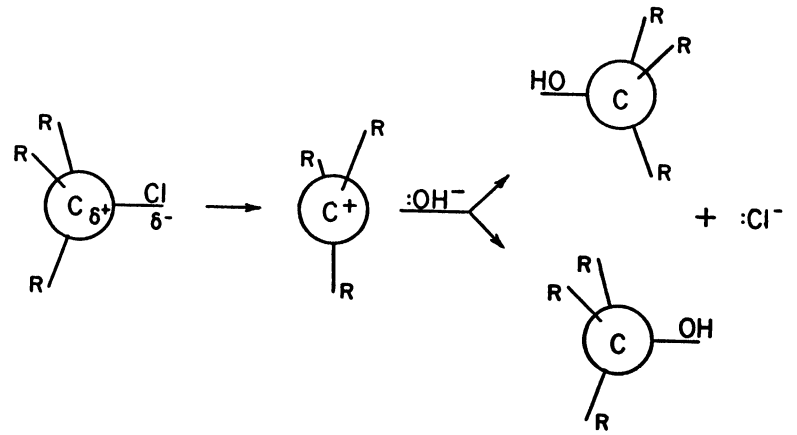
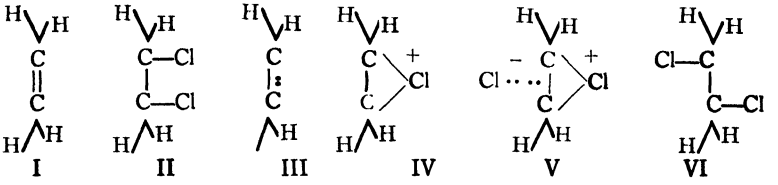


FIGURE 22 25. Unimolecular reaction between $(CH_3)_3CCl$ and OH^- ion. R represents CH_3.

the structures as shown in figure 22.25. The rate of hydrolysis is independent of the concentration of the OH^- ion. It depends entirely on the rate (relatively slow) at which *tert*-butyl chloride ionizes to give a positive carbonium ion, which has three groups *in the same plane* as the central carbon atom to which they are attached. The OH^- can attack from either side of that plane. If the three groups on the carbon atom are all different from one another, and from –OH, the result will be a racemic mixture of optical isomers. Furthermore, an optically active compound hydrolyzed by this mechanism, in which the first stage is ionization, will become optically inactive unless highly polar groups are present which tend to direct the OH^- ion preferentially to one side (see section 32.15).

We may now turn to the consideration of stereochemistry as it applies to certain of the reactions at the olefin double bond. If the ethene molecule is regarded in the old conventional manner (figure

15.1), addition of a molecule of Cl_2 would be expected to take place in a single step by opening one bond in I to yield II. However, kinetics of the reaction show that the reaction takes place in several



steps. As stated in section 17.4, one of the bonds is a π electron pair (III) which forms a positively charged, cyclic chloronium ion (IV) by union with Cl^+ ion. This ion is then attacked "from the rear" by a molecule of Cl_2 or by a Cl^- ion, as indicated in V. Addition of chlorine to ethene is thus seen to be *trans* as shown in VI rather than *cis* as shown in II. One of the carbon atoms may be regarded as undergoing a Walden type of inversion. After the addition, rotation can occur about the single C–C bond to the extent permitted by the groups already present in the molecule.

SUGGESTED READING

American Chemical Society Committee on Nomenclature, "Rules of Carbohydrate Nomenclature," *Chem. Eng. News,* **26,** 1623-1628 (1948).

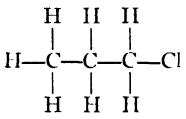
Bates, F. J., *Polarimetry, Saccharimetry, and the Sugars,* National Bur. Standards *Circular C440,* U. S. Govt. Print. Office, Washington, D. C., 1942.

PART 3

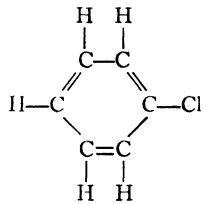
The Classification of Carbon Compounds

The amazing thing about organic chemistry is the immense number of compounds included in it. There is an almost endless number of compounds which consist of carbon and hydrogen, combined with just a few other elements.

Fortunately, as explained in the second part of this book, the carbon compounds can be grouped into a relatively few distinct families, depending on their structures, and this simplifies our study to an enormous degree. For example, when an organic chemist glances at the following two compounds,



and



he classifies them immediately among the *chain* and *ring* compounds, respectively. This helps him to compare the properties of these compounds with the properties of other compounds of similar structure.

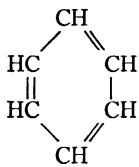
We shall find, however, that the organic chemist, in some cases, is not as much interested in the shapes of these molecules as he is in the fact that they both contain the halogen atom, chlorine. He may, therefore, classify both these compounds in a certain family which will be called the "halogen compounds." Other methods of classification which are sometimes employed are outlined in the next chapter, and constitute the principal problem in the third part of our text.

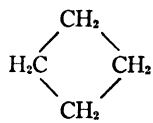
23. THE COMMON METHODS OF CLASSIFICATION IN ORGANIC CHEMISTRY

23. 1. Classification according to General Structure. In our study of the architecture of carbon compounds we have emphasized two broad types of structures, one of which we call chain compounds and the other, ring compounds.

Before proceeding to other methods of classification, it may be wise to recall that the cyclic compounds may be of two types:

Type I	Type II	
	Cyclic	
Open-Chain	a. *Aromatic Compounds*	b. *Alicyclic Compounds*
Aliphatic Compounds	(section 19.1)	(section 11.1)
(section 10.4)		





These examples illustrate the possible arrangements of the carbon atoms in organic compounds, as far as the general architecture is concerned. For a classification of this kind it is only necessary to consider general outlines.

Aliphatic. The word aliphatic is derived from *aleiphatos,* which means fat in Greek. The name has been applied to the chain compounds because some of them were originally obtained from fats,

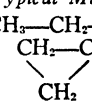
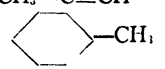
such as butter and lard. To the modern chemist, the word aliphatic simply means a string of carbon atoms in straight-chain or branched-chain formation. It does not mean that the compound has any "fatty" characteristics.

Aromatic. This term is applied to all cyclic compounds containing the benzene ring, or rings with similar properties (section 36.3). Most of the benzene derivatives isolated in the early days of organic chemistry had a pleasant odor and for a while it was thought that an aromatic odor was a characteristic of all benzene compounds. However, not all benzene derivatives have an aromatic odor. Some have practically no odor, and others have very bad odors.

Alicyclic. In chapter 11 we described certain ring compounds that strongly resemble the open-chain compounds in properties. Because of their similarity to chain compounds they are called closed-chain derivatives. They are also known as alicyclic (aliphatic-cyclic).

In most of the following chapters, our attention will be about equally divided between the aliphatic and aromatic compounds. The alicyclic compounds are of little importance in an elementary study of organic chemistry.

23. 2. Classification according to Homologous Series. Up to this point, most of our time has been devoted to the study of chains and rings that can be made from carbon atoms and hydrogen atoms. The families of compounds which we have studied in detail are the following. and it will be recalled that they are all hydrocarbons:

Name of Family	*General Formula*	*Typical Member*
Paraffin hydrocarbons	C_nH_{2n+2}	$CH_3—CH_2—CH_3$
Cycloparaffin hydrocarbons	C_nH_{2n}	
Olefin hydrocarbons	C_nH_{2n}	$CH_3—CH=CH_2$
Acetylene hydrocarbons	C_nH_{2n-2}	$CH_3—C\equiv CH$
Benzene hydrocarbons	C_nH_{2n-6}	

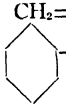
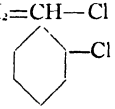
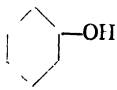
Each of these families of compounds is known as a homologous series, for reasons explained in section 10.7. In every homologous series, each member differs from the next succeeding member by CH_2, as in the paraffin family, CH_4, $CH_3–CH_3$, $CH_3–CH_2–CH_3$, $CH_3–CH_2–CH_2–CH_3$, etc.

All the members of any one homologous series have the same general characteristics, the differences being only that of degree. As the molecules in a series grow larger the solubility may increase or decrease, and the reactivity may increase or decrease, but the essential nature of all the compounds in the series is the same.

The principle of homology has proved useful as a method of classification in organic chemistry, as we have already seen. It allows us to arrange a multitude of compounds into just a few families or series.

23. 3. Classification according to Composition. From now on, we must use still another common method of classifying organic compounds. We are now to begin the study of interesting classes of compounds which owe their characteristic properties to the fact that, in addition to carbon and hydrogen, they also contain elements such as oxygen, sulphur, nitrogen, the halogens, and others.

These compounds will be classified in general according to the most important elements or groups present in the molecule; that is, the classification is based on the *composition* of the molecule. For example, compounds containing only C and H atoms are known as *hydrocarbons*. If the compound also contains a Cl atom this element may stand out as the most important one in the molecule, and we may therefore refer to it as a *halogen* compound. As we have already found (section 9.4), chain compounds containing an –OH group are called *alcohols,* and we shall learn presently that when the –OH group is attached to an aromatic ring structure the compound is called a *phenol.*

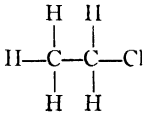
Hydrocarbons	*Halogen Compounds*	*Alcohols and Phenols*
CH_4	$CH_3—Cl$	$CH_3—OH$
$CH_3—CH_3$	$CH_3—CH_2—Br$	$CH_3—CH_2—OH$
$CH_2=CH_2$	$CH_2=CH—Cl$	
		

The names of many of the important classes of compounds in organic chemistry can be found by simply glancing at the chapter headings in the rest of this book.

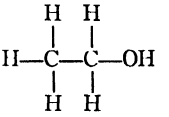
When a compound contains two or more characteristic elements or groups it is called a mixed compound. The substance $CH_2=CH–CH_2Cl$ is a mixed compound, for it is both an olefin and a halogen compound.

24. ALKYL RADICALS AND ARYL RADICALS

24. 1. Introduction. Whenever we met a new compound in part 2 of this book, we tried to name it as a substitution product of some structure with which we were already familiar, for at that time we were stressing the architecture or shapes of compounds. The following substances were named as indicated:



Chloroethane
(Ethyl chloride)



Hydroxyethane
(Ethyl alcohol)

in order to show their relation to ethane, CH_3–CH_3, which was studied in section 9.7. They were regarded as derived from ethane by replacing an H atom of that structure by another element or group of elements. This illustrates the fundamental point of view of the organic chemist and is the system we have consistently employed thus far.

As organic chemists, we like to keep our attention fixed on the importance of structure, which has proved so useful in the development of organic chemistry. However, it is often convenient to think of the presence of a certain element as the important thing, and that the ring or chain to which it is attached is of secondary importance. These two different ways of looking at the same molecule are illus-

trated by the following two formulas that can be used for chloroethane:

Chloroethane, or ethyl chloride

Formula (A) focuses attention on the structure of the molecule; the Cl atom is shown as replacing the H atom in a member of the *paraffin family of hydrocarbons.*

Formula (B) directs our attention to the fact that a reactive Cl atom is in the molecule; the molecule is more clearly designated as a member of the *halogen class of compounds.* Accordingly, we give the name *ethyl* to the radical, $-C_2H_5$; and the substance C_2H_5–Cl, ethyl chloride, is then regarded as consisting of two parts just as sodium chloride, Na–Cl, is always thought of as composed of two units. It is evident that the *ethyl* radical is nothing more than the paraffin hydrocarbon CH_3–CH_3 with one H atom removed.

24. 2. Alkyl Radicals. The radicals, like $-C_2H_5$, which are paraffin hydrocarbons with one H atom missing, are known as alkyl radicals.

Paraffin Hydrocarbons		*Alkyl Radicals*	
CH_4	Methane	CH_3—	Methyl
CH_3—CH_3	Ethane	C_2H_5—	Ethyl
CH_3—CH_2—CH_3	Propane	C_3H_7—	Propyl
CH_3—CH_2—CH_2—CH_3	Butane	C_4H_9—	Butyl
etc.		etc.	

The alkyl radicals are named by replacing the ending -ane by -yl in the name of the hydrocarbon. They have a valence of one, being found combined always with one atom of a univalent element like chlorine, or with one univalent radical like –OH.

To represent *any* alkyl radical the chemist uses the symbol R. Thus, R–Cl is an alkyl chloride, and stands for any of the compounds CH_3–Cl, methyl chloride, C_2H_5–Cl, ethyl chloride, etc. In the same way, R–OH stands for all alcohols such as CH_3–OH, methyl alcohol, and R–CN is any alkyl cyanide such as CH_3–CN, methyl cyanide.

The use of R to represent an alkyl radical is quite common in chemical literature. The student should be warned, however, that

it is also used as a symbol for other radicals. For example, if the author of an article wishes to designate a series of compounds such as CH_3–CH_2–Cl, CH_3–CH_2–CH_2–Cl, and CH_2=CH–CH_2–Cl by R–Cl, that is his privilege. (The unsaturated compound in this list is not an alkyl chloride.)

For an additional illustration, consider an alkyl chloride containing three carbon atoms. The general formula is R–Cl, but this time it represents C_3H_7–Cl which may be either of these

Propyl chloride Isopropyl chloride

for we found in section 10.5 that there are two isomers of C_3H_7–Cl.

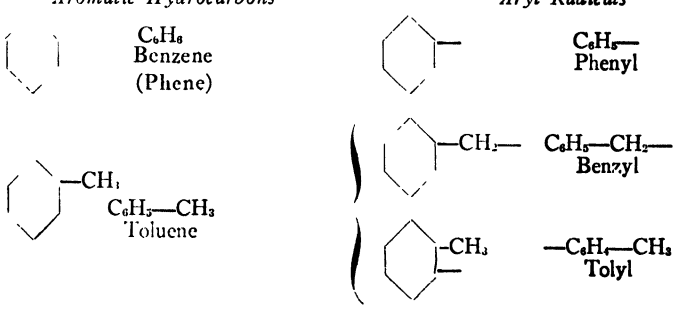
24. 3. Alkanes, Alkenes, and Alkynes. If we call R an alkyl radical, and define it as a paraffin hydrocarbon minus one H atom, then a paraffin hydrocarbon itself is R–H. On this basis, the *paraffin* hydrocarbons are also called *alkanes*.

Whenever someone develops a new family name, like alkanes, for the paraffin hydrocarbons, we can always work out corresponding names for the olefins and acetylenes. The following table explains this plan.

HYDROCARBON FAMILIES

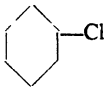
Common Name	*Systematic Name*	*General Formula*	*Typical Member*
Paraffin	Alkane	C_nH_{2n+2}	CH_3—CH_3 Ethane
Olefin	Alkene	C_nH_{2n}	CH_2=CH_2 Ethene
Acetylene	Alkyne	C_nH_{2n-2}	CH≡CH Ethyne

24. 4. Aryl Radicals. The aryl radicals bear the same relation to the aromatic cyclic compounds as the alkyl radicals do to the aliphatic chain compounds:

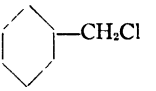


The aryl radicals are the aromatic hydrocarbons with one H atom missing. They have a valence of one, just like the alkyl radicals.

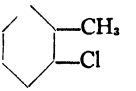
To represent *any* aryl radical, the chemist may use the symbol Ar. Thus, Ar–Cl is any aryl chloride and stands for such compounds as these:



Phenyl chloride



Benzyl chloride

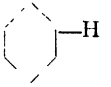


Tolyl chloride

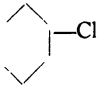
The student should notice particularly that the radical corresponding to benzene itself is not called benzyl, but is called phenyl, for the reason given in section 19.4.

Just like the chain compounds, aromatic hydrocarbons can be regarded as Ar–H. Also, when a compound consists of both a nucleus and a side chain, like toluene, it can be written Ar–R:

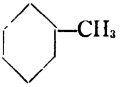
Ar
Phenyl



Ar—H
Benzene
(Phene)



Ar—Cl
Phenyl chloride



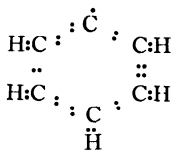
Ar—R
Toluene

24. 5. Carbonium Ions and Carbanions. In the chapters which follow, we shall study not only classes of compounds but also the procedures by which we can pass from one class of compound to another class. This means that we shall constantly apply the principles explained mainly in chapter 17 ("how molecules react") and chapter 20 ("nuclear reactions"). A brief review of those chapters will show that the reactions of chain compounds (aliphatic chemistry) are believed to be mostly *free radical* reactions as described in section 17.12, whereas the reactions of benzene compounds (aromatic chemistry) are explained as a result of *ionic* reactions as described in section 20.2.

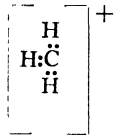
It will soon become evident that free radical reactions are common to both chain and ring structures and ionic reactions are likewise common to both fields of chemistry. Free radicals have already been

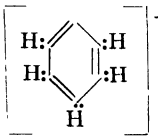
described in section 10.3, which should be reviewed. Free radicals representative of aliphatic and aromatic chemistry are these:

Free methyl radical

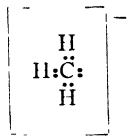

Free phenyl radical

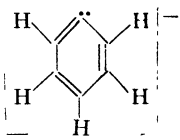
At this point, we shall briefly review several terms covering *ions* which have been introduced elsewhere in this book (see Index) and are illustrated by the following ionic structures:


Methyl ion


Phenyl ion

Carbonium ions


Methyl ion


Phenyl ion

Carbanions

A *carbonium* ion is one in which a carbon atom has released a valence electron, so that the resulting ion has a positive charge (section 10.3). A *carbanion* is a negative ion, in which the negative charge is due to the fact that a carbon atom in the structure has acquired an electron to complete a valence pair. An example is the negative ion in phenylsodium, $Na^+[:C_6H_5]^-$. Another illustration is the negative ion in sodium cyanide, $Na^+[:C:::N]^-$. (The student should carefully compare the structures given for the phenyl ions and the free phenyl radical.)

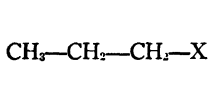
24. 6. Alkylation. The carbonium ion is currently thought to be the key figure in many reactions of commercial importance. One of these reactions was described in section 20.5, where the catalyst in the Friedel-Crafts synthesis forms an "intermediate complex" with a carbonium ion. The Friedel-Crafts synthesis is referred to as an *alkylation* because it involves introduction of an alkyl radical into a ring structure; it can just as well be referred to as an *arylation* since it is introduction of a ring structure into a chain compound.

The petroleum industry employs alkylation reactions in which only open chain structures are involved. This will be discussed in section 32.17.

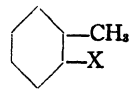
25. HALOGEN COMPOUNDS

25. 1. Introduction. In part 2 we learned how halogen atoms can be inserted into carbon compounds and how their reactivity enables the chemist to do that building up and tearing down of molecules which is his pride and joy. In this chapter, we shall engage in a more thorough study of the behavior and reactivity of the halogen atom.

The general nature of the compounds to be described in this chapter is shown by the following examples, in which X stands for any of the halogens — fluorine, chlorine, bromine, and iodine.



An aliphatic halogen compound.

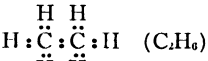


Aromatic halogen compounds. Halogen in side chain. Halogen in nucleus.

We shall consider the chain compounds first.

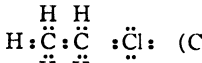
25. 2. Alkyl Halides. The simplest halogen compounds are those in which one X atom replaces one H atom in a chain compound. Examples we have met quite often are methyl chloride, CH_3–Cl, and ethyl chloride, CH_3–CH_2–Cl. These compounds are known as alkyl halides, for they may be represented by the general formula R–X, in which R is the symbol of the alkyl radical (section 24.2) and X is the symbol of the halogen atom.

The importance and structure of these halogen compounds were discussed earlier in the book in section 9.4. It was explained that the paraffin hydrocarbons are relatively inactive because of the firmness of the C–H bond, but their reactivity is increased when the H atom is replaced by Cl:



(C_2H_6)

Ethane
(Very stable)



$(C_2H_5—Cl)$

Chloroethane, or ethyl chloride
(Relatively active)

It is thought that the activity of the Cl atom in these halogen compounds is due to a looser bond between C and Cl than between C and H. The chlorine atom exerts a greater attraction on the electron pair (:) than does the hydrogen atom, and the resulting displacement of the electrons toward the electronegative Cl atom leaves the rest of the molecule slightly electropositive; that is, the C_2H_5–Cl molecule is polar whereas the C_2H_6 molecule is nonpolar (section 10.1). A greater polarity, as we have often observed, is accompanied by a greater chemical reactivity.

Because of the reactivity of the halogen atom in the alkyl halides, these compounds are of great importance in synthetic organic chemistry. They react very easily with metals and metallic compounds, as may be seen in the following cases:

1. $CH_3—CH_2—Cl + 2Na + Cl—CH_3 \rightarrow \underset{\text{Propane}}{CH_3—CH_2—CH_3} + 2NaCl$

This, it will be recalled, is the Wurtz synthesis (section 10.2) for building up larger molecules.

2. $CH_3—CH_2—Cl + KOH/water \rightarrow \underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} + KCl$

This is a method for preparing alcohols (section 9.4).

3. $\underset{\text{Chloropropane}}{CH_3—CH_2—CH_2—Cl} + KOH/alcohol \rightarrow \underset{\text{Propene}}{CH_3—CH=CH_2} + KCl + H_2O$

This is a method for preparing compounds in the olefin series (section 14.2).

In addition to these reactions, a highly important reaction will be described in section 34.10 in connection with the preparation of the

Grignard reagents. These are made by adding the halogen compound to a metal (usually magnesium) suspended in a solvent under carefully controlled conditions.

There is a considerable variation in the rate at which alkyl halides will react with other substances, depending on the chain length and on the halogen atom in the molecule. Thus, methyl halides (CH_3X) react much faster than the homologs with longer chains of carbon atoms and iodides react faster than other halides. Most organic chemists prefer to work in the laboratory with bromides or iodides because of their greater reactivity, if their cost is not prohibitive.

It would require many pages to list all the interesting things that can be done with the simple halogen compounds. Instead of doing so, we shall ask the reader to refer to larger books for more details.

The student who is making his first acquaintance with organic chemistry by reading this book will soon become aware of an intricate, closely woven relationship existing among the various classes of carbon compounds. This has just been indicated by the equations which show how the halogen compounds can be used to prepare both alcohols and olefins, as well as higher paraffin hydrocarbons.

In order to explain the relationships among the various classes of compounds we are not going to be practical in the sense that the equations and reactions we shall write can always be translated into processes useful in chemical industries. Our chief object is to show how the classes of compounds are related to each other, even though the evidence for the existence of the relations described is sometimes obtained from difficult procedures in the laboratory.

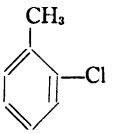
25. 3. Preparation of Alkyl Halides. Now that we have seen how useful alkyl halides can be, we should also find out how the alkyl halides themselves can be made. Instead of listing a series of reactions showing how to make the halogen compounds, we shall refer the student to the other places in this book where their preparation is described. This will make the relation of the halogen compounds to the other classes of compounds more evident.

In section 15.2 we found that H–X (in other words HCl, HBr, etc.) can be added to the double bond, C=C, in an olefin hydro-

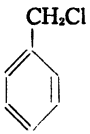
carbon. Some halogen compounds can be made on a large scale by this method because the olefins are a by-product of gasoline refining, and are, therefore, very cheap.

In section 27.3 the preparation of halogen compounds from alcohols, by replacement of the –OH group by a halogen atom, will be described. This is also a favorite method of preparation, because many alcohols can be obtained in large quantities from natural substances.

25. 4. Aryl Halides. Among the aromatic compounds, as we have already indicated in the introduction to this chapter, there are two general types of halogen derivatives — those in which the halogen atom is in the nucleus, and those in which the halogen atom is in the side chain.



ortho-Chlorotoluene
1-Chloro-2-methylbenzene

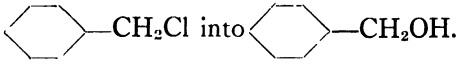


Benzyl chloride
Chloromethylbenzene

Both of these compounds can be represented by the general formula Ar–X; they consist of the aryl radical and the halide radical.

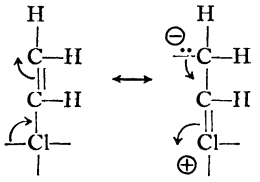
Once again, we find that the position of the halogen atom in the compound is of great importance. The chlorine atom in the nucleus is very stable, so stable in fact that chlorobenzene, , does not react with KOH except under pressure and at high temperature, whereas we have observed that a boiling solution of KOH converts C_2H_5–Cl into C_2H_5–OH quite easily.

The side-chain chlorine atom is even more reactive than when the benzene ring is not present. Water alone will convert

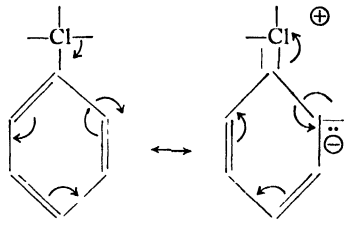


These observations are readily explained with the assistance of the electronic structure of a few typical compounds. First, the student should review what was said about vinyl chloride in section

17.3 (especially the electron structure in figure 17.4), where it was shown that the halogen atom is *conjugated* with the double bond.



Vinyl chloride
Chloroethene

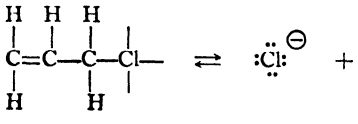


Chlorobenzene

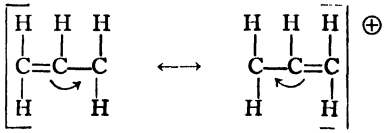
Resonance structures are, therefore, possible, as shown here. As a result, the C–Cl bond is shortened because of its partial double-bond character and the molecule is made more compact (figure 18.5). The C–Cl bond in vinyl chloride is accordingly abnormally stable and is far less reactive than the C–Cl bond in ethyl chloride, CH_3CH_2–Cl.

The same reasoning explains the great stability of the halogen atom attached to the benzene ring. The extensive resonance possibilities of chlorobenzene are shown in figure 21.1, which should be reviewed. A more compact and more stable C–Cl bond results from this resonance effect. It will be observed that the chlorobenzene molecule contains a conjugate system which is seven atoms long, most of it in the ring structure, and that the effect of the Cl atom is felt by the last atom in that system; the last atom now has an excess of negative charge, which makes it receptive to attack by an electrophilic reagent as described in section 20.2. This phenomenon will be referred to again under *vinylogy* (section 32.14).

Now we turn to the *enhanced* reactivity of the C–Cl bond, which is illustrated by the bond in the allyl chloride molecule:



Allyl chloride
3-Chloro-1-propene



Resonance structures
of the allyl ion.

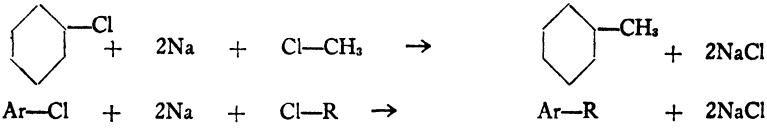
In the introduction to this chapter and in section 10.1, it was explained that the C–Cl bond is polar and that in chemical reactions the Cl tends to separate and react as an ion. If it separates from the allyl chloride molecule during a reaction, the other fragment is a carbonium ion. Resonance structures can be written for this ion, as indicated, whereas such resonance is not possible for the molecule from which the ion originated.

We have repeatedly stressed the fact that resonance stabilizes *a molecule* (section 18.5) in that the molecule will then have a lower energy content; the same thing is true of *an ion* for which resonance forms can be written. In order to cause the chloride and allyl ions to recombine and form allyl chloride, a certain resonance energy must be added, which is considerable because the two resonance structures are equivalent, and this "complete" resonance yields enhanced stability (section 18.5). Once the ions are developed during a reaction, they, therefore, tend to remain ions. This is theoretical support for the experimental observation that the C–Cl bond is abnormally active in allyl chloride; it is many times as active as the corresponding bond in propyl chloride, $CH_3CH_2CH_2$–Cl.

If the *vinyl* radical, CH_2=CH–, is separated from the halogen atom by more than one –CH_2– group, it has no effect on the halogen atom. For example, in the ion from such a molecule as CH_2=CH–CH_2–CH_2–Cl, the flip-flop possibility is lost which enables the electrons from the electron source (section 17.3) to reach the other end of the ion.

If the structure of benzyl chloride is now examined, it will be seen that it contains the same type of atomic arrangement as allyl chloride, namely, a –CH_2– group between a double bond and a halogen atom. It, therefore, contains a reactive chlorine, as stated before.

Although the chlorine atom, when attached to the ring, will not react with some of the reagents with which it reacts when in chain compounds, it will behave in a more normal manner towards metals. We have already called attention to the Fittig synthesis (section 20.7), by which the benzene ring can be linked with other radicals,



and by the same method two rings can be linked:

Phenyl chloride Diphenyl

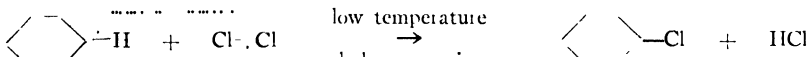
Diphenyl is a crystalline solid (it melts at 71° C. and boils at 254°C.) and is more properly known as *xenene,* but this name is seldom used. It has many properties of considerable interest, of which we shall mention a most important one in section 32.10. Its thermal properties are favorable for its use in certain types of "steam" engines in which it replaces the steam.

25. 5. Preparation of Aryl Halides. The inquisitive student may have noticed that when we discussed the preparation of the *alkyl* halides, such as CH_3–CH_2–CH_2Cl, we did not mention the direct substitution process that we made so much "theoretical" use of in chapter 9:

$$CH_3—CH_2—CH_3 + Cl_2 \xrightarrow[\text{sunlight}]{\text{high temperature}} CH_3—CH_2—CH_2Cl + HCl$$

This is not a good method for preparing individual members of the aliphatic series of halogen compounds, because it is difficult to control the reaction in such a way as to insert just one, two or three halogen atoms into the molecule. Besides, in a chain of several carbon atoms a number of isomers may be formed (section 10.5), which it might be difficult to separate.

In the aromatic series, however, this direct substitution is employed very frequently:



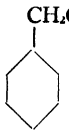
$C_6H_6 + Cl_2 \rightarrow C_6H_5—Cl + HCl$

Phenyl chloride
Chlorobenzene

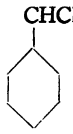
The experimental conditions for substitution in a chain are different from the conditions necessary for substitution in the ring, as shown by the preceding reactions. The mechanism of halogenation of an open-chain compound has already been described (section

20.2) and this description need not be repeated. It will be recalled that it is a photochemical reaction with a *free radical* mechanism. Halogenation of the benzene ring (section 20.2) is an *ionic* reaction which requires catalysts known as halogen carriers. The carrier described in the earlier chapter was $AlCl_3$, but iron filings is more generally used (the catalyst in that case is an iron chloride). Sometimes it is best to halogenate ring structures in the absence of light. Substitution of H atoms in the ring by iodine is generally more difficult than with the other halogens, but when the ring contains certain radicals, substitution even by iodine takes place rapidly, as will be shown later in section 28.2.

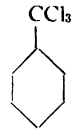
When we wish to introduce a halogen atom into an aromatic compound that contains both a nucleus and a side chain, we must use one of the two sets of experimental conditions which have just been outlined in order to direct the halogen atom into the correct position. If toluene is chlorinated in the dark and at low temperature, the Cl atom goes into the nucleus, but if chlorine is passed into toluene in sunlight, the following compounds are formed:



Benzyl chloride



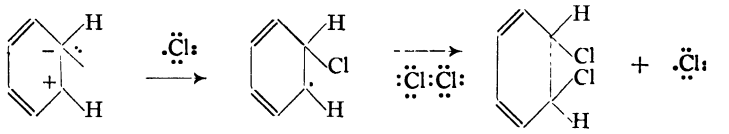
Benzal chloride



Benzo trichloride

These products are mentioned here because they illustrate the use of the names *benzyl, benzal,* and *benzo* for three radicals that occur often in other classes of compounds (see *benzyl* alcohol, *benzal*dehyde, and *benzo*ic acid in the Index).

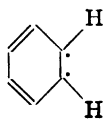
25. 6. Addition of Halogen to Benzene. We have seen that when chlorine is mixed with benzene in the absence of light, but in the presence of a halogen carrier, such as aluminum chloride, the reaction that takes place is ionic, with *substitution* of chlorine for hydrogen. However, the ring structure will slowly *add* chlorine when exposed to sunlight. The ultimate product is benzene hexachloride, as already mentioned in section 19.2. The reaction is thought to be a typical photochemical reaction (section 17.13 and 20.2) with a free radical mechanism:



(I) Benzene (An excited form) (II) Free radical (III) Benzene dichloride

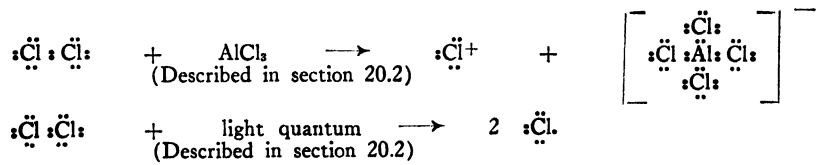
The intermediate complex formed with the chlorine atom (free radical) under the activating influence of light presumably uncouples the pair of π electrons in one of the double bonds of the benzene molecule (I). The resulting free radical (II) reacts with a chlorine molecule to give a molecule of benzene dichloride (III) and a free chlorine atom. This atom then reacts with benzene (I) to continue a cycle of the type described in section 17.13.

Instead of writing (I) with an "uncoupled" electron pair, it may perhaps be easier to visualize the excited structure as a *diradical* form of the type to be described in section 26.4. The double bond in (I) would then be written



25. 7. Fluorine Compounds. Fluorine is the most electronegative of the elements and chemically the most active (see table 8.2). Its activity is so great that comparatively little was done with it in the laboratory until the urgency of the development of fluorine compounds required for the "atomic" bomb in World War II brought about a thorough study of how to tame it.

We have found that, in its reactions with hydrocarbons, chlorine can behave as an ion or as an atom:

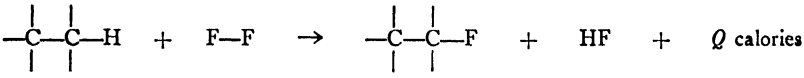


(Described in section 20.2)

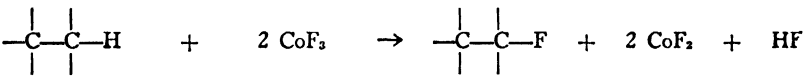
(Described in section 20.2)

Since fluorine is so highly electronegative (electron attractive), it is probably very difficult to form the F^+ ion in chemical reactions. Most fluorinations are, therefore, thought to be atomic (free radical) reactions.

Another important characteristic is the high heat of reaction of fluorine with hydrocarbons. In a substitution, for example, the heat (Q) developed per mole of product is higher than that required to break the C–C bond (see table 17.1). Fluorinations with

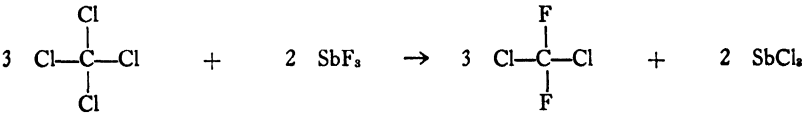


F_2 are, therefore, accompanied by decomposition of the product unless the reaction is carefully controlled by such means as dilution with an inert gas to dissipate the heat of reaction. A common practice developed in World War II was to fluorinate with salts such as CoF_3 or AgF_2. The reaction takes place as follows:



The salt can be regenerated by treatment with excess fluorine.

Fluorinations such as those described before generally tend to go to completion, that is, substitution of all the H atoms usually takes place. Compounds containing a restricted number of F atoms are often made by special methods; one such method is an *exchange reaction* with a corresponding chlorine compound. Thus, to make fluoroethane, CH_3CH_2F, it is convenient to treat chloroethane, CH_3CH_2Cl, with potassium fluoride in a suitable solvent. Another example is the following:



Carbon tetrachloride
Tetrachloromethane

Freon-12
Dichlorodifluoromethane

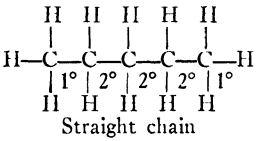
In this reaction, a small amount of antimony pentafluoride, SbF_5, is used as a catalyst. The product is one of the Freons which is used as a refrigerant (section 9.1).

Fluorine compounds are the most stable of the alkyl halides, the order of stability of which is RF > RCl > RBr > RI. For example, methyl chloride (CH_3Cl) can be converted slowly to the corresponding alcohol (section 9.4) by a concentrated alkali solution, but the reaction does not take place with methyl fluoride (CH_3F).

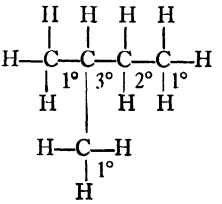
A remarkably stable compound is tetrafluoroethene, $CF_2=CF_2$, which can be polymerized to a plastic (section 46.11) marketed under the name of Teflon. This is so stable that it is used to make gaskets for engines, and bottle-cap linings inert to nearly all chemical reagents.

26. TRIVALENT CARBON

26. 1. Effect of Structure on Polarity. Now that we have seen the importance of the *presence* of foreign elements in carbon compounds, we shall also consider more thoroughly the effect of their *position* in the compound. If we write down some examples of the straight-chain and branched-chain hydrocarbons mentioned in chapter 10,



Straight chain



Branched chain

we can point out an important structural factor which we have intentionally overlooked up to this point.

In the straight-chain compound, it will be observed that the C atoms at the ends of the chain are connected to only *one* other C atom. These are called primary carbon atoms, and are marked by the symbol 1°. All the carbon atoms inside the chain are connected to *two* other C atoms, and are called secondary carbon atoms; they are labeled 2°. In the branched-chain compound we have not only 1° and 2° carbon atoms, but also a tertiary type, labeled 3°, which is connected to *three* other C atoms.

This distinction may not seem to be important, until we bring in the following related facts. It has been found that when the H atom is on a 3° carbon atom it is more reactive than an H on a 2° carbon atom, and this is in turn more reactive than an H on a 1° carbon atom. The strength of the C–H valence bond *decreases* when the carbon atom is united with other carbon atoms.

To explain this behavior, we refer to the electron structure of a typical hydrocarbon, such as propane. The carbon atom is more electronegative (electron-attractive) than the hydrogen atom (table 8.2). It is even more electronegative toward the CH_3 group than it is toward the H atom (in section 21.7 we referred to the CH_3 group as having electron-release characteristics). The result of the competition between the dipoles H+→C and CH_3+→C is that the electron pair in the C:H bond at the 2° carbon atom may be considered to be displaced in the direction C :H. This means that the 2° carbon atom has a looser hold on the H atom to which it is attached; the C–H bond is made more polar by the presence of CH_3 groups on the same carbon atom. When propane is chlorinated, the 2° hydrogen atoms are more easily replaced than the 1° hydrogen atoms, that is, the reaction products contain more 2-chloropropane than 1-chloropropane.

The activity of the 3° hydrogen atom in isobutane, $(CH_3)_3C$-H, is even more remarkable than that of the 2° hydrogens in propane. Although alkanes as a class are resistant to oxidation, mild oxidizing agents will easily convert isobutane to the corresponding alcohol, $(CH_3)_3C$-OH. Isobutane can also be sulphonated (section 20.3) and nitronated (section 20.4).

Other elements, such as chlorine, when placed in 1°, 2°, or 3° positions in the molecule will also show these same variations in activity. Of the following halogen compounds,

$CH_3—CH_2—CH_2—Cl$

1-Chloropropane
(*n*-Propyl chloride)

$CH_3—CH(Cl)—CH_3$

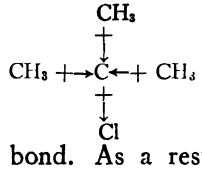
2-Chloropropane
Isopropyl chloride
(*sec*-Propyl chloride)

$CH_3—C(CH_3)(Cl)—CH_3$

2-Chloro-2-methylpropane
(*tert*-Butyl chloride)

the last one is the most active, which is simply another way of saying that its Cl atom is most loosely held to carbon from the chemical standpoint. These are generalizations; the deviations from the rules will not be discussed in this book.

The Cl atom is more electron-attractive than the carbon atom. In the case of the tertiary compound, the dipole directions show that the electron release by the CH_3 groups tends to increase electron density at the central carbon atom. This carbon atom, therefore, has a much smaller attraction for the electron pair in the C:Cl bond. As a result, the chlorine atom tends to leave the molecule with that electron pair as a chloride ion. In other words, *tert*-butyl chloride readily goes through ionic reactions.



For a mental picture of all this, it may be said that when a carbon atom has three carbon radicals attached to it, these groups use up so much "valence force" that the fourth valence of the carbon atom is weakened.

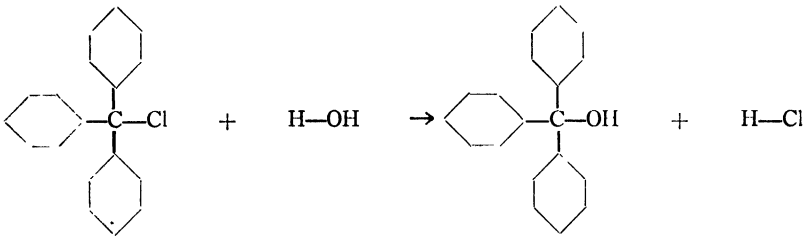
When the rate of hydrolysis of *tert*-butyl chloride was measured

$$Na^+ :OH^- + (CH_3)_3\overset{\delta+}{C} :\overset{\delta-}{Cl} \rightarrow (CH_3)_3C:OH + Na^+ :Cl^- \quad (S_N1 \text{ reaction})$$

it was found to be a unimolecular reaction, whereas the corresponding hydrolysis of methyl chloride (section 17.4) is bimolecular. In other words, when the experimental rate data are calculated from equations 17.6 and 17.7, they are found to fit equation 17.7. The explanation is that the hydrolysis takes place in two stages. In the first step, there is a comparatively slow ionization which is unimolecular and results in $(CH_3)_3C^+$ and Cl^- ions; the second step, which is very fast, consists principally of a reaction between ions. The first step is said to be rate-determining since it controls the overall speed of the reaction; in fact, it is so much slower than the second that the velocity data do not show any characteristics of the bimolecular reaction which takes place in the second stage (review sections 17.10 and 22.16).

26. 2. Trivalent Carbon. The principles discussed in the preceding section are well illustrated by triphenylmethyl chloride, the structure of which is as follows. Since this compound is a derivative

of $(C_6H_5)_3CH$, which is sometimes called *tritane,* it may also be found referred to as trityl chloride.

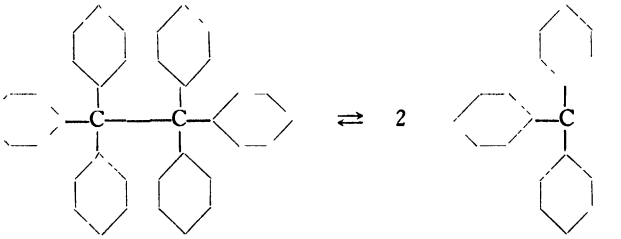


Triphenylmethyl chloride
Triphenylchloromethane

Triphenylmethyl alcohol
Triphenyl carbinol

The Cl atom is so loosely held in this compound that on standing in water it is hydrolyzed to the corresponding alcohol. The compound also reacts with silver nitrate almost as readily as sodium chloride does, which would indicate that it ionizes into $(C_6H_5)_3C^+$ and Cl^-, triphenylmethyl ion and chloride ion.

An interesting reaction of triphenylmethyl chloride is the condensation brought about by zinc, when it is dissolved in such a solvent as benzene. This reaction is similar to the Wurtz and Fittig syntheses (sections 10.2 and 20.7). The resulting compound, hexaphenylethane, is remarkable for its activity. It has been determined that in solution it is dissociated as follows to the extent of about 10 per cent:



Hexaphenylethane

Triphenylmethyl

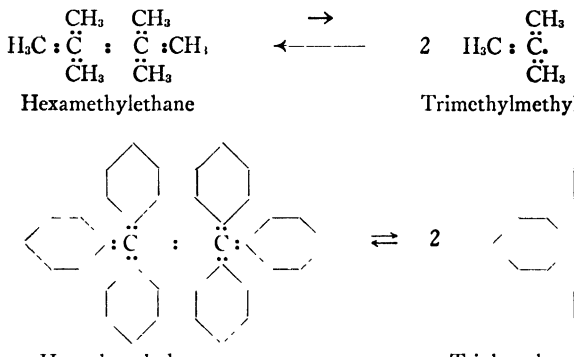
Triphenylmethyl is a distinct chemical substance, the existence of which is beyond doubt, and it contains a carbon atom the valence of which is only three. It is one of the very few instances of *trivalent* carbon. The great activity of hexaphenylethane in solution is probably due to the triphenylmethyl which is present. It reacts with

almost anything in order to fill the valence quota of four on its central carbon atom.

Triphenylmethyl is a *free radical.* Triphenylmethyl is named as a derivative of the methyl radical, CH_3–, which itself, of course, does not exist in the free state except for very brief periods. If we represent the phenyl group by Ph the formula of triphenylmethyl is Ph_3C. This should not be confused with triphenylmethane, which is Ph_3CH.

A series of compounds similar to triphenylmethyl have been prepared.

If we compare the dissociation products of hexamethylethane and hexaphenylethane,



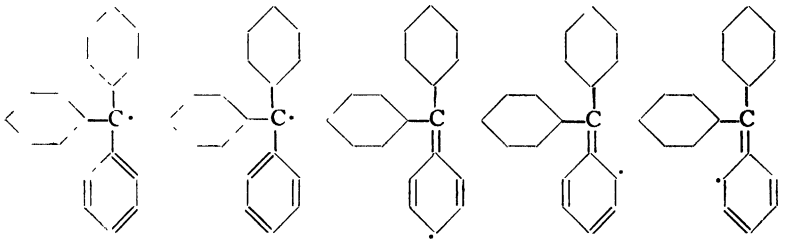
Hexamethylethane Trimethylmethyl

Hexaphenylethane Triphenylmethyl

we note that in each case the central carbon atom has an odd electron. Triphenylmethyl has considerable stability due to the presence of ring structures which permit an extensive amount of stabilizing resonance with this odd electron. Such stabilizing resonance possibilities do not exist for trimethylmethyl, and it is so unstable that we use a very small arrow for the right-hand direction in the preceding reaction.

26. 3. Resonance with an Odd Electron. In order to obtain a picture of the extent of resonance possible in triphenylmethyl, the reader should observe that there are two resonance possibilities for each ring; these are the Kekulé structures A and B, as in benzene (section 19.3). The odd electron can enter into resonance possibilities with each of these, because of conjugation (section 18.1)

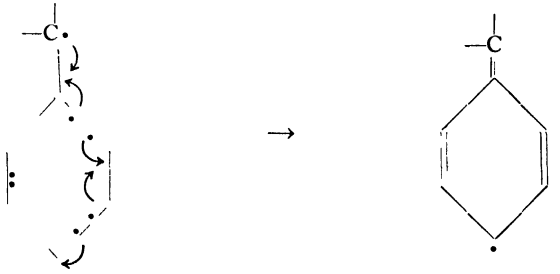
with the double bonds, to give structures I, II, and III. Since there are three rings in each structure, the possibilities can be multiplied



A B I (from A or B) II (from A) III (from B)

(For simplicity, resonance structures for only one ring are shown)

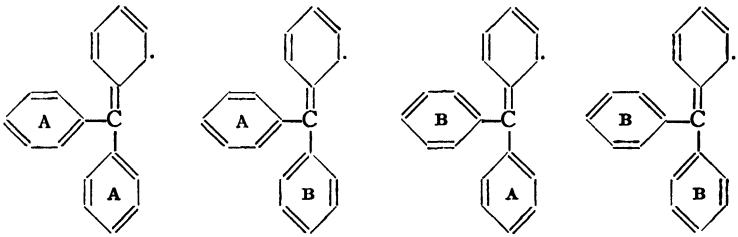
by three, the odd electron being found in nine positions *in addition* to that on the central carbon atom. The odd electron in these structures appears at the *o*- and *p*- positions. The student should work out the structures with pencil and paper, using a system somewhat similar to that described in section 21.5. This can be illustrated by the formulation of structure I, as follows, keeping in mind that each straight-line bond represents a pair of electrons:



It will be seen that a conjugate system of double and single bonds is necessary for such an interaction of electrons. The electron pairs shown in this example are the π electrons described in section 17.3 (see especially part (*e*) under figure 17.3*b*).

The odd electron tends to spread through the entire molecule of *triphenyl*methyl rather than attach itself only to the central carbon atom; this distinguishes it from its behavior in *trimethyl*methyl. We noted in the preceding paragraph that the odd electron can occupy ***nine*** positions in the three ring structures. In each of these positions

the electron can be associated with *four* different resonance forms as follows, making possible the existence of thirty-six structures of this type (the letters A and B as usual indicate the two Kekulé structures for benzene). Similarly, *eight* resonance structures with the odd electron at the central carbon atom can be written, making a total of forty-four.



The many triphenylmethyl structures which are possible produce so much resonance energy that the molecule is fairly stable. Even more stable molecules of similar type have been studied, in which there are more complex rings with a larger number of double bonds, permitting still greater resonance possibilities (such a ring structure is naphthalene, section 36.5).

It is believed that these principles explain why the dissociation of a chain compound like $(CH_3)_3C–C(CH_3)_3$ is very small, whereas the degree of dissociation of a benzene derivative represented by $Ar_3C–CAr_3$ is relatively large. The resonance energy of the dissociation products ($2\,Ar_3C$) of the benzene compounds stabilizes them because this relatively large amount of energy must be supplied to the dissociation products in order to recombine them to $Ar_3C–CAr_3$.

26. 4. Other Odd Electron Structures. In chapter 9, which introduced part 2 of this book, much emphasis was placed on the constancy of valence of carbon, which was said to have a valence of four in nearly all of its compounds. We have now discussed some of the exceptions, but it is obvious that the exceptions indicate even more strongly the normal tendency of the carbon atom toward quadrivalence.

The student should review the various places in this book where deviations from the normal valence behavior have been described.

Free radicals were first mentioned in section 10.3, where they were compared with free atoms. The methyl radical, $\cdot CH_3$, was written with an odd electron. As stated in this chapter, free radicals may be regarded as compounds containing trivalent carbon. This is based on the definition of valence elaborated on in section 3.1, that is, the combining power of an element. More strictly, one might say that only the carbon atom in a carbonium ion (section 24.5) is trivalent, since such a carbon atom holds only 3 pairs of electrons, whereas in a free radical there are 3½ pairs.

In certain experiments, the methyl radical has been found to have a life of the order of 0.01 second. It rapidly unites with another methyl radical to form ethane, $CH_3:CH_3$.

In sections 17.11 to 17.13, it was shown that when the structure of a molecule is such that it absorbs certain wavelengths of light, the resultant activation may lead to formation of free radicals, and these may initiate chain reactions. Free radicals propagate a chain reaction by giving up their activation energy to molecules, breaking them down, in turn, to free radicals.

In sections 17.4, 25.5, and 25.6, it was explained that free-radical reactions are prevalent in the chemistry of saturated chain compounds, especially substitution reactions, whereas the unsaturated olefin group in a molecule and the benzene structure lead to reactions of an ionic mechanism.

It is of interest now to mention briefly a group of compounds which have a *diradical* type of structure. These are structurally related to oxygen, which has the electron configuration $:\ddot{\underset{\cdot}{O}}:\ddot{\underset{\cdot}{O}}:$ although it may be found more generally written $:\ddot{O}::\ddot{O}:$ or $O{=}O$. The structure $:\ddot{\underset{\cdot}{O}}:\ddot{\underset{\cdot}{O}}:$ is also sometimes used; it makes more apparent that the odd electron may interact with an electron pair of the neighboring atom to produce a three-electron bond in addition to the two-electron bond. Two such bonds are possible in the oxygen molecule, and it is believed that the stability of such molecules is due to these bonds. The reason for calling this type of structure a diradical will be evident after a review of the radicals shown in table 10.1, in that it has *two* odd electrons.

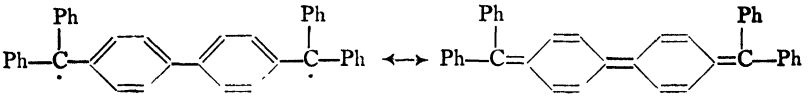
A fundamental assumption about the duet of electrons which make a chemical valence bond is that the two electrons have opposite spins (section 7.5). Such electrons are said to be *paired.* A molecule in which all the electrons are paired is *diamagnetic.* The oxygen molecule contains two electrons which are not paired; they spin in the same direction and the molecule is *paramagnetic.* These terms refer to the *magnetic susceptibility* of the molecule. If the magnetization induced in a body has a value I when placed in a field in which the magnetizing force is H, the magnetic susceptibility is the ratio I/H. If the ratio is greater than one the molecule is said to be paramagnetic, whereas if the ratio is less than one it is called diamagnetic.

Paramagnetism is due to an excess of electrons spinning in one direction. Most molecules have paired electrons, but are feebly diamagnetic because of the characteristic behavior of electrons, rotating in their orbits, called precession (look up precession of the planets in an astronomy book).

Since paramagnetism is a property characteristic of an unpaired electron, it is a useful test for odd electron structures and consequently for free radicals. The existence of triphenylmethyl was postulated originally on the basis of its chemical properties, before the development of electron valence theory, but there is now this physical property which proves its structure.

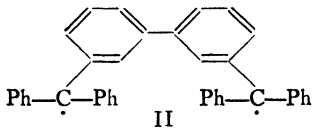
If now we refer back to the possible electronic structures of the double bond in ethene (section 17.3), we shall see that it is possible to write a structure analogous to that of oxygen, namely, $\dot{C}H_2$–$\dot{C}H_2$, which is known as the dot-dot structure; a similar diradical type of structure can also be written for butadiene (section 18.10), thus, $\dot{C}H_2$–CH=CH–$\dot{C}H_2$, and such "excited" structures may conceivably be formed under the influence of high temperature or photochemical activation. They would have such a fleeting existence that it would be difficult to prove their presence, even by spectroscopic means.

It is possible to prepare molecules in which two such unpaired electrons are known to be present. In the following structures, to save space, certain of the phenyl rings are represented by Ph:



I Ia

This compound is not paramagnetic



II

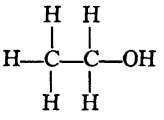
This compound is paramagnetic

Formula I is that of a compound which can be written with unpaired electrons, but as shown in Ia these electrons can interact through a conjugate system of double and single bonds. In formula II, where the end groups are *meta,* such resonance interaction is not possible (the student should prove this to himself with pencil and paper). The odd electrons in II are, therefore, fixed and the compound has been found to be paramagnetic. Like free $\cdot CH_3$ radicals, these molecules will tend to react with each other, but measurements show that there is an appreciable dissociation to free diradicals at ordinary temperatures.

27. ALCOHOLS

27. 1. The Hydroxy Group. As already explained, our plan in part 3 of this book is to spend less time on the architecture of compounds and more time on the reactive elements they contain. In this chapter we begin the study of oxygen compounds, and among them first the class of alcohols.

There are two ways of looking at alcohols, as shown by the two ways ethyl alcohol is written:



Ethanol

$C_2H_5—OH$

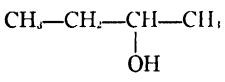
Ethyl alcohol

According to one system, ethyl alcohol is a compound derived from the hydrocarbon, ethane, by replacing an –H atom with the –OH group. It is named ethanol to indicate it is an alcohol derived from ethane, the ending *-ol* being used as a designation for alcohols.

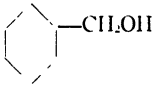
In the other system, ethyl alcohol is considered as derived from water, H–O–H, by replacing an –H atom with the ethyl radical, $-C_2H_5$. Any such alcohol can be represented by R–OH or R–O–H.

The –OH group is called either *hydroxy* or *hydroxyl.* In this book, we shall use the first name.

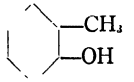
Before reading further, the student should turn back to the first page in chapter 25 and compare the halogen compounds we listed at that time with the following compounds containing –OH groups:



An aliphatic alcohol (—OH in a chain compound)



An aromatic alcohol (—OH in a side chain of an aromatic compound)

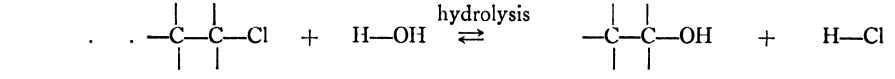


A phenol (—OH in nucleus of an aromatic compound)

As indicated by these examples there are two kinds of alcohols. The aliphatic alcohols are those in which the –OH group replaces an H atom in an open-chain compound. The aromatic alcohols are those in which an –OH group replaces an H atom in the *side chain* of an aromatic compound.

When the –OH group replaces an H atom in the *nucleus* of an aromatic compound, the product is called a phenol. The phenols will be discussed in the next chapter, because they are quite different from alcohols. In chapter 25, we found that the Cl atom, also, has different properties, depending on whether it is in the side chain or nucleus of a compound.

There is a direct relation between the –OH compounds to be described now and the halogen compounds we have already studied, for they can often be converted into each other under the proper conditions:

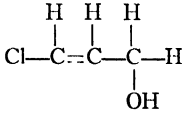


As a matter of fact, many hydroxy compounds of commercial importance are manufactured by first introducing a Cl atom into an open-chain compound and then replacing the active Cl atom by an –OH group by this process of hydrolysis.

It is only on rare occasions, as we shall see later (section 27.4*c*) that the C–H bond in liquid hydrocarbons can be directly converted to C–OH without first replacing the H atom by a more active atom or group of atoms.

27. 2. How to Name Alcohols. We have already indicated (sections 10.10 and 14.3) that when the –OH group is the principal "functional" group in a molecule, the ending -ol is used in the main part of the name of the compound. For this reason, we write for CH_3CH_2OH ethanol instead of hydroxyethane. Similarly, we assign to $CH_3–CH_2–CHOH–CH_3$ the name 2-butanol instead of 2-hydroxybutane; in this example *butan* shows there are four carbon atoms in the chain, and *ol* shows it is an alcohol. The –OH group is on the second carbon atom.

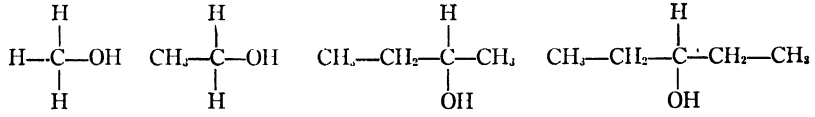
By this systematic method it is a comparatively simple matter to name fairly complex compounds such as this:



3-Chloro-2-propen-1-ol

This is a halogen compound (chloro), and an olefin (en), as well as an alcohol (ol). It is also a three-carbon chain (prop) and the numbering is started from the right-hand end in order to give the functional group (–OH) the lowest number.

One of the old methods for naming alcohols that is still quite often used is based on an old name for wood alcohol, which used to be called carbinol. Other alcohols are named as derived from carbinol, as in these illustrations:



Carbinol
Methanol
Wood alcohol
Methyl alcohol

Methylcarbinol
Ethanol
Grain alcohol
Ethyl alcohol

Methylethylcarbinol
2-Butanol
(a butyl alcohol)

Diethylcarbinol
3-Pentanol
(an amyl alcohol)

The carbon atom in the C–OH bond is called the carbinol carbon atom.

These examples also indicate a third common way to name alcohols, that is, according to their source. Until recently, the only commercial source of methanol was the distillation of wood and,

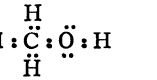
consequently, it is known as wood alcohol. Ethanol is still obtained in large quantities from the fermentation of cereals and grains, such as rye, barley, and corn, and is, therefore, called grain alcohol. The five-carbon alcohols, corresponding to pentane and called pentanols, were originally obtained from starch fermentation and named amyl alcohols, because the Latin word for starch is amylum.

Lastly, the alcohols are often named in such a way as to indicate their two-component structure. Thus, methyl alcohol consists of the methyl radical, CH_3–, and the hydroxy radical, –OH, which is the "alcohol" group. The simple alcohols are to be regarded as hydroxides of hydrocarbon radicals. The alcohols derived from the paraffin series, such as CH_3–OH, C_2H_5–OH, etc., are alkyl hydroxides, R–OH.

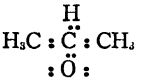
The aromatic alcohols should give no difficulty in regard to nomenclature. As an illustration, —CH_2CH_2OH is phenylethyl alcohol, or 2-phenyl-1-ethanol, or hydroxyethylbenzene.

27. 3. Alcohols as Acids or Bases. The alcohols have polar characteristics, and the lower alcohols in particular behave very much like water toward certain reagents. The lower alcohols will dissolve many inorganic substances which are water soluble.

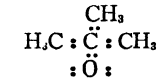
Most of their chemical behavior is easily understood and explained when alcohols are considered electronically. There are three types of structures, analogous to those described in section 26.1, which can be illustrated by the following compounds:



Methanol
Methyl alcohol
A 1° alcohol



2-Propanol
Isopropyl alcohol
A 2° alcohol

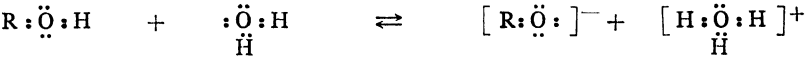


2-Methyl-2-propanol
tert-Butyl alcohol
A 3° alcohol

The oxygen atom is highly electronegative, and tends to draw the electron pairs from both the CH_3 and the H atom. Consequently, there is a measurable tendency for the H atom to lose its interest in the electron pair of the O:H bond and become an ion.

The ionization of an alcohol may be written as a decomposition of ROH to give the RO^- ion and the H^+ ion. A discussion which

will be given in sections 31.5 and 31.7 will demonstrate that it is better to consider the ionization in water soluton as the result of the following interaction:



An alcohol reacts as an acid to yield hydronium ion (hydrated H^+ ion).

The hydrated H^+ ion will be referred to again in section 31.5.

It will be seen that the oxygen atom in water is somewhat more prone to share its electron pair with the H^+ ion than the oxygen atom in the alcohol molecule. It will be explained in section 31.7 that, according to the electron theory of acids and bases, water can be regarded as a base when it furnishes an electron pair in a reaction; in this instance, the alcohol is acidic in that it yields the H^+ ion. The acidity of alcohols is very weak. The ionization constants of the lower alcohols in water have been measured and indicate a very small concentration of the hydrated hydrogen ions.

The structure of the hydrated hydrogen ion is similar to that of other ions to be described soon, such as the ammonium ion (section 31.5). It is, therefore, called *hydronium* ion, and is a member of the large family of *oxonium* ions.

The tendency to lose the H^+ ion, in other words, the acidity of alcohols, is greatest in the 1° alcohol and least in the 3° alcohol. The lower acidity of the 3° alcohol has been explained as the result of electron release by the $-CH_3$ group (section 26.1), which causes an increased density of electrons around the carbinol carbon atom. This makes the oxygen atom in the $-\overset{|}{C}OH$ group more basic. The H^+ is more firmly held, which means lower acidity. The greater stability of the 3° alcohols in this respect is illustrated by the sodium reaction. When an active metal, like sodium, is added to an alcohol, the hydroxy H atom is replaced, since it is acidic:

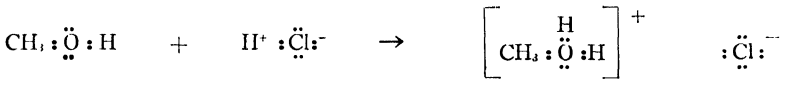
$$2\,CH_3OH + 2\,Na \rightarrow \underset{\text{Sodium methylate}}{2\,CH_3ONa} + H_2$$

This reaction takes place most rapidly with 1° alcohols, less rapidly with the 2°, and least rapidly with the 3° type. The product is a

salt which belongs to the class of *alcoholates*. It is preferable to call them *alkoxides* and then, the sodium compound is *sodium methoxide*.

The organic chemist makes wide use of the fact that he can insert a metal so easily into a carbon compound. Such compounds can easily be made to react with compounds containing halogen atoms, to produce larger molecules. An example of such a preparation will be given later, in the study of ethers (section 29.3). The alcoholates resemble the hydroxides of inorganic chemistry, such as NaOH, in their method of preparation. Since alcoholates are salts of extremely weak acids they hydrolyze in water to give basic solutions.

The availability for reaction of the free pairs of electrons on the oxygen atom of an alcohol is made evident by the ease of formation of valence bonds with electron-seeking reagents. An alcohol reacts



An alcohol reacts as a base to yield a salt

with acids to form salts which can be isolated at low temperatures (about —50°C.). These are *oxonium* salts; the structure of the positive ion should be compared with that of the hydrated H^+ ion. It is obvious that in this reaction an alcohol is acting as a base to form a salt, whereas in the reaction with sodium it acts as an acid to form a salt. Acids and bases will be discussed more fully in section 31.5.

At ordinary temperatures, oxonium salts like the one described before, are generally very unstable. The C–OH bond is weakened by the presence of the *additional* hydrogen atom, which draws away part of the negative charge normally on the oxygen atom. A molecule of HOH splits off from the complex ion, leaving a methyl ion (in the preceding example) to react with chloride ion:

$$CH_3OH + H^+Cl^- \rightleftarrows CH_3Cl + H_2O$$

This is the reaction referred to in section 25.3. The reaction takes place most readily with the 3° alcohols because, as already stated, the carbinol carbon atom in a 3° alcohol has an abnormally high electron density. This accentuates the negative properties of the oxygen atom, which is then even more susceptible to attack by an

electron-seeking reagent, such as the H^+ ion. The chlorine compound is not prepared so readily by this method as the other halogen compounds. A drying agent must be used to absorb the water by-product; otherwise the process would reverse itself with the regeneration of the alcohol, because this is a reversible reaction.

27. 4. Other Properties of Alcohols. There is evidence that most of the activity of the alcohols is due to the activity of the R–OH bond rather than the RO–H bond. At any rate both bonds react readily as we shall see in the following examples, so that the chemical properties of the alcohols are to be summed up in the type formula R–O–H, analogous to H–O–H for water.

27. 4a. Reaction with PX_3. When alcohols are treated with one of the chlorides of phosphorus the entire –OH group is replaced:

$$3\ C_2H_5{-}OH + P{-}Cl_3 \rightarrow 3\ C_2H_5{-}Cl + H_3PO_3$$

Phosphorus trichloride — Ethyl chloride — Phosphorous acid

This reaction is probably to be attributed to the strong affinity of phosphorus for oxygen. This is one of the standard methods by which –OH groups are replaced by halogen atoms in many kinds of compounds. When PBr_3 and PI_3 are used, the corresponding bromine and iodine compounds are formed. Since many alcohols are obtained in vast quantities from natural sources, it is evident that this reaction is a most important method for making the halogen compounds which occupied our attention in the last few chapters.

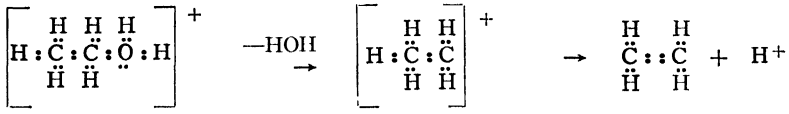
27. 4b. Dehydration. In discussing the properties of alcohols, we have up to now stressed the OH group alone. Now we must look at the behavior of the molecule as a whole.

Alcohols can often be dehydrated, as follows:

$$H{-}C(H){-}C(H){-}H + \text{dehydrating agent } (H_2SO_4 \text{ or } Al_2O_3 \text{ at high temp.}) \rightarrow H{-}C{=}C{-}H + H_2O$$

The requirement here is that the C–OH is next to a carbon atom holding an H atom. This is a convenient way to prepare olefins, as we pointed out in section 14.2.

The dehydration reaction takes place through intermediate formation of an oxonium ion, due to the proton (H^+) from the acid catalyst "sitting down" on one of the electron pairs of the oxygen atom. This oxonium ion then splits off water as it usually does, yielding



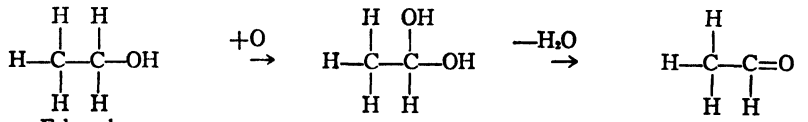
An oxonium ion — A carbonium ion — Ethene

a carbonium ion which is even less stable and, in turn, proceeds to eliminate H^+ ion. (If the catalyst used is sulphuric acid, the transient compounds formed from these ions would be successively ethyldihydrogenoxonium sulphate and ethyl sulphate.)

The H^+ ion, which is eliminated, reacts with an acid radical to regenerate a molecule of the acid catalyst, or it can attack another molecule of the alcohol to decompose it to an olefin. The student should compare this high-temperature reactivity of an acid toward an alcohol (at about 180°C.) with the activity at lower temperature described in section 27.3, where it was shown that CH_3OH and HCl eliminate a molecule of water to give the CH_3Cl molecule.

On a commercial scale, alcohols are often dehydrated by passing their vapor over an aluminum oxide catalyst at about 350°C. This catalyst is similar in its action to the H^+ ion. The student is also advised to read ahead in section 29.3 for still another mechanism by which alcohols may be dehydrated, that is, to yield *ethers*.

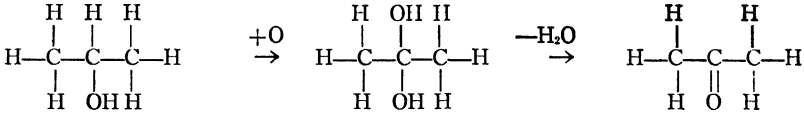
27. 4c. Oxidation. Most alcohols are easily oxidized, but the course of the reaction depends on the position of the –OH group in the molecule, that is, whether it is primary, secondary, or tertiary. Let us see what happens when these three types of alcohols are oxidized by oxidizing agents, such as chromic acid (an acid solution of $K_2Cr_2O_7$, potassium dichromate). These are the probable steps in the oxidation of a primary alcohol:



Ethanol — Ethanal (An aldehyde, section 30.2)

When an –OH is present on the same carbon atom, the H atom in the group H–C–OH is easily oxidized to HO–C–OH. Two –OH groups on the same carbon atom generally form an unstable system, although there are known exceptions to the rule (see chloral, section 30.6); it is believed that the intermediate product in the oxidation of an alcohol has such a structure. It eliminates water to form a compound which is called an aldehyde. The student is advised against reading ahead to find out more about aldehydes until we begin definitely to study them. It is sufficient for the present just to note their structure.

When a secondary alcohol is oxidized we again assume that the H atom in the group H–C–OH is unusually active and can easily be oxidized directly to OH:



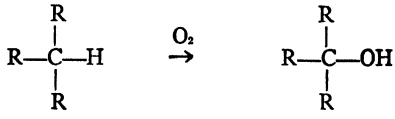
2-Propanol

Propanone
(A ketone, section 30.2)

When the two –OH groups on the same carbon atom eliminate a molecule of water, a ketone is formed. Here again, it is sufficient to notice that the product of oxidation of a 1° alcohol is different from the product of oxidation of a 2° alcohol, and that the difference is due to the *position* of the –OH group in the molecule.

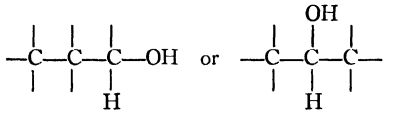
A tertiary alcohol, when oxidized, cannot go through any such process as the primary and secondary alcohols, as is perfectly evident by inspecting the formula of 2-methylpropan-2-ol (section 27.3). Strong oxidation of such a compound will break it down completely to carbon dioxide and water.

As a matter of fact, a tertiary alcohol can itself often be prepared by the oxidation of the corresponding hydrocarbon:

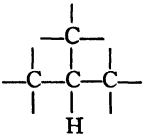


To understand why this is possible, the student is referred to section 26.1, where we explained the greater activity of the C–H bond when the carbon atom has three radicals attached to it.

In this discussion, we have shown two types of examples in which the C–H bond, so famous for its stability, can be transformed into C–OH. In one case the C–H link was loosened by the presence of –OH on the same carbon atom, and in the other case it was loosened by the presence of three other carbon atoms:



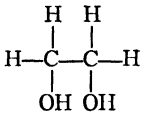
Case I



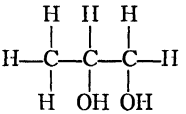
Case II

In all of these examples the H atom is easily oxidized to OH.

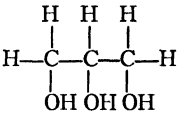
27. 5. Polyhydric, or Polyatomic Alcohols. Although carbon compounds are usually unstable when two or more –OH groups are on the *same* carbon atom, many important and quite stable compounds are known in which several –OH groups are attached to *different* carbon atoms. Here are just a few examples, with their systematic and common names:



Ethanediol
Ethylene glycol



1,2-Propanediol
Propylene glycol



1,2,3-Propanetriol
Glycerol
Glycerin

These are known as polyhydric or polyatomic alcohols to distinguish them from the alcohols which have been described up to this point. The alcohols containing only one –OH group in the molecule are called monohydric or monatomic. The diatomic alcohols are called *glycols*.

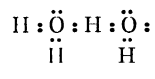
Ethylene glycol and glycerol are used in large quantities commercially as sweetening agents, in antifreeze mixtures, in cosmetics, in dynamite, etc. In general, the polyhydric alcohols have the same chemical properties as the monohydric, except that, in certain cases, they will react with more of a specific reagent.

27. 6. Aromatic Alcohols. The alcohols containing benzene rings behave in general like the ordinary aliphatic alcohols. The simplest compound in this class is , which is the phenyl derivative of methanol. It can be called phenylmethyl alcohol, or phenylmethanol, or phenylcarbinol, but is generally known as *benzyl* alcohol. The benzyl radical is defined in section 24.4.

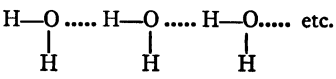
Benzyl alcohol gives most of the characteristic reactions of the –OH group which have just been described. The ring part of the compound, however, does not behave normally; that is, it is not possible to sulphonate and nitrate it as described in section 20.4, because the alcohol group is sensitive to oxidation and these reagents may cause oxidation and decomposition of the molecule.

The aromatic alcohols usually have a pleasant, ethereal odor.

27. 7. The Hydrogen Bond. It has been known for many years that water tends to combine with itself to form polymers, or giant molecules; this is the phenomenon referred to as association (section 8.9*d*). A satisfactory mechanism for the polymerization of water was not available until the electron theory of valence was proposed. It is now understood that H:Ö:H molecules are linked through hydrogen bridges, thus,



or



The important characteristic of the hydrogen bond is that an H atom acts as a bridge between two highly electronegative elements like oxygen, chlorine, and nitrogen, which hold unshared electron pairs.

In the index of this book, the reader will find a number of references to phenomena in which the hydrogen bond plays an essential part. These phenomena had no satisfactory explanation until recent years, because the hydrogen bond according to the older theories required that the hydrogen atom should have a valence of two (–H–), to which very few chemists would agree.

The hydrogen bond is currently believed to be due to the ability of pairs of electrons on small elements (such as oxygen) to share a proton between them. This gives rise to dipole forces, measurements

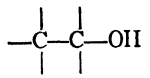
of which are in substantial agreement with the conventional picture of the hydrogen bridge. It is an electrostatic effect.

Alcohols polymerize in the same way; if we represent any alcohol by R:Ö:H the continuous chain in the liquid phase is

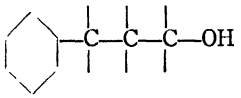
H:Ö: H:Ö: H:Ö:, etc.
R R R

28. PHENOLS

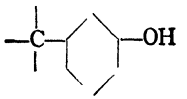
28. 1. Introduction. In the last chapter we showed that the difference between an *alcohol* and a *phenol* is in the position of the –OH group. The –OH group of an alcohol is attached to a C atom in a chain, whether the chain is a simple one or is joined to a benzene ring in the form of a side chain. The –OH group of a phenol is directly attached to a C atom in the benzene ring itself:



An aliphatic alcohol



An aromatic alcohol



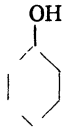
A phenol

These different positions result in different properties of the same group, as we shall soon demonstrate.

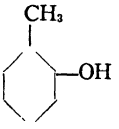
The simplest phenol is phenol itself. It is the compound derived from benzene; its name is obtained from the old name for benzene, which used to be called phene (section 19.1).

Phenols, just like the alcohols, may be looked on as derived from water, H–O–H, by replacing one H atom with an aryl radical (section 24.4), so that the general formula is ArOH.

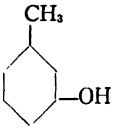
We can also define phenols as derived from aromatic hydrocarbons by replacing an H atom in the *nucleus* with an –OH group. Representative compounds are shown as follows.



Phenol
Carbolic acid
Hydroxybenzene
m.p. 43°



o-Cresol
o-Hydroxytoluene
o-Methylphenol
m.p. 30.8°



m-Cresol
m-Hydroxytoluene
m-Methylphenol
m.p. 10.9°

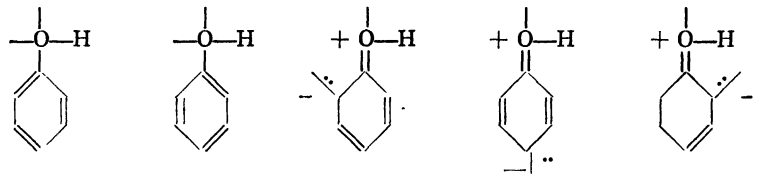
p-Cresol
p-Hydroxytoluene
p-Methylphenol
m.p. 35°

These examples of phenols containing but one –OH group are known as monohydric phenols, to distinguish them from the polyhydric phenols to be described later in this chapter.

All four compounds listed here are found in coal tar. They all have penetrating odors, and are all used as antiseptics as well as intermediates in many industrial processes. The toluene derivatives are known as the *cresols* because they are found in wood creosote.

28. 2. Properties of Phenols. In the phenols, the –OH group is so firmly linked to carbon that it cannot be made to enter readily most of the reactions described for alcohols in section 27.4. Moreover, phenols are much more acidic than alcohols. The chemically active bond in phenols can be shown by ArO–H, whereas we found the properties of alcohols represented better by R–OH than by RO–H.

The acidity of phenol can be explained with the aid of the resonance theory, the usual Kekulé structures A and B being in resonance with structures I, II, and III:



A B I (from A) II (from A or B) III (from B)

These structures are worked out by the scheme described in section 21.5. They contribute resonance energy which increases the stability of the phenol molecule, but what we wish to emphasize is the fact that the average state of the molecule is one in which the O atom is positively charged because of the shifting of negative elec-

trons into the ring. The electropositive H atom is, therefore, held less firmly, which accounts for the stress laid on the ArO–H bond in the preceding paragraph.

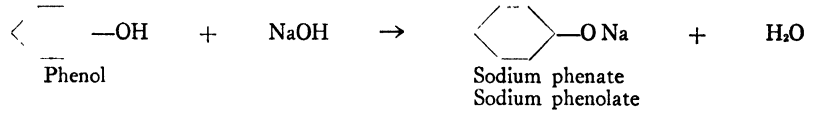
The ionization of phenol in water leads to the formation of hydrated hydrogen ions (section 31.5) and phenate ions:

$$\underset{\text{Phenol}}{C_6H_5O{-}H} + HOH \rightleftarrows \underset{\text{Phenate ion}}{C_6H_5O^-} + H{\cdot}H_2O^+$$

Resonance in the phenate ion is even more effective than in phenol itself because absence of the H^+ ion from structures A and B allows shifting of three unshared valences instead of only two. This promotes stability of the phenate ion, thus decreasing the tendency for the preceding reaction to go to the left and giving phenol acid characteristics.

There are no resonance possibilities of this type in alcohols, like C_2H_5OH, which, therefore, have a much smaller tendency to lose H^+ ions and behave like acids. The reader should review section 26.2 and note how an analogous reasoning explained the greater dissociation tendency of hexaphenylethane than that of hexamethylethane.

Because of its acid properties, phenol reacts with inorganic bases to form salts:



Phenol

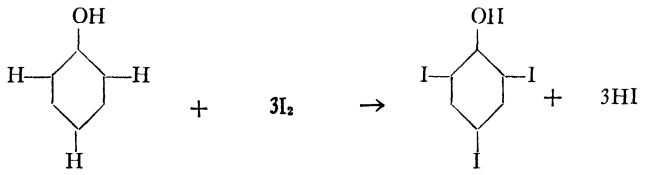
Sodium phenate
Sodium phenolate

Because phenol is a stronger acid than alcohol, the phenolates are more saltlike and more stable than the alcoholates of section 27.3. Although phenol is definitely an acid, it is one of the weakest of acids. Its salts are decomposed even by carbonic acid, which is very weak indeed (in general, an acid is liberated from its salts by stronger acids).

Now that we have seen how the nature of the –OH group is modified by the simple fact that it is attached to the nucleus, let us take the other side of the question and find out how the presence of –OH in the ring modifies the properties of the ring itself.

The presence of –OH in the nucleus has a great activating effect on the *o*- and *p*- positions for the reason shown in the resonance

structures I, II, and III earlier in this chapter. Normally, iodine does not directly replace hydrogen atoms in the nucleus, but phenol reacts with an alkaline solution of iodine in water almost instantly and quantitatively. The mechanism is probably similar to that already described for reactions resulting in substitution in the ring (section 20.2). A positive fragment (in this case, I^+) attacks the nucleus at a point of high electron density to form an unstable complex ion, which then expels a proton that pairs with a negative iodide ion to form HI. The reaction is written briefly as follows, the final product being triiodophenol.

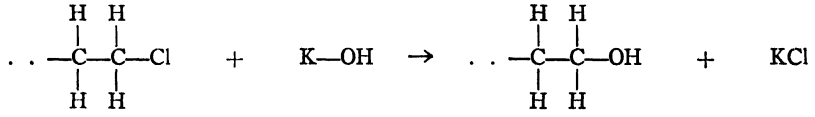


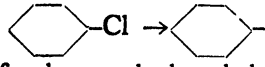
Phenol — 2, 4, 6-Triiodophenol

This reaction may be used for estimating the quantity of phenol in a solution.

Another example of this activating effect of –OH on other positions in the ring is that shown by the preparation of the high explosive, *picric acid*. This compound is made by nitrating phenol (see section 20.4 for the meaning of nitration). Three $-NO_2$ groups are inserted into the ring in the positions occupied by the iodine atoms in triiodophenol. Phenol is much easier to nitrate than benzene itself.

28. 3. Preparation of Phenols. One of the favorite laboratory methods for the preparation of alcohols is the hydrolysis of halogen compounds, thus,

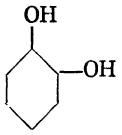


This is not easily accomplished when the halogen atom is in the ring,  , because the Cl atom in the ring is firmly attached and does not react readily (section 25.4). Methods recently adapted by the chemical industries, using high pressure and

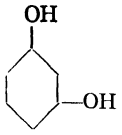
high temperatures, however, have made this reaction the standard procedure for introducing the –OH group into the benzene ring for the preparation of phenols.

At present, phenol is used in great quantities for manufacturing Bakelite resins and other processes. The supply from coal tar is insufficient and, therefore, it is also made synthetically.

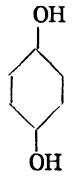
28. 4. Dihydric Phenols. The three dihydroxybenzenes have the following formulas and names:



o-Dihydroxybenzene
Pyrocatechol



m-Dihydroxybenzene
Resorcinol

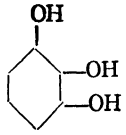


p-Dihydroxybenzene
Hydroquinone
Quinol

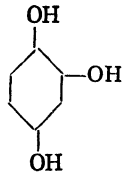
These are important substances in the dye industry and in photography. Hydroquinone particularly is employed as a photographic developer. They are all easily oxidized.

When we study the dyes, we shall take up the structure of the dihydric phenols in greater detail.

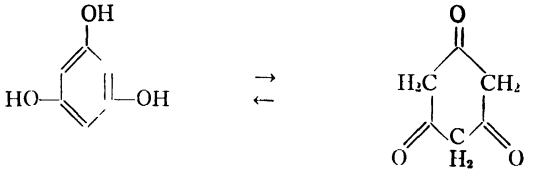
28. 5. Trihydric Phenols. There are also three trihydroxybenzenes and, like the dihydric phenols, they are known generally by their common names rather than by their systematic names. Like the dihydric phenols, they are easily oxidized and are useful as reducing agents.



1, 2, 3-Trihydroxybenzene
Pyrogallic acid
Pyrogallol



Hydroxyhydroquinone
1, 2, 4-Trihydroxybenzene



(enol form) (keto form)

1,3,5-Trihydroxybenzene
Phloroglucinol

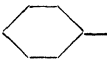
Pyrogallic acid is readily oxidized. It is used in quantitative analysis for estimating the amount of oxygen in a gas mixture. Phloroglucinol is an excellent example of a compound which exhibits *tautomerism* (section 32.11); this is indicated in these formulas by a dynamic equilibrium between *keto* and *enol* forms. The compound takes part in reactions as if it had either structure.

The student may find it interesting to consult larger texts to find out how these polyhydric phenols obtained their names.

29. ETHERS

29. 1. Introduction. Although this chapter will be very brief the compounds to be described form an important branch of organic chemistry.

In the two preceding chapters we found that alcohols and phenols are to be thought of as H–O–H derivatives, in which *one* of the H atoms is replaced by a radical:

CH_3—OH An alcohol  A phenol

The ethers complete the possibilities; they are compounds in which *both* H atoms of water are replaced by radicals. We can have aliphatic ethers R–O–R, aromatic ethers Ar–O–Ar, and aliphatic-aromatic ethers R–O–Ar, as shown by the following examples:

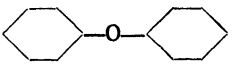
Aliphatic Ethers

CH_3—O—CH_3
Dimethyl ether

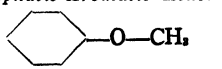
CH_3—O—C_2H_5
Methyl ethyl ether

CH_3CH_2—O—CH_2CH_3
Diethyl ether

Aromatic Ether


Diphenyl ether

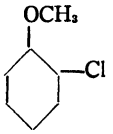
Aliphatic-Aromatic Ether


Methyl phenyl ether

Dimethyl ether is referred to as a *simple* ether, in contrast with methyl ethyl ether which is called a *mixed* ether, because there are two different radicals in it. People usually refer to diethyl ether

simply as ether, just as they call ethyl alcohol simply alcohol. Diethyl ether is the most common of the ethers.

Naming the ethers is generally a simple problem. In the form R–O–R, or Ar–O–Ar, all we need do is name the radicals on each side of the oxygen bridge. Thus, CH_3–O–CH_2–CH_3 is methyl ethyl ether. In certain more complicated cases, like this one, the –OR



group is called the *alkoxy* radical. In this particular instance, the compound is *o*-chloro-methoxybenzene. Similarly, –OC_2H_5 is *ethoxy* and –OC_6H_5 is *phenoxy*.

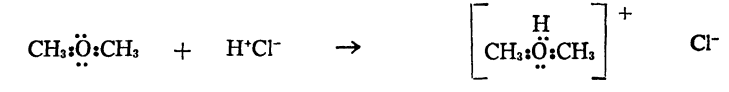
Brief mention may also be made of a system of nomenclature, employed principally for certain rather complicated molecules, in which the oxygen atom is regarded as a substituent for a –CH_2– group of a chain of carbon atoms (either open-chain or closed-chain). According to this system, diethyl ether is 3-oxapentane, indicating that the oxygen atom is the third member in a chain of five members. Another example will be found in section 29.4 in the alternative name for 1, 4-dioxane.

29. 2. Properties of Ethers. As a class the ethers are stable compounds. In fact, the ethers are often used as solvents in which other, very reactive substances are dissolved, that is, they often serve as a reaction medium, just as water is a common medium for reactions in inorganic chemistry.

This is the first place in this book where we have found a chain of carbon atoms, . . . –C–C–O–C–C– . . . which is interrupted by a foreign element. The chain C–O–C contains the oxygen bridge. The interesting thing, then, is to find out how strong is the oxygen bridge compared to the rest of the chain.

As we have already pointed out, the ethers are stable compounds and, therefore, the oxygen bridge must also be stable. The C–O–C link, however, is weaker than the C–C link because of a very im-

portant factor. The oxygen atom still has two unshared pairs of electrons, which offer points of attack to electron-seeking reagents. The ethers accordingly form salts similar to those described in section 27.3. These salts are stable only at quite low temperatures



Dimethyl ether — Dimethyl ether hydrochloride; Dimethylhydrogenoxonium chloride

An ether acts as a base to form a salt

(about –100°C.) and are practically completely dissociated at ordinary temperatures. (The student should refer to the sulphonium salts, section 34.4.) The ether molecule can also add a second molecule of HCl to form a dihydrochloride in which the oxonium ion has a positive charge of two.

Although the ether salts are unstable, they offer an explanation for at least part of the usefulness of ethers as a reaction medium. The intermediate complexes formed with dissolved reagents generally serve to activate them. It will be evident that an ether cannot combine with itself through hydrogen bridges, as water and alcohols (section 27.7), but can associate with other compounds containing loosely held hydrogen. The Grignard reaction (section 34.10) makes extensive use of the tendency of ethers to form molecular complexes through the unshared electron pairs on its oxygen atom.

On exposure to air, ethers slowly form explosive peroxides of the structure R :Ö:Ö: R or R :Ö: R. Ordinary diethyl ether is usually
:Ö:

sold in bottles containing iron wire, which is oxidized preferentially to protect the ether. Distillation of an ether containing peroxides is dangerous, because the peroxides are concentrated by distillation and explode when most of the ether has been distilled off. This is true of many compounds containing the ether linkage.

Except for the activity of the C–O–C bond, ethers have hydrocarbon characteristics and are quite soluble in hydrocarbons.

When acted on by hot hydrogen iodide, an ether can be broken as follows,

$$\underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + H—I \rightarrow \underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} + \underset{\text{Ethyl iodide}}{CH_3—CH_2—I}$$

the break occurring at the oxygen atom. An intermediate oxonium compound is first formed, as described for hydrogen chloride, and this breaks down to give the products indicated here. The best halogen acid for this cleavage is HI.

29. 3. Preparation of Ethers. The Williamson method for preparing ethers is a general one and depends on alcohols for the raw materials. The ethylate and iodide are both made from alcohols as

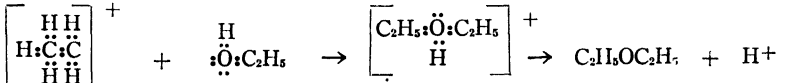
$$\underset{\text{Sodium ethylate}}{C_2H_5—ONa} + \underset{\text{Methyl iodide}}{I—CH_3} \rightarrow \underset{\text{Methyl ethyl ether}}{C_2H_5—O—CH_3} + NaI$$

shown in section 27.3. This method is especially useful for preparing *mixed* ethers.

Ethers can be prepared easily from some alcohols by dehydration of two molecules of the alcohol. Several catalysts are available for

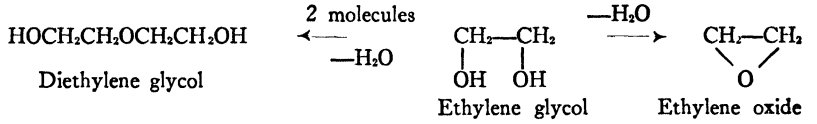
$$\underset{\text{Ethyl alcohol}}{C_2H_5—OH} + HO—C_2H_5 \xrightarrow{\text{Catalyst}} \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + H_2O$$

this process, such as Al_2O_3 at an optimum temperature. At a certain temperature, the product of dehydration of an alcohol is an olefin, as explained in section 27.4b, where it was shown that an acid catalyst causes formation of an unstable *carbonium* ion. This section should be reviewed. At 180°C., the carbonium ion expels a proton to yield an olefin. At 140° C., however, the carbonium ion reacts with a second molecule of the alcohol to give an intermediate



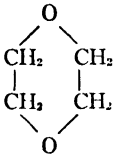
oxonium ion which is unstable and expels a proton to yield an ether. The positively charged fragments, during these reactions, are paired with the negative ions of the catalyst, such as the sulphate ions of sulphuric acid.

29. 4. Other Representative Ethers. An industrially important ether is diethylene glycol, a straight-chain condensation product of



ethylene glycol (section 27.5). An inner anhydride of ethylene glycol is ethylene oxide, which is a cyclic ether widely used as an intermediate in chemical processes and as a fumigant. These reactions illustrate the interrelations of the compounds rather than their commercial methods of preparation.

The cyclic ether known as *1, 4-dioxane* may be regarded as derived from two molecules of ethylene glycol by elimination of two molecules of water, or from diethylene glycol by removal of a molecule of water from the terminal OH groups. Among the important straight-chain ethers used in large quantity as solvents for lacquers are *Cellosolve* and *Carbitol.*



1, 4-Dioxane
1, 4-Dioxacyclohexane

$HOCH_2CH_2OC_2H_5$

Cellosolve
Monoethyl ether of ethylene glycol

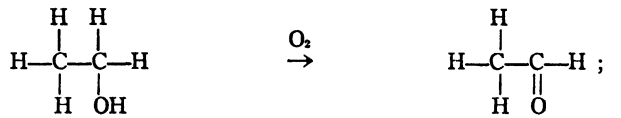
$HOCH_2CH_2OCH_2CH_2OC_2H_5$

Carbitol
Monoethyl ether of diethylene glycol

30. ALDEHYDES AND KETONES

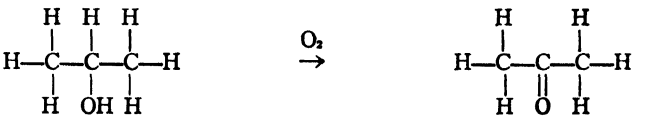
30. 1. Introduction. The alcohols, described in the last few chapters, the aldehydes and ketones to be presented in this chapter, and the acids to be studied in the next chapter, are all very closely related. We must keep this in mind while reading about the properties of aldehydes and ketones, because their chemistry will be difficult to understand unless we do so.

Before proceeding any further, the student should review what has been said about primary (1°) alcohols and secondary (2°) alcohols in section 27.4c. At that time, we showed that both types of alcohols can be oxidized to compounds containing the $-\overset{\overset{O}{\|}}{C}-$ group:



Ethyl alcohol
Ethanol

Acetaldehyde
(An aldehyde)



Isopropyl alcohol
2-Propanol

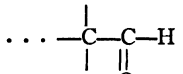
Acetone
(A ketone)

Since the –OH group is *at the end of the chain* in a 1° alcohol, that is where the $-\overset{\overset{O}{\|}}{C}-$ group is found in the oxidation product. The resulting compound is called an aldehyde, and $-\overset{\overset{O}{\|}}{C}-H$ or –CHO is called the *aldekyde* group.

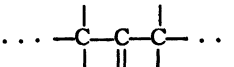
In a 2° alcohol the –OH group is *inside the chain,* and accordingly that is where the $-\overset{\overset{O}{\|}}{C}-$ group is found when the compound is oxidized. The resulting product is called a ketone, and, when present in such a substance, $-\overset{\overset{O}{\|}}{C}-$ is called the *keto* group.

The student should now turn to section 31.2 in the next chapter and note how simple it is to pass from an aldehyde or ketone to an acid. It is easy to prepare aldehydes and ketones from alcohols, and we can easily go one step further to the next series of compounds, the acids. The relations between aldehydes, ketones, and acids will be commented on later. For the present, it is sufficient to note their structural similarity.

30. 2. The Carbonyl Group. The $-\overset{|}{C}=O$ group is one of the most important in organic chemistry, and has been given the name *carbonyl.* It is found in many types of compounds, as one can readily see by thumbing over the pages in the rest of this book. It will be met frequently in many different ways; the student must therefore be careful at this point to make sure he understands its position in the aldehydes and ketones.

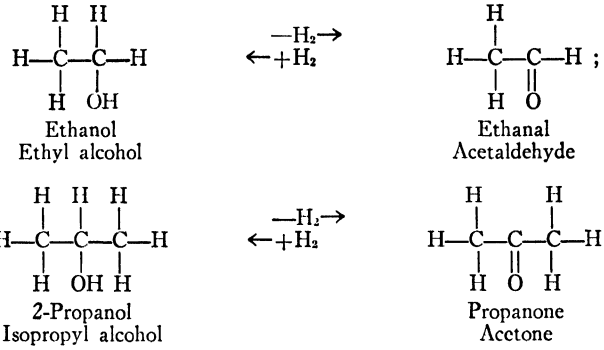


In an aldehyde, CO is bound to an H atom and to a C atom



In a ketone, CO is bound on both sides to C atoms

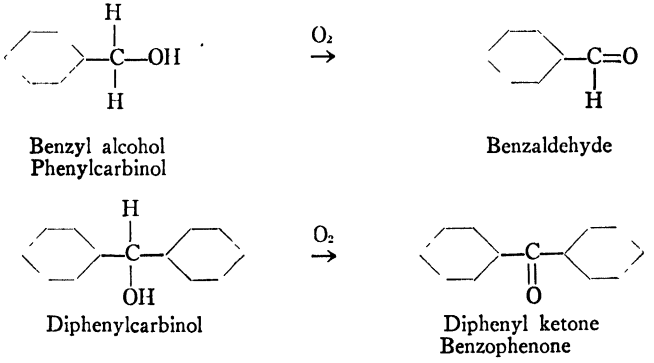
30. 2a. Formation from Alcohols. Although the method of formation of the $-\overset{|}{C}=O$ group in aldehydes and ketones has already been described in section 27.4*c,* in the study of the oxidation of alcohols, perhaps a more instructive illustration is the following:



When the vapors of alcohols are led over a suitable catalyst at an elevated temperature there is a direct removal of two atoms of hydrogen, as shown. This is known as *dehydrogenation.* We shall find very shortly that these H atoms can be put back again by the process of *hydrogenation,* and the alcohols are regenerated. The dehydrogenation process explains how the aldehydes, as a class, obtained their family name. The word aldehyde is a contraction of *al*cohol *dehyd*rogenated.

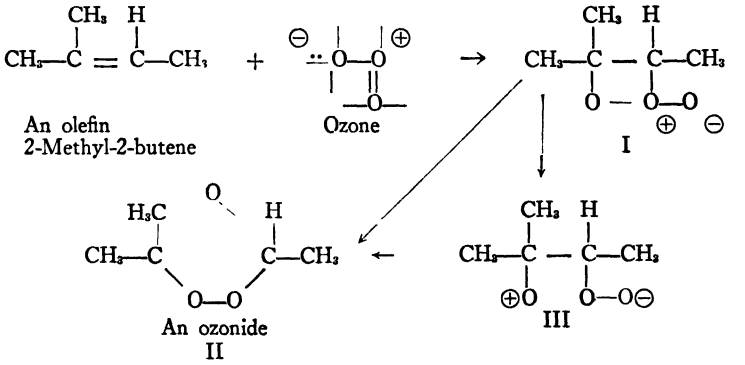
A commercial preparation of acetaldehyde from acetylene will be described later under the chemistry of acetic acid (section 31.9).

Aromatic aldehydes and ketones are also closely related to alcohols, as can be seen from the following examples:



30. 2b. Formation from Olefins by Ozonolysis. Ozone (O_3) is electronically analogous to carbon dioxide, the resonance possibilities

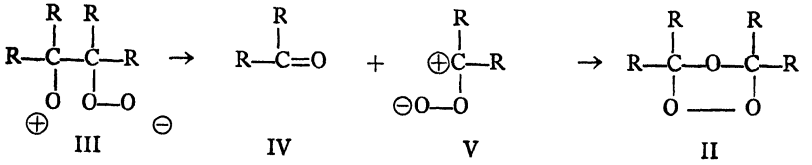
of which should be reviewed in section 18.5. Ozone is an angular molecule (the angle is about 125°), whereas the three atoms in the carbon dioxide molecule form a straight line. The polar nature of the ozone molecule, together with the ready polarizability of the C=C group as described in section 17.4, probably accounts for the ease with which olefins quantitatively absorb ozone from a stream of air or oxygen which has been ozonized (structure I). It has been proposed that structure I rearranges directly to structure II by breaking the C–C bond, but a more recent theory postulates the intermediate dipolar ion structure III, such as is described under *glycine* in section 33.8.



Ozonides are generally not isolated, because of their explosive properties, but are broken down by addition of water to various products, principally aldehydes and ketones if the hydrolysis is performed in the presence of reducing agents, such as zinc dust, to remove peroxides and prevent further oxidation to acids. The olefin shown in the reaction would yield acetaldehyde, CH_3–CHO, and acetone, CH_3–CO–CH_3. By proper choice of the olefin, it is possible to obtain two molecules of an aldehyde or two molecules of a ketone, instead of the mixture of the two. Since the products are easily identified, it is obvious that this reaction makes it possible to determine the location of a double bond in an olefin molecule of unknown structure. Similar reactions take place with acetylene hydrocarbons.

The theory indicated by structure III assumes (as in the case of II) that the hydrolysis causes breaking of the C–C bond. However,

the initial fragments can undergo a number of different rearrangements characteristic of the solvents in which the reaction takes place.



III IV V II

The theory explains the formation of II, since the fragment V is a dipolar ion which will add across the C=O bond of the ketone IV by a mechanism which will be described in the next few pages (section 30.5).

30. 3. Oxidation and Reduction. The reader who has studied modern inorganic chemistry may sometimes be confused by the fact that many organic chemists still use these two terms in the old-fashioned sense. For example, we just showed how dehydrogenation of ethyl alcohol (CH_3–CH_2OH) yields acetaldehyde (CH_3–CHO). This is usually called an oxidation because the compound formed in this reaction has a higher oxygen content than the original molecule, which has been at the same time deprived of hydrogen. The alcohol contains 34.8 per cent oxygen as compared with 36.4 per cent in the aldehyde.

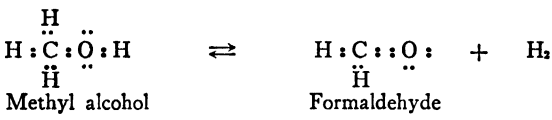
Similarly, hydrogenation of acetaldehyde is often called a reduction reaction, because hydrogen is added and the oxygen content thus decreased. Reduction, to many organic chemists, is a reaction involving hydrogen in which the hydrogen content is increased.

In modern terminology, oxidation and reduction refer, respectively, to the loss or gain of electrons by an element or its compounds. As an illustration, when a sodium atom combines with a chlorine atom as shown in figure 4.3, the sodium is oxidized (loss of electron) while the chlorine is reduced (gain of electron):

$$Na^0 + Cl^0 \rightarrow Na^+Cl^-$$

This is an oxidation, although it does not involve oxygen, the oxidation state of the sodium atom being raised from 0 to +1. The chlorine atom gains an electron and is said to pass to a lower state of oxidation, to a charge of —1. Oxidation and reduction take place simultaneously.

Applying these principles to compounds of carbon is not quite so simple because of the tendency of carbon to form covalent rather than ionic compounds. Electrons in carbon compounds are usually shared rather than transferred, but a calculation of the *oxidation number* of the carbon atom may arbitrarily be made by use of the oxidation numbers of the elements which are attached to carbon, as in the following examples:



The H atom, in most of its compounds, is referred to as having an oxidation state of +1, as in hydrochloric acid, $H^+ Cl^-$. The carbon atom in methyl alcohol may, therefore, be said to have an oxidation state of —2; this charge is the sum of —3 due to the electrons gained from the three hydrogen atoms, and +1 due to an electron donated to the oxygen atom. There is no actual transfer of electrons, but carbon is looked upon as slightly more electron-attractive than hydrogen, and oxygen more electron-attractive than carbon (see table 8.2).

Conversion of the alcohol to the aldehyde is, therefore, an oxidation, the carbon atom being raised to an oxidation state of 0; this is the sum of —2 due to the H atoms, and +2 due to the oxygen atom. In the reverse reaction, formation of the alcohol from the aldehyde, the process is a reduction.

This conception of oxidation states of the elements has wide usefulness in inorganic chemistry, with ionic compounds, but, as already stated, its application in organic chemistry is quite limited. As carbon tends to share electrons, it is often meaningless to attempt to assign a definite oxidation state or oxidation number to carbon in its compounds. However, oxidation-reduction systems are an important factor in modern biochemistry (see cystine-cysteine in section 34.2 and cozymase in section 44.5).

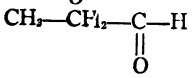
30. 4. Nomenclature. Typical aldehydes and ketones which occur in the straight-chain and cyclic families of compounds are shown in tables 30.1 and 30.2.

Aldehydes, like most organic compounds, can be named in two different ways, one method giving the common names and the other method resulting in the systematic names. In order to understand

how the aldehydes received their common names, it is necessary to know something about the relationship between aldehydes and organic acids. This will be discussed later in this chapter in connection with the chemical properties of the aldehydes.

The systematic names are obtained as usual from the longest chain

TABLE 30.1. ALIPHATIC ALDEHYDES

	Systematic Name	*Common Name*
	Methanal	Formaldehyde
	Ethanal	Acetaldehyde
	Propanal	Propionaldehyde

AROMATIC ALDEHYDES

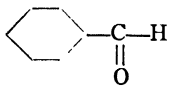
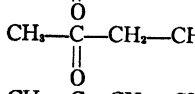
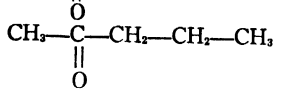
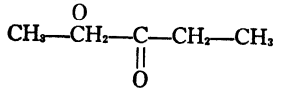
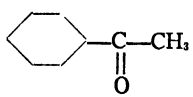
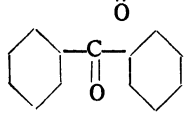
	Systematic Name	*Common Name*
	(No system used)	Benzaldehyde Oil of bitter almonds

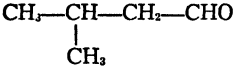
TABLE 30.2. ALIPHATIC KETONES

	Systematic Name	*Common Name*
	Propanone	Dimethyl ketone (Acetone)
	Butanone	Methyl ethyl ketone
	2-Pentanone	Methyl propyl ketone
	3-Pentanone	Diethyl ketone

AROMATIC KETONES

	Systematic Name	*Common Name*
	(No system used)	Methyl phenyl ketone (Acetophenone, or hypnone)
		Diphenyl ketone Benzophenone

of carbon atoms containing the aldehyde group, with the 1 position assigned to the aldehyde group. The aldehyde group is regarded as a "functional" one (section 10.10); its presence in the molecule is designated by the ending *-al* which is used in the main part of the name as follows:



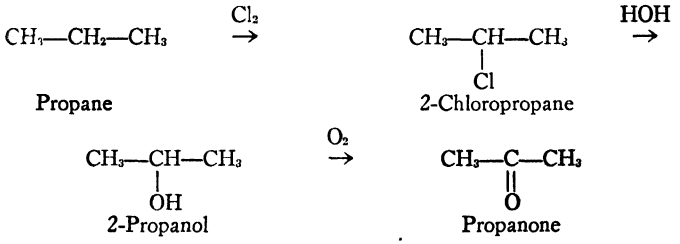
3-Methylbutanal

In relatively simple compounds like this one, it is not necessary to use a numeral with -al because it is at the beginning of the chain.

In the nomenclature of aldehydes, frequent use is made of the Greek alphabet (compare the names of acids in section 31.3), carbon atom 2 being marked *alpha*. The scheme can be represented by this skeleton structure: C–C–C–C–CHO. On this basis, 3-methyl-
$\delta\ \gamma\ \beta\ \alpha$
butanal would be called β-methylbutanal.

The systematic naming of ketones follows the method developed for all the other classes of compounds which have a simple chain structure. The name is obtained by counting the number of C atoms in the chain, writing down the name of the corresponding hydrocarbon, and adding the suffix *-one* in place of *-e*. A number is then added to show the position of the C=O bond in the chain. As illustrated by the two formulas of pentanone, this number is not necessary until we reach the compound with a chain of five carbon atoms.

In the following series of compounds,



notice that a number is used in the name only when the element (–Cl), or group (–OH), can be present in other parts of the molecule than the place shown.

The names of the ketones which we have listed in the column of common names are often called systematic names by experts. It is apparent that for those compounds which we have used for illustrative purposes, this method of naming ketones is quite systematic. The name indicates the typical structure of a ketone, R–C–R, that
O
is, a radical on each side of the C=O bond.

Dimethyl ketone is called a *simple* ketone, because the two radicals attached to the C=O group are the same. When the two radicals

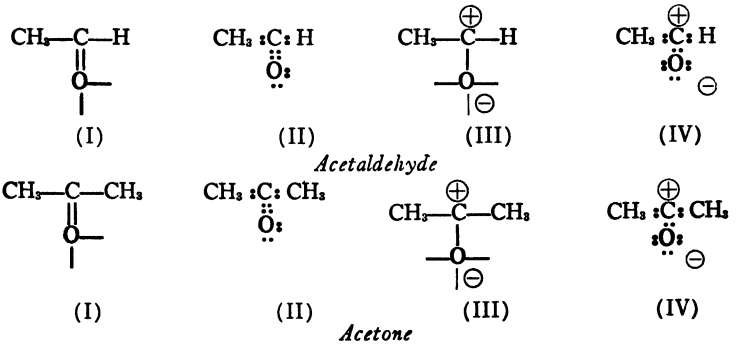
are different, as in methyl ethyl ketone, the group name *mixed* ketone is used. Compare this with the naming of ethers.

The simplest chain ketone, CH_3–CO–CH_3, is almost always called acetone. The simplest ketone of the benzene series is known as acetophenone and is sometimes referred to as *hypnone* because it is useful as a hypnotic in medicine.

30. 5. Properties of Aldehydes and Ketones. Formaldehyde (HCHO), the simplest aldehyde, is a gas and acetaldehyde (CH_3 CHO), the next member of the family, boils at about 21°C. Higher aldehydes are liquids or solids. Although the ketones differ from the aldehydes in the position of the C=O bond, this difference does not bring about many important variations in properties. Most of the common aldehydes have a disagreeable odor, whereas ketones are liquids or solids with pleasant, aromatic odors; in other respects, they are similar physically.

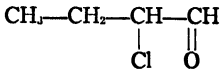
As we have already stated, the C=O bond is present in many types of compounds, but it is most active in an aldehyde molecule. From the following illustrations, it will be apparent that the reactivity of aldehydes is due almost entirely to the nature of the C=O bond. The ketones are not quite as reactive as the aldehydes, but the general nature of their chemistry is the same.

The reactivity of aldehydes and ketones is easy to understand if we relate their properties to their electron structures. The double bond in the $\overset{|}{\underset{|}{C}}{=}O$ group is like the double bond in the $-\overset{|}{C}{=}\overset{|}{C}-$ group (section 17.4) in that we can write for it either a normal covalent structure or a polarized structure. Formulas I and II are

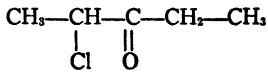


two different ways of showing that there are unshared electron pairs on the oxygen atom. Formulas III and IV show the polarized structures. Aldehydes and ketones can be considered as resonance hybrids of II and IV, and from dipole-moment measurements, they appear to have about 50 per cent ionic character. Accordingly, either the normal covalent or the polarized structure can be used for the formula of an aldehyde or ketone, but it is better to keep in mind the polarized structures when studying the chemistry of these compounds.

30. 5a. Reactions as a Hydrocarbon. Aldehydes and ketones show the principal characteristic property of hydrocarbons, namely, substitution of H atoms by the halogens (section 9.1). The important observation in this chapter is that substitution takes place most readily with the H atoms on α-carbon atoms. Chlorination of butanal and of diethyl ketone, for example, yields the following products:

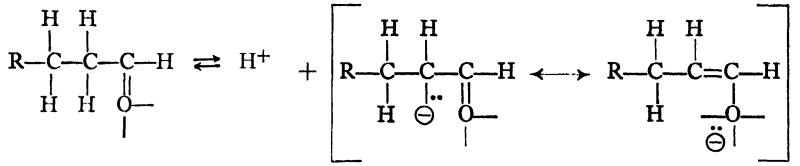


α-Chlorobutanal
2-Chlorobutanal



Ethyl α-chloroethyl ketone
2-Chloro-3-pentanone

The *alpha* hydrogen atoms are more loosely held, more "acidic," more reactive, and, therefore, more readily replaced by halogen than are the other hydrogen atoms in the molecule. This activity of a C–H bond when it is adjacent to the C=O group will be discussed in some detail in section 32.11 under *tautomerism* and in section 45.4, a proof of the mobility of the *alpha* hydrogen atom will be presented. In this section, we shall briefly examine the phenomenon on the basis of the principles of resonance which have already been used for analogous interpretations. In a recent chapter (section 28.2), we found that the acidity of phenol can be explained by the resonance possibilities of the phenate ion, the stability of which favors ionization of phenol even though the effect is rather small. Similarly, if acetaldehyde or acetone should ionize, they may give rise to resonance structures. For an aldehyde, the resonance possibilities of the negative ion may be shown as follows, if an H^+ ion should be removed from the *alpha* carbon atom:

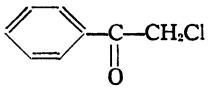


(V) (VI)

Resonance structures of an aldehyde ion

These resonance structures (which are not possible by interaction of the $-\overset{|}{C}=O$ group with carbon atoms more distant than *alpha*) tend to stabilize the ion and may be considered responsible for the slight acidity of an aldehyde. A similar reasoning can be applied to ketones, in which the alpha hydrogen atoms also have acid properties. In structure (V), it will be seen that the unshared electron pair on the *alpha* carbon atom offers a point of attack for an electron-seeking reagent. The reaction with chlorine probably occurs through an *ionic* mechanism like that described in section 20.2, the positive fragment of the chlorine molecule, Cl^+ $:Cl^-$, adding to the *alpha* carbon atom in structure (V) and the negative chloride ion pairing with an H^+ ion to give HCl as by-product.

Halogenation products of acetone are lacrimatory. Examples are bromoacetone, $CH_2Br–CO–CH_3$, and *sym*-dichloroacetone, $CH_2Cl–CO–CH_2Cl$. The prefix *sym* means symmetrical. In chemical warfare terminology, these compounds are tear "gases," but the first is a liquid and the second a solid. One of the most powerful of lacrimators is known in chemical warfare as CN; it is also used for riot control and "burglar-proofing." It is a crystalline solid (m.p. 54°C.) of the following structure:

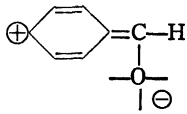


α-Chloroacetophenone

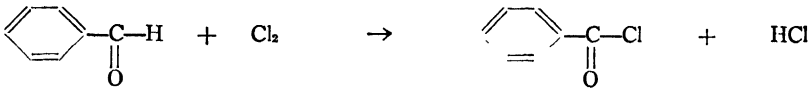
This compound is also known as ω-chloroacetophenone, because the prefix *omega* is often used to designate the last carbon atom in a chain (ω is the last character in the Greek alphabet).

If the student will review section 21.5, in which the possible resonance structures of nitrobenzene are worked out, he will see that the

benzene ring in that compound is essentially positive in character due to withdrawal of electrons by the nitro group. Similarly, in benzaldehyde the CHO group withdraws electrons to give polarized structures, such as



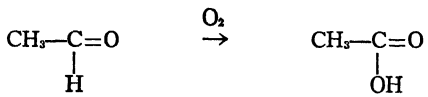
Because of lowered activity of the nucleus, when benzaldehyde is chlorinated under conditions which normally promote nuclear substitution (section 25.5), the H atom in the –CHO group is acted on before chlorine atoms enter the nucleus:



Benzaldehyde Benzoyl chloride

Benzoyl chloride is a member of the family of acid chlorides (section 31.8*c*) and is a useful reagent for organic syntheses.

30. 5b. Oxidation. Aldehydes, in general, can be oxidized without much trouble:



Acetaldehyde Acetic acid

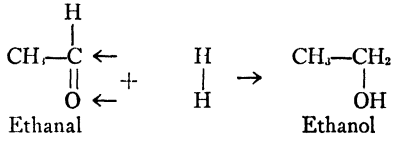
It is from this property of easy oxidation to acids that aldehydes derive their common names. An aldehyde is named from the acid to which it can be oxidized. Acetaldehyde (or acetic aldehyde) is convertible to acetic acid, formaldehyde to formic acid, and so on. It will be seen that the aldehyde and its corresponding acid have very similar structures; the two molecules differ only by one oxygen atom.

A substance which is easy to oxidize is a correspondingly strong reducing agent. This strong reducing action of aldehydes is used in one of the methods for detecting aldehydes in unknown substances. Aldehydes reduce the copper in "Fehling's solution" to cuprous oxide and the silver in ammoniacal silver nitrate to metallic silver.

Silver mirrors can be made by the interaction of formaldehyde and certain silver solutions on glass.

Whereas the aldehydes are easily oxidized, the ketones are oxidized only with some difficulty. They cannot, therefore, be detected by their action on solutions of silver or copper salts. The changes that take place in the oxidation of a ketone are much more complex than those taking place in the oxidation of an aldehyde, and we shall, therefore, reserve its discussion for the next chapter.

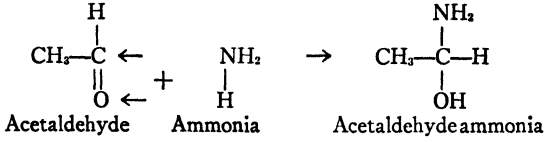
30. 5c. Addition to the C=O Group. By far the most important characteristic of the C=O bond in aldehydes and ketones is its tendency toward addition reactions. In that respect it resembles the C=C bond which we described in detail in the chapter on double bonds (chapter 15) and in section 17.4. The following reaction is a *reduction*:



Thus, when an aldehyde is treated with active hydrogen, it easily adds on one molecule of hydrogen to form the corresponding alcohol. In this illustration, acetaldehyde is reduced to ethyl alcohol. Notice that the *hydrogenation,* or reduction of aldehydes to alcohols, is exactly the reverse of the *dehydrogenation,* or oxidation of alcohols to aldehydes which was mentioned at the beginning of the chapter.

In the same way, ketones are also reduced to alcohols. As we showed earlier in this chapter, aldehydes give 1° alcohols on reduction whereas ketones give 2° alcohols.

Aldehydes and ketones form many *double compounds* with such substances as hydrogen cyanide, sodium iodide, sodium bisulphite, etc. A typical case is the addition of ammonia to acetaldehyde when the two substances are brought together in certain solvents:

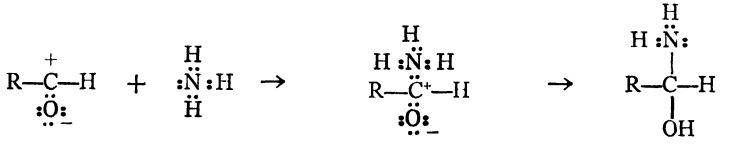


The aldehyde-ammonias are crystalline substances which are easily purified and are sometimes used as sources of pure aldehyde. On

gentle warming in dilute acid, the original substances are regenerated from the double compound and the aldehyde can be distilled from the mixture in pure form.

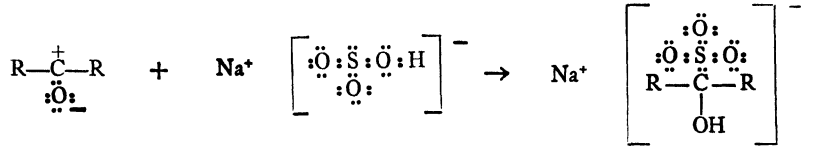
Formaldehyde, however, the simplest of the aldehydes, does not behave this way with ammonia. Instead, it reacts with ammonia to form a complex substance known in medicine as urotropine, and the reaction is not a simple addition process. Ketones, likewise, form complex condensation products with ammonia.

In studying the addition of other substances to the C=O group in aldehydes and ketones, it must always be kept in mind that the reaction just described between an aldehyde and ammonia is typical. The adding molecule splits up in such a way that its *H atom or other positive fragment goes to the oxygen end of the C=O,* while the *rest of the molecule attaches to the carbon atom.* The mechanism can be made clear by referring to the electronic structures of an aldehyde and a ketone shown in formulas IV (the student should turn back a few pages to these formulas), where it is seen that the molecules can be either electron-seeking at the C end of the C=O bond, or electron-donating at the O end. The principal tendency is electron-seeking, in which respect the C=O bond differs from the C=C bond described in section 17.4, which should be reviewed. Aldehydes and ketones, in other words, react readily with molecules (or ions) containing an unshared electron pair:



(Unstable) An aldehyde-ammonia

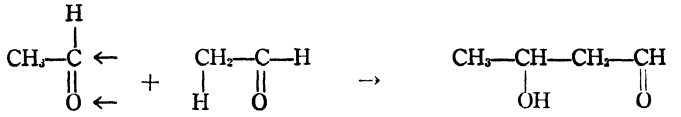
Similarly, when aldehydes and ketones react with sodium bisulphite to form a double compound,



A ketone-sodium bisulphite

the combination takes place through a C–S linkage, in which the positively charged carbon "sits down" on the unshared electron pair of the sulphur atom. A rearrangement then takes place by migration of an H atom (more exactly, a proton) as in the case of the ammonia compound which was described previously.

30. 5d. Condensation. The aldehydes and ketones are so susceptible to the formation of addition products that they even show a marked tendency to combine with themselves, thus:

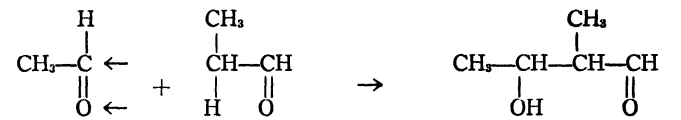


Two molecules of acetaldehyde — Aldol (An aldehyde, and an alcohol)

This building up to the double molecule takes place readily in dilute alkalies.

The important feature of this addition reaction is the fact that it is one of the methods at the disposal of the chemist in his laboratory, and probably of plants in nature, for lengthening the carbon chain by adding carbon to carbon. This particular type of reaction is known as the *aldol condensation.* It is a good example of synthesis in organic chemistry (section 10.2).

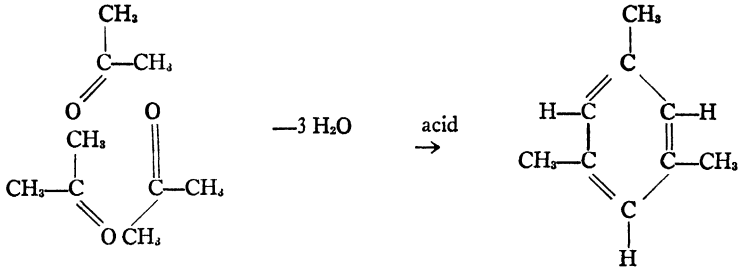
When aldehydes containing more than two carbon atoms are condensed, it is the C atom next to the –CHO group which participates in the synthesis, for the reason given in part *a* of this section, namely, the relatively great activity of hydrogen on an *alpha* carbon atom:



Ethanal — Propanal — 2-Methyl-3-hydroxybutanal

With strong alkalies, aldehydes condense to complex, yellow substances of a strong resinous odor.

Ketones, as well as aldehydes, can be put through the aldol condensation process and for a description of the products obtained the student is referred to larger books on organic chemistry. One such condensation is as follows:



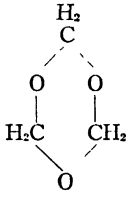
Three molecules of acetone — Mesitylene (see table 19.1)

This reaction is of importance because it illustrates the ease with which we can pass from the straight-chain (aliphatic) series of compounds to a member of the cyclic (aromatic) series.

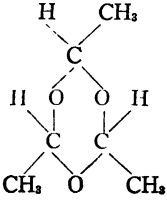
In the aldol condensation, as already explained, two or more molecules combine to form larger molecules through a C–C bond. Some aldehydes, however, combine by formation of an oxygen link between carbon atoms, as shown, in general, by the following scheme:

$$\ldots {}^{+}C{-}O^{-}\ldots {}^{+}C{-}O^{-}\ldots {}^{+}C{-}O^{-}\ldots {}^{+}C{-}O^{-}\ldots$$

In this way, cyclic compounds of the following types can be easily made:



Trioxane
Trioxymethylene $(CH_2O)_3$
(Three molecules of formaldehyde)



Paraldehyde $(CH_3CHO)_3$
(Three molecules of acetaldehyde)

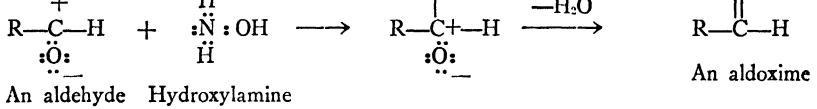
These compounds are not so stable as the compounds in which C–C links are formed; for example, paraldehyde quickly reverts to acetaldehyde when it is boiled and, under the proper experimental conditions, trioxane can be used as a convenient source of formaldehyde for chemical reactions.

Formaldehyde (and possibly other aldehydes) combines with itself to form long-chain molecules as well as the cyclic compounds just described. These are called polyoxymethylenes and have the following general structure,

$$—CH_2—O—CH_2—O—CH_2—O—CH_2—O—CH_2—$$

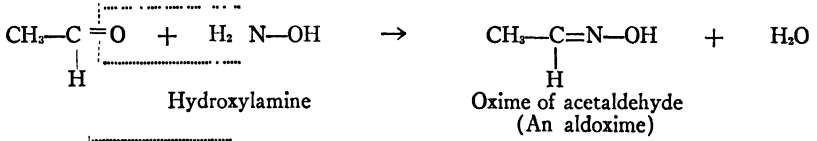
the principal variations being in the nature of the end groups and the length of the chain. The chains contain from forty to perhaps one hundred CH_2O units, with –OH or $–OCH_3$ groups at the ends. They are solids, readily converted back to formaldehyde on heating. Compounds of this type are called *polymers,* from the Greek meaning many parts of the same thing (compare *isomer* in section 10.5). The general subject of polymerization will be discussed in section 46.9.

30. 5e. Replacement of O in the C=O Group. In aldehydes and ketones, the oxygen atom of the C=O group can be completely replaced. This is not to be construed as an operation in which the O atom is chopped off. In most of the reactions, the mechanism is clearly one in which an intermediate compound is formed, similar to the formation of an aldehyde-ammonia (section 30.5); the intermediate complex then splits off an oxygen-containing fragment, such as water:

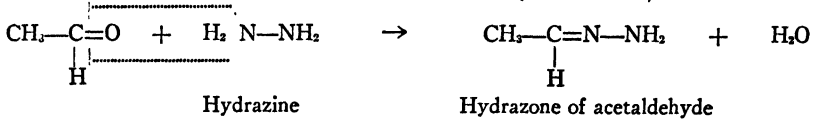


An aldehyde Hydroxylamine An aldoxime

In condensed form, the reaction with hydroxylamine is as follows.



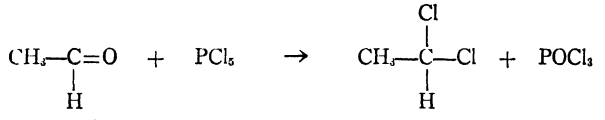
Hydroxylamine Oxime of acetaldehyde (An aldoxime)



Hydrazine Hydrazone of acetaldehyde

Another important reaction in this category is that with hydrazines, which is also written here in condensed form, without showing the intermediate complex.

By the action of phosphorus pentachloride, PCl_5, the oxygen atom is replaced by two chlorine atoms:

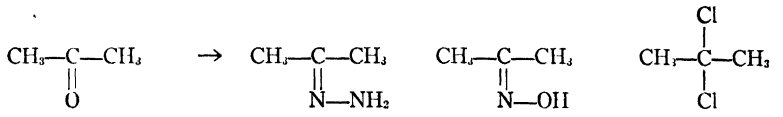


Ethanal
Acetaldehyde

1, 1-Dichloroethane

This is a standard method for attaching two Cl atoms to one carbon atom. The student should compare this reaction with the action of PCl_3 on alcohols (section 27.4*a*) and also note the relation between 1, 1-dichloroethane and 1, 2-dichloroethane in section 15.2.

The ketones form oximes and hydrazones, and react with PCl_5 in the same way as aldehydes do. The following compounds correspond to those already pictured for the aldehydes:



Acetone

Acetone hydrazone

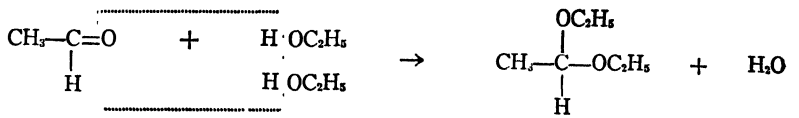
Acetoxime
(A ketoxime)

2,2-Dichloro-
propane

Hydroxylamine and hydrazine have played an important part in the historical development of organic chemistry, in that they helped to identify and elucidate the structures of complex compounds containing the aldehyde group, $-\underset{\displaystyle H}{\overset{|}{C}}=O$, and the keto group, $-\overset{|}{C}=O$.

The oximes and hydrazones are often solids, easy to crystallize, with definite melting points and crystal shapes. After the melting points of a large number of these compounds had been tabulated, it was a simple matter to identify an aldehyde or ketone from the melting point of its oxime or hydrazone.

When an aldehyde and an alcohol are mixed and heated in the presence of certain acid catalysts an *acetal* is formed:



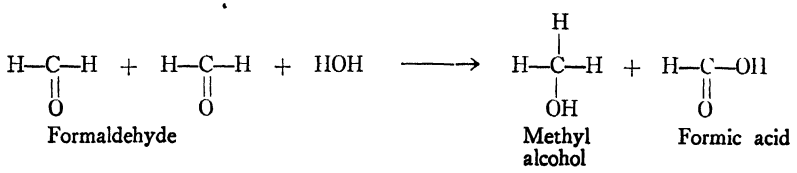
Acetaldehyde

Ethyl alcohol

Acetal

The compound described here is *acetal,* itself, but many other compounds in this acetal series are known. For example, the product of the reaction between formaldehyde and ethyl alcohol is called *ethylal.* The acetals have an ether type of structure, and are quite stable to alkalies, but are easily hydrolyzed by acids. The acetal reaction will be considered in more detail in the chemistry of the sugars (section 40.7).

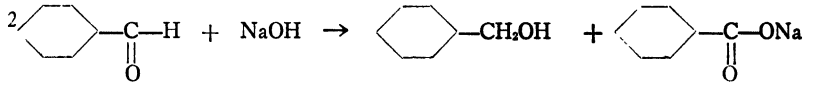
30. 5f. Cannizzaro Reaction. In part *b* of this section, we observed that an aldehyde is easily *oxidized* to an acid, and in part *c,* we found that an aldehyde can be *reduced* to an alcohol. An aldehyde, therefore, occupies an intermediate state between oxidation and reduction. With the proper assistance, two molecules of an aldehyde can interact in a way known as mutual oxidation and reduction. One molecule oxidizes the other to an acid while it is reduced to an alcohol:



The reaction takes place when the aldehyde is warmed with aqueous sodium hydroxide. The initial phase of the reaction consists in the attack on the polarized form of the C=O group by an OH^- ion of the alkali, the mechanism of which we have already extensively described in this chapter. The subsequent reactions are rather complex and we do not have the space available to consider them. Since the reaction takes place in a basic solution, the products contain the salt of the acid rather than the free acid.

The interaction of two similar molecules to give other dissimilar products, as in the Cannizzaro reaction, is referred to as *dismutation* or *disproportionation.*

It should be observed that the experimental conditions for the Cannizzaro reaction are those which promote the *condensation* reactions described in part *d* of this section. A condensation, however, takes place only with aldehydes in which there is an *alpha* carbon atom. Formaldehyde has no *alpha* carbon atom; nor has benzaldehyde, which, therefore, dismutates when heated with alkali:



Benzaldehyde Benzyl alcohol Sodium benzoate

30. 6. Representative Aldehydes and Ketones.

Formaldehyde (see table 30.1) is the simplest aldehyde. Since it contains only one carbon atom it does not have some of the characteristics of other aldehydes which contain a chain of carbon atoms. For example, it cannot react with halogens in the same way as the other aldehydes do, because of the absence of the carbon chain. It reacts with itself in the Cannizzaro reaction (this chapter) and, unlike other aldehydes, it combines with phenols to form hard condensation products of which Bakelite (section 46.10) is an example.

Formaldehyde, CH_2O, has been condensed by special treatment to a sugar of the composition $(CH_2O)_6$ similar to sugars from plants. It was formerly believed by some that a similar synthesis takes place in plants,

$$CO_2 + H_2O \rightarrow H{-}CHO + O_2 \quad \text{and} \quad 6\,H{-}CHO \rightarrow C_6H_{12}O_6$$

carbon dioxide and water being absorbed by the plant and converted to formaldehyde, and the formaldehyde put through an aldol condensation (section 30.5*d*) with the formation of sugars and starches.

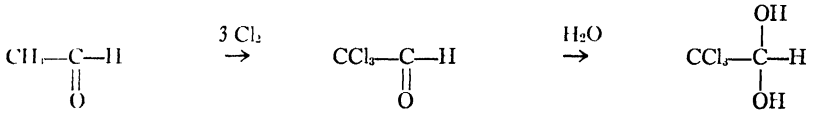
Formaldehyde is a gas. It is available in a 40 per cent solution in water called *formalin.* Formaldehyde candles, used for disinfecting, are polymerized formaldehyde (section 30.5*d*); the solid polymer is known as *paraformaldehyde.*

Acetone, $CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3$, is the simplest ketone. It is obtained by the dry distillation of wood, from the products of fermentation of starch and molasses induced by certain bacteria, and also by treatment of the propylene (section 15.5*c*) in cracked petroleum oils. It is one of the most widely used commercial solvents.

Glyoxal, $H{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}H$, is the simplest of the di-aldehydes. It is interesting in that it is a simple combination of two aldehyde groups. It can be obtained by oxidizing the simplest di-alcohol glycol (sec-

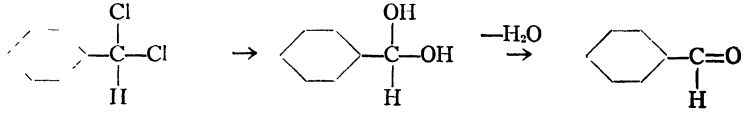
tion 27.5), and gets its name from the fact that it can be further oxidized to oxalic acid (section 31.13). Glyoxal is the simplest organic compound which has color (section 42.14). It melts at 15°C. and boils at 50°C. The crystals are yellow and the vapor is green.

Chloral can be obtained by chlorination of acetaldehyde. It is a

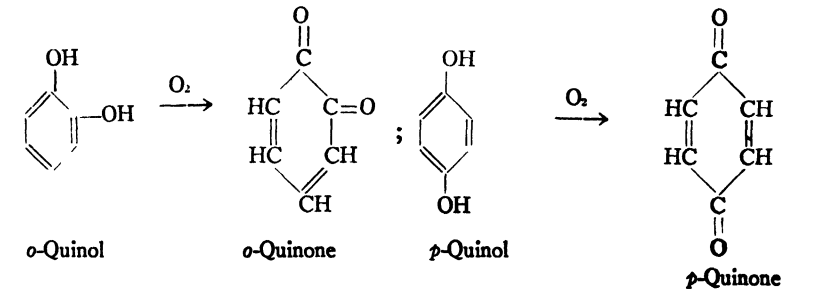


liquid which forms a stable hydrate with water when in aqueous solution. The hydrate is so stable that it can be obtained from the solution as a crystalline solid. This is an exception to the generalization (section 27.4*c*) that two OH groups on the same carbon atom form an unstable system. Chloral hydrate has been used in medicine as a soporific.

Benzaldehyde is known as oil of bitter almonds. It is present in bitter almonds, combined with glucose and hydrogen cyanide. It can be prepared from benzal chloride (section 25.5) by hydrolysis in weak alkalies:



Quinones. In the chapter on phenols (section 28.4), we described several derivatives of benzene containing two –OH groups. When these are oxidized, they are converted to ketones of the following type:



These quinones do not belong to the benzene series of compounds. As we took great pains to show in section 19.2, the benzene compounds owe their characteristic properties to the symmetrical nature of the alternate single and double bonds in the ring. Oxidation of the diphenols breaks up this arrangement in the ring and, therefore, the reaction which is characteristic of the nucleus is no longer present.

The quinones are cyclic compounds, but they have the properties of olefin hydrocarbons in the straight-chain series and also the properties of ketones. They are unusual in that they are highly colored, and when we take up the question of dyes (section 42.2), we will find that the theory of color in dyes is closely associated with the "quinoid" structure.

31. CARBOXY ACIDS

31. 1. Introduction. Acids have been defined in various ways. Some of these definitions are: an acid turns blue litmus red; an acid contains H atoms that are replaceable by metals or by positive radicals, as in the change from hydrochloric acid, HCl, to sodium chloride, NaCl; an acid is a substance which dissociates in water solution, yielding hydrogen ions, thus, $HCl \rightleftarrows H^+ + Cl^-$.

Modern ideas concerning the structure of atoms and molecules cast doubt on the theory that the acidity of acids is due to a simple ionic dissociation, such as we have illustrated for HCl. However, we have not changed in our belief that certain H atoms in a molecule have unique properties (like the replaceability by metals), which we call acid properties. We shall refer to this again later (section 31.6).

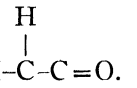
Organic acids differ from inorganic acids in that they are compounds of carbon, in addition to being acids. The following compounds are typical organic acids:

H_2CO_3	HCN	C_6H_5OH	$C_2H_4O_2$
Carbonic acid	Hydrocyanic acid	Carbolic acid (Phenol)	Acetic acid

The composition of acetic acid is $C_2H_4O_2$, and it is correctly listed as an organic acid. It is used quite often, however, in the routine laboratory work of inorganic chemistry, and in the textbooks of inorganic chemistry it is written $HC_2H_3O_2$.

Why isn't acetic acid more generally written $C_2H_4O_2$? The answer is that the inorganic chemist, when he writes the formula of an acid, likes to single out that particular H atom which has acid properties, and experience has shown that only one of the four H atoms in acetic acid is acidic. A typical salt obtained from acetic acid is sodium acetate, $NaC_2H_3O_2$.

Once again we find that the organic chemist is not content with the simpler formulas of inorganic chemistry. If *one* of the H atoms in acetic acid is different from the others, this must be due to a unique position of that one H atom in the molecule, and we ought to show its position when we write the formula of the compound. From a study of the properties of acetic acid which we shall give in this chapter, it is clear that the structure of the acetic acid molecule is to be represented thus,



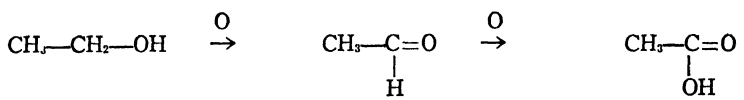
It consists of a methyl group, $-CH_3$, linked to what is called a carboxy group,

The H atom in the carboxy group has acid properties when the compound is dissolved in water, and this H atom is the one that is replaceable by metals:

$$CH_3—COOH + NaOH \rightarrow CH_3—COONa + H_2O$$

(Compare the structure of the carboxy group with the structure of the aldehyde group given in section 30.2. The H atom in the aldehyde group does not have acid properties.)

31. 2. Formation of Carboxy Acids. We have already learned how the carboxy group can be made in the laboratory. In section 27.4*c*, we showed that alcohols can be oxidized to aldehydes; similarly, aldehydes are easily oxidized one step further to acids:



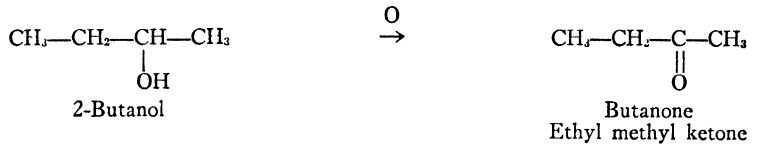
Ethyl alcohol
Ethanol

Actaldehyde
Ethanal

Acetic acid
Ethanoic acid

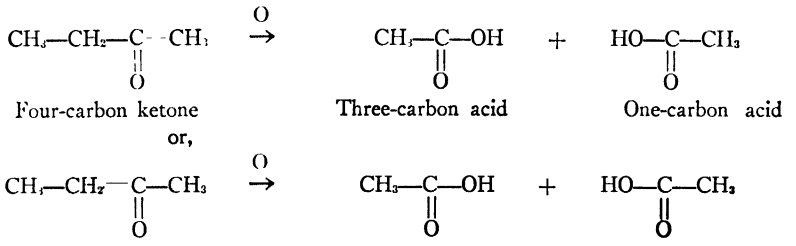
The principal thing to remember about this reaction is that the alcohol must be a primary alcohol, that is, one with the –OH group on the last carbon atom in the chain. In such cases, the acid formed has the same number of carbon atoms as the alcohol with which we start.

When a secondary alcohol is oxidized, a ketone is formed:



2-Butanol — Butanone (Ethyl methyl ketone)

Ketones are not as easily oxidized to acids as the aldehydes. However, when oxidation does take place, a *mixture* of acids will result because the chain of carbon atoms will break at the C=O group:



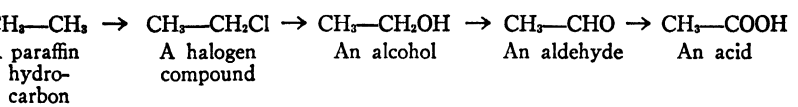
Four-carbon ketone — Three-carbon acid — One-carbon acid

or,

Two molecules of a two-carbon acid

As indicated, the chain can be broken on either side of the C=O group; the reason for this will be given later (section 32.11). The two carbon atoms at the point where the chain is broken are converted into carboxy groups, so that no matter where the break occurs, two acid molecules are formed. It is evident, therefore, that when we oxidize a secondary alcohol, the acids formed have a smaller carbon content than the alcohol with which we start.

The relationship between the carboxy acids and the other series of compounds we have studied can be shown as follows:



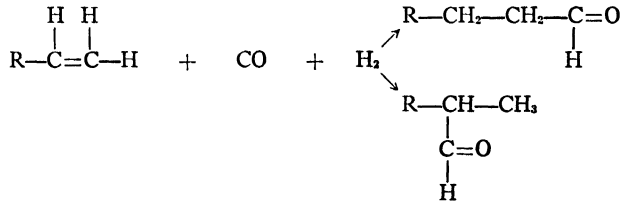
The student should note here the course of events in the transformation of one $-CH_3$ group in CH_3-CH_3 to the carboxy group, –COOH, in CH_3–COOH. As already explained, if we use a longer chain of

carbon atoms, like CH_3–CH_2–CH_3, in the original hydrocarbon, it is possible to prepare a ketone (instead of the aldehyde) in this series of reactions — in which case a mixture of acids is obtained.

The index of this book may be referred to for additional methods by which carboxy acids can be made. As stated before (section 25.2), most of the preparations described in this book illustrate chemical theory rather than commercial practice. The commercial operations described as follows, however, are of sufficient importance to the national economy to merit at least a brief mention.

The *Fischer-Tropsch* synthesis uses as raw materials a mixture of one part carbon monoxide and two parts hydrogen ($CO + 2\ H_2$). This mixture, called *synthesis gas*, contains twice as much hydrogen as *water gas*, which is made from steam and hot coke. When synthesis gas is passed over a catalyst (cobalt or iron) at a temperature a little over 200°C. and at pressures of 1 to 10 atmospheres, a mixture of mostly paraffin and olefin hydrocarbons is produced. Oxygenated compounds, alcohols, aldehydes, acids, can be obtained in good yield by varying the conditions.

In the *Oxo* process, a mixture of CO and H_2 is added to an olefin double bond in the presence of a catalyst (dicobalt octacarbonyl) at pressures of 100 to 300 atmospheres and temperatures in the range of 120 to 180°C. The olefins are obtainable from the Fischer-Tropsch reaction. The Oxo process has also been called *hydroformylation*, because the mixture of CO and H_2 behaves like a molecule of formaldehyde, H–CHO, which splits up into H– and the formyl group, –CHO, and then adds across the double bond (section 15.2).



The aldehydes made by this reaction can be reduced to alcohols and oxidized to acids. The reaction also yields ketones.

31. 3. How to Name Carboxy Acids. Just as the –OH group is referred to as either hydroxy or hydroxyl, the –COOH group is called either carboxy or carboxyl. We use the shorter name in this book.

The nomenclature of acids related to the principal type hydrocarbons is apparent from tables 31.1 and 31.2. The common names of the acids, in most cases, indicate their original sources in nature. Formic acid is obtainable by distillation of red ants, the Latin name of which is *formica*; acetic acid is present in vinegar, the Latin name of which

TABLE 31.1. ALIPHATIC ACIDS

Corresponding Hydrocarbon	*Carboxy Acid*	*Common Name*	*Systematic Name*
CH_4 Methane	$H-C(=O)-OH$	Formic acid	Methanoic acid
CH_3-CH_3 Ethane	$CH_3-C(=O)-OH$	Acetic acid	Ethanoic acid
$CH_3-CH_2-CH_3$ Propane	$CH_3-CH_2-C(=O)-OH$	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-CH_3$ Butane	$CH_3-CH_2-CH_2-C(=O)-OH$	Butyric acid	Butanoic acid
$CH_3-(CH_2)_{16}-CH_3$ Octadecane	$CH_3-(CH_2)_{16}-C(=O)-OH$	Stearic acid	Octadecanoic acid
$CH_3-CH=CH-CH_3$ 2-Butene	$CH_3-CH=CH-C(=O)-OH$	Crotonic acid	2-Butenoic acid
$CH\equiv C-CH_3$ Propyne	$CH\equiv C-C(=O)-OH$	Propiolic acid	Propynoic acid

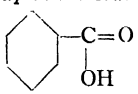
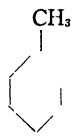
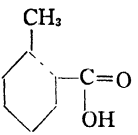
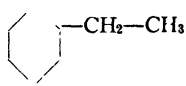
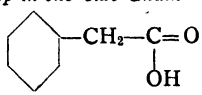
is *acetum*; and butyric acid gets its name from the Latin *butyrum* butter.

In systematic nomenclature, the main part of the name is derived from the name of the longest chain of carbon atoms containing the –COOH group, and this group is always written at the end of the chain. The carboxy group is regarded as the "chief function" (section 10.10) in the molecule and its presence is indicated in the main part of the name by calling the compound an -oic acid, thus: CH_2Cl-CH_2-COOH, 3-chloropropanoic acid. The carboxy group does not require a numeral because the carbon atom in the carboxy group is assigned the 1 position in the chain.

Sometimes the *-ane* is dropped completely from the name of the corresponding straight-chain hydrocarbon of the paraffin series, as in the use of heptoic acid instead of heptanoic acid for the compound the skeleton of which is C–C–C–C–C–C–COOH. This, however, is not the official procedure. The student should also observe in the table how the position of the C=C group, that is, the *ene* group, is indicated when it is present in a carboxy acid molecule.

The Greek alphabet is used instead of numbers in an older systematic method for naming acids which contain substituent elements

TABLE 31.2. AROMATIC ACIDS

Corresponding Hydrocarbon	*COOH Group in the Nucleus*
Benzene Phene	 Benzoic acid
 Toluene Methylbenzene Phenylmethane	 *o*-Toluic acid *o*-Methylbenzoic acid
COOH Group in the Side Chain	
 Ethylbenzene Phenylethane	 Phenylacetic acid

or groups. The lettering starts at the first carbon atom after the COOH group, thus: $\overset{\delta}{C}-\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-COOH$. According to this method CH_2Cl-CH_2-COOH is called β-chloropropionic acid, the older common names being used as last names. As already explained, according to the new systematic procedure this compound is 3-chloropropanoic acid. The Greek-alphabet method of designating the carbon atoms in the chain is used more often for acids than for other types of compounds.

31. 4. Properties of Carboxy Acids. The straight-chain acids in which the chain of C atoms is small are liquids of pungent odor. Formic acid and acetic acid have sharp, irritating odors and the next few acids in the series have terribly rancid odors. The acids with a chain of ten carbon atoms ($C_9H_{19}COOH$) or more are waxy solids at room temperature, and the odor diminishes with the increasing chain until it is practically absent in stearic acid, $C_{17}H_{35}COOH$, the substance used in candles.

The melting points of the first ten straight-chain acids are given in table 31.3, and it will be seen that the molecule with an even number of carbon atoms has a higher melting point than the next member of the series with an odd number of carbon atoms (see figure 12.8). There is no such irregularity in the boiling points, for the reason given in section 12.4

TABLE 31.3. STRAIGHT-CHAIN ACIDS (R—COOH)

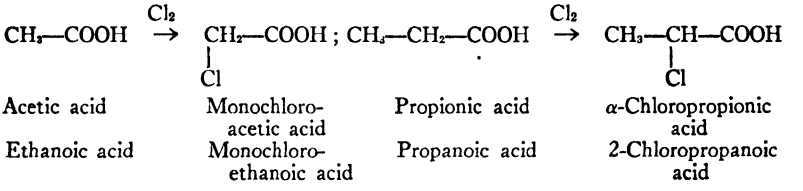
Acid	*Formula*	*Melting Point °C.*	*Boiling Point °C.*
Formic	H—COOH	8.4	100.7
Acetic	CH_3—COOH	16 6	118.1
Propionic	CH_3—CH_2—COOH	—22	141.1
Butyric	CH_3—$(CH_2)_2$—COOH	—7.9	163.5
Valeric	CH_3—$(CH_2)_3$—COOH	—58.5	187
Caproic	CH_3—$(CH_2)_4$—COOH	—1.5	205
Heptylic	CH_3—$(CH_2)_5$—COOH	—10	223 5
Caprylic	CH_3—$(CH_2)_6$—COOH	16	237 5
Nonylic	CH_3—$(CH_2)_7$—COOH	12	254
Capric	CH_3—$(CH_2)_8$—COOH	31.5	269

The lower acids are water-soluble, but as the chain of C atoms is lengthened, the solubility in water decreases. The characteristics of the compounds will, of course, approach the properties of the corresponding hydrocarbons as the chain grows larger and the –COOH group at the end of the chain becomes a comparatively insignificant part of the molecule.

The aromatic acids, that is, compounds derived from benzene hydrocarbons, are generally colorless, odorless, crystalline, and only slightly soluble in water. In the table of representative acids in this series (table 31.2), the student should note that we have listed examples in which the –COOH is in the *nucleus* or in the *side chain*, as in benzoic acid and in phenylacetic acid, respectively. There is very little difference in the chemical nature of the –COOH group in these two positions.

The chemical properties of the acids naturally consist of the two sets of characteristics shown (a) by the hydrocarbon from which they are derived, and (b) by the carboxy group.

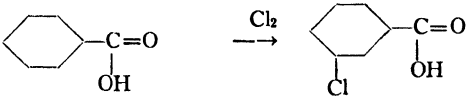
31. 4a. Hydrocarbon Properties. Let us examine first the chemical properties depending on the hydrocarbon part of the molecule. The open-chain compounds, as usual, are easily halogenated:



In fact, chlorination of these compounds is easier than that of the hydrocarbons themselves. We also found this to be true of the halogenation of aldehydes and ketones (section 30.5*a*). When a long-chain acid is treated with chlorine, the most susceptible point of attack is the α-carbon atom as shown.

The halogenated acids are important because they can be used for many syntheses, as explained in section 25.2 for halogen compounds in general.

The acids containing the benzene nucleus are halogenated, nitrated, and sulphonated as described in sections 20.3 and 20.4:



m-Chlorobenzoic acid

The presence of the negative –COOH group in the ring, however, makes the introduction of other negative groups a little more difficult.

31. 4b. Carboxy Group Properties. The other chemical characteristics of acids which we shall describe are the reactions of the carboxy group, $-\overset{|}{\underset{OH}{C}}=O$. This unit contains two other groups that we have already studied, namely, the carbonyl group, $\overset{|}{C}=O$, and the hydroxy group, –OH.

These subgroups, however, do not have exactly the same properties when acting together in acids as they do when present separately in aldehydes or ketones (chapter 30) and in alcohols (chapter 27). In the case of aldehydes and ketones we found the principal property of the C=O group is its reducing ability (section 30.5*c*) and its ability to add on other substances so as to open its double bond. This "additive" tendency of C=O is much less pronounced when it is present in the carboxy group of acids. The typical properties of the OH group, however, are retained to a large extent when it is present in the carboxy group. This will become evident later in the chapter, when we describe the various types of compounds that can be derived from acids (section 31.8).

There are many chemical transformations in which the $-\overset{|}{\underset{|}{C}}=O$ / OH group can take part, and most of this chapter will be devoted to the study of these reactions. The most important characteristic of the carboxy group, however, is its acidity. Before we examine the carboxy group to find out what it is that brings about this acidity, let us first discuss what is meant by an acid.

31. 5. Proton Theory of Acids and Bases. For many years it was taught that an acid is a substance which can liberate hydrogen ions (H^+) when in solution, due to an ionic dissociation of the type, $HCl \leftrightharpoons H^+ + Cl^-$. The greater the "degree of dissociation," the greater the "strength" of the acid. (The student should review the structure of the H atom in figure 6.1 and note that the hydrogen ion, H^+, is simply a proton, a unit positive charge of electricity.)

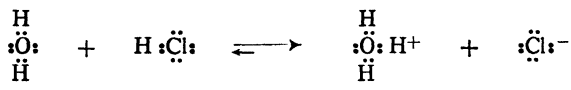
Similarly, it was taught that a base is a substance that dissociates in aqueous solution to produce hydroxyl ions (OH^-), thus: $NaOH \rightleftarrows Na^+ + OH^-$. A solution is commonly said to be basic if it contains hydroxyl ions.

Modern ideas of atoms and molecules have led us away from the belief that there are *free* H^+ ions in an acid solution. The HCl molecule is covalent, as shown in section 8.8, with the structure $H:\ddot{\underset{\cdot\cdot}{Cl}}:$. It is not an ionic molecule like $Na^+:\ddot{\underset{\cdot\cdot}{Cl}}:^-$ (figure 8.1), which simply falls apart when dissolved in water, $Na^+Cl^- \rightarrow Na^+ + Cl^-$. This disintegration of the sodium chloride molecule is the modern picture of an ionic dissociation. Since HCl, however,

is a covalent rather than an ionic molecule, it is not likely that it will ionize the way NaCl does.

When HCl is dissolved in water, it probably reacts with the water as follows:

$$H_2O + HCl \rightleftharpoons H_2O.H^+ + Cl^- \quad \text{or,}$$



This reaction is practically complete in the direction of the arrow to the right. The HCl molecule donates its proton, that is, H^+ ion, to the water molecule and forms a *hydrated* hydrogen ion. This is the entity that appears in solution instead of the *bare* H^+ ion. This is the *hydronium* ion referred to in section 27.3.

According to this theory, an acid is a substance capable of donating protons, and a base is a substance that accepts protons. Water, from this point of view, can be regarded as a base because it takes up the protons from the HCl molecules dissolved in it. The OH^- ion obtainable from an alkali in solution is also a base, because it tends to react with protons to form water ($H_2O.H^+ + OH^- \rightarrow 2\,H_2O$). It will be seen that this theory of acids and bases depends on the donating and accepting of hydrogen ions. This ion is the central figure in the theory.

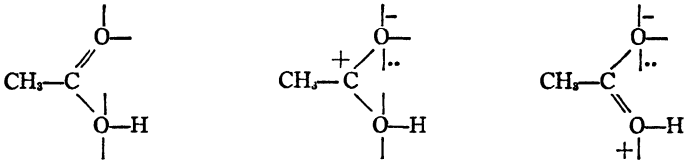
When HCl is dissolved in water ($H_2O + HCl \rightleftharpoons H_2O.\,H^+ + Cl^-$) there is practically no tendency for the reverse reaction to take place to form HCl molecules. The right-hand reaction is nearly complete and, for this reason, we state that hydrochloric acid is a strong acid. The Cl^- ion in this solution is not basic, because it does not react with (accept) the hydrogen ions.

With acetic acid the conditions are quite different:

$$\underset{\text{Acetic acid}}{CH_3—COOH} + H_2O \rightleftharpoons H_2O.H^+ + \underset{\text{Acetate ion}}{CH_3—COO^-}$$

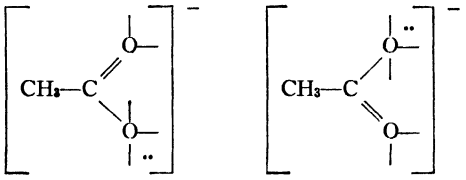
The negative ion in this case tends to react with H^+ ions to form molecular acetic acid. The reaction to the left predominates and, since there are relatively few hydrated H^+ ions in solution, compared with the status in hydrochloric acid solution, the solution of acetic acid is said to be weak. Moreover, the acetate ion is said to be basic, because it readily accepts H^+ ions.

31. 6. Acidity of the Carboxy Group. Now that we have seen what constitutes an acid we can proceed to the study of the acidity of the carboxy group. The explanation is exactly like that given for phenol (section 28.2) and is based on resonance of the acetic acid molecule, the resonance formulas of which are written according to the procedure given in section 18.6:



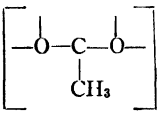
The shift of electrons away from the –OH group leaves the O atom in that group with a positive charge and the H atom is accordingly less firmly held. In its average state, the *acetic acid molecule*, therefore, has considerable ionic character, and it reacts with water according to the equilibrium shown in the preceding paragraph.

The *acetate ion* also shows resonance (compare the remarks about the phenate ion in section 28.2) and the resonance in this case is complete, because the two structures are exactly equivalent (section 18.5):



The resonance energy is, therefore, greater than for the undissociated CH_3–COOH molecule. This excess energy must be supplied by the H^+ ion in order to react with the acetate ion to form the undissociated molecule. All this leads to the fact that the molecule CH_3–COOH has an appreciable tendency to remain dissociated in water to give an acid solution even though a weak one, whereas the –OH group normally has acid properties which are almost negligibly small (section 27.3).

The student should also refer to the discussion of the nitro group (section 20.4) for the description of a symbolism by which we can indicate the symmetrical nature of the acetate ion as follows:

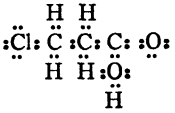


Another explanation for the acidity of the carboxy group makes use of the theory of *inductive effects* (section 17.2). There is reason to believe that in a molecule of this type the chain of carbon atoms exerts a strong pull on the electron pairs in the direction of the arrow, $\xleftarrow{\qquad}$ C–C–C=O. Displacement of the electrons away from the hydrogen

OH

(of the –COOH) makes the hydrogen more free to assume the condition of the hydrogen ion.

This effect is more pronounced when an electronegative element, like chlorine, is present in the chain, thus



The direction of the dipole which is formed is Cl←C, that is, the chlorine atom is more electron-attractive than the carbon atom. According to modern theory, the other electron pairs joining the C atoms in the chain are also affected. There is an "induced" electrical effect throughout the chain, which ultimately is felt by the H atom in the –COOH group at the other end of the molecule. This H atom has even more freedom to wander because of the presence of a strongly negative element somewhere in the chain. This means a higher acidity. The greater the distance of the negative group in the chain from the –COOH group, the smaller is the induction effect, and for this reason $CH_2Cl–CH_2–COOH$ is a weaker acid than $CH_3–CHCl–COOH$.

The relative strengths of acids are usually stated in terms of the *dissociation constant.* This constant is obtained from the law of mass action with reasonable accuracy for weak acids in dilute solution. If

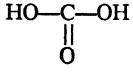
the dissociation of a weak acid, HA, is represented by $H_2O + HA \rightleftarrows H_2O.H^+ + A^-$, then

$$K = \frac{[H_2O.H^+]\,[A^-]}{[HA]}$$

K is the dissociation constant and the quantities in brackets are the concentrations of the reacting substances. The effect of the solvent H_2O molecules can be neglected in the case of dilute solutions of weak electrolytes.

The dissociation constants for a number of representative acids are shown in table 31.4. The open-chain acids all have about the same degree of acidity, as illustrated by the data for acetic acid and butyric acid. Acidity of the open-chain acids increases rapidly, however, when *electronegative* elements are present in the chain, as shown by the chloroacetic acids. Trichloroacetic acid, CCl_3–COOH, is practically as strong as HCl, but no accurate data are available for strong acids, because their behavior in solution does not follow the simple form of the law of mass action. (For information concerning the equilibrium of strong acids, the student is referred to recent texts on physical chemistry in which the "activity coefficient" is defined.) The benzene ring is electronegative in character, like the Cl atom, and consequently benzoic acid, C_6H_5–COOH, also, is somewhat stronger than acetic acid.

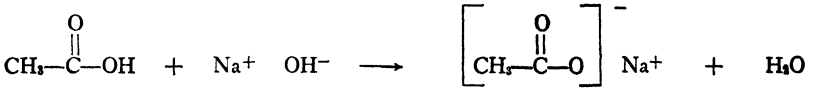
TABLE 31.4. DISSOCIATION CONSTANTS OF ACIDS (AT 25° C.)

Substance	*Formula*	*Dissociation Constant*
Hydrochloric acid	H—Cl	Complete dissociation
Formic acid	H—COOH	0.000 17
Acetic acid	CH_3—COOH	0.000 018
Propionic acid	CH_3—CH_2—COOH	0.000 014
Butyric acid	CH_3—CH_2—CH_2—COOH	0.000 015
Chloroacetic acid	CH_2Cl—COOH	0.001 5
Dichloroacetic acid	$CHCl_2$—COOH	0.050
Trichloroacetic acid	CCl_3—COOH	Complete dissociation
Benzoic acid		0.000 063
Carbonic acid		0.000 000 35
Phenol (carbolic acid)		0.000 000 000 13
Hydrocyanic acid	H—CN	0.000 000 000 72
Water (for comparison)	H—OH	0.000 000 000 000 01

31. 7. Electron Theory of Acids and Bases. We have described in these pages what is generally known as the *proton* theory of acids and bases. This theory is included in a theory of much wider scope, according to which any molecule is an acid if it can accept an electron pair, and any molecule is a base if it can donate an electron pair. For an example, we can refer to section 8.5, where a reaction is shown in which boron trichloride is the acid and ammonia is the base. According to this *electron* theory, the hydrogen ion, or proton, is an acid because it is an acceptor of an electron pair, as in the reaction $H^+ + :\ddot{O}:H \rightarrow H:\ddot{O}:H^+$, where water is the base.

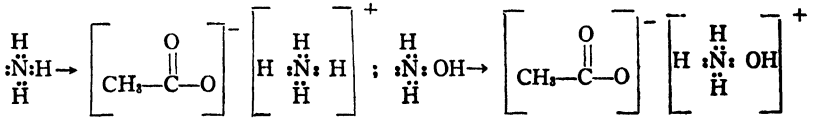
31. 8. Compounds Derived from Carboxy Acids. The student should review sections 31.4*a* and 31.4*b*, where the general nature of the chemical properties of carboxy acids was briefly described. In the paragraphs which follow, we shall discuss the carboxy group in detail.

31. 8a. Formation of Salts and Soaps. The acid nature of the carboxy group is shown by the ease with which *salts* are formed through the interaction of these organic acids with bases:



Acetic acid — Sodium acetate

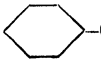
This is a *neutralization*, exactly as defined in inorganic chemistry, that is, a reaction between an acid and a base to form a salt and water. The following weaker bases also react with acetic acid to yield the corresponding salts:



Ammonia — Ammonium acetate — Hydroxylamine — Hydroxylamine acetate

It was shown in section 30.5*e* that hydroxylamine reacts with the C=O group in aldehydes and ketones to form *oximes*. The C=O group is much less reactive when in the carboxy group and the bases

preferentially react with the proton. The student should read again the brief section 31.7.

The salts of the carboxy acids are generally crystalline substances. The salts of the open-chain acids with a large number of C atoms in the chain, like sodium stearate, CH_3–$(CH_2)_{16}$–COONa, are called *soaps*, which will be discussed further in section 31.10. The sodium salt of benzoic acid,  –COONa, is used as a food preservative.

The salts of the open-chain acids, when fused with a strong alkali *lose their carboxy group*:

$$CH_3—CH_2—COONa + NaOH \rightarrow CH_3—CH_2—H \text{ (or } CH_3—CH_3) + Na_2CO_3$$

Sodium propionate — Ethane

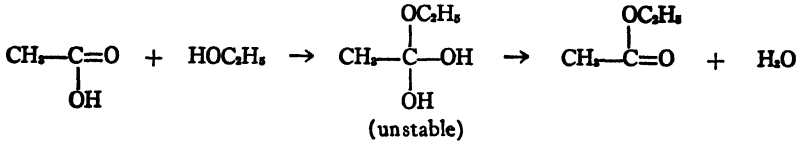
This is of interest, because it gives the chemist a method of *reducing* the length of the carbon chain by one carbon atom. To pass from propane to ethane, we can convert CH_3–CH_2–CH_3 to CH_3–CH_2–COOH by the reactions outlined in section 31.2, and then take off the –COOH group as just indicated. The phenomenon of decarboxylation, discussed under malonic acid in section 31.13, should also be referred to.

31. 8b. Formation of Esters. The carboxy acids react with alcohols to form *esters*. These compounds are analogous to salts in structure, but differ from salts in properties. The following reaction indicates the formation of a typical member of this family of compounds:

$$CH_3—\underset{\displaystyle OH}{\underset{|}{C}}=O + HOC_2H_5 \rightarrow CH_3—\underset{\displaystyle OC_2H_5}{\underset{|}{C}}=O + H_2O$$

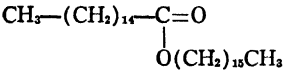
Acetic acid — Ethyl alcohol — Ethyl acetate

This looks like the neutralization of an acid by a base to form a salt as described before, but the mechanism of the reaction is probably different. Ester formation probably occurs in two stages, the first stage of which is the addition of the alcohol to the C=O group of the acid, just as in addition to aldehydes (section 30.5*c*). The second stage is the splitting off of water to form the ester as follows:



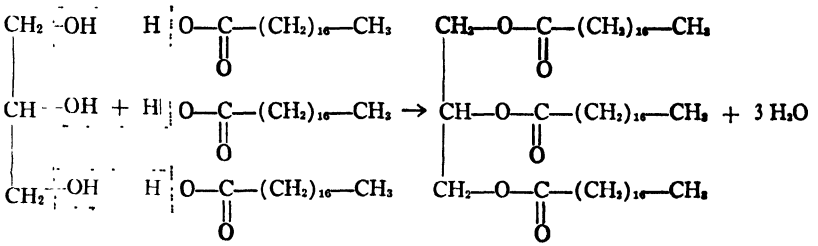
The instability of compounds with two –OH groups on the same carbon atom has already been pointed out in section 27.4*c*. Esters formed from the lower open-chain acids and the lower alcohols are sweet-smelling liquids, used for flavoring and as solvents for lacquers.

The *waxes* are essentially esters of the long-chain acids and the long-chain alcohols. For example, spermaceti is a crystalline wax obtained from sperm oil of the whale; one of its ingredients is cetyl palmitate:



the ester of a C_{16} acid, known as palmitic acid, and of a C_{16} alcohol, called cetyl alcohol.

Fats are the esters of the open-chain acids and of glycerol. This alcohol contains three –OH groups, and can, therefore, react with three molecules of a carboxy acid:



These substances occur plentifully in nature in fats and oils, such as tallow, lard, olive oil, butter, etc. In most cases, the acid part of the ester has a long chain, like stearic acid, or palmitic acid CH_3-$(CH_2)_{14}$-COOH. Butter fat, however, contains a high percentage of the ester of butyric acid, which is only a four-carbon acid, CH_3-$(CH_2)_2$-COOH. It is curious that acids built up of odd numbers

of carbon atoms have not been found in fats and oils which occur in nature.

The fats were among the first compounds thoroughly studied in the early days of organic chemistry and substances isolated from them were known as "fatty" or aliphatic, in contrast with the "aromatic" compounds obtained from coal tar. It was a long time before it was discovered that the "fatty" materials and "aromatic" materials differ only in that the first are open-chain compounds whereas the second are mostly cyclic compounds of the benzene series (section 23.1).

Although we now know many thousands of open-chain compounds which are not at all fatty and bear no relation to fats in appearance, they are still often referred to as fatty compounds, because they have a chain structure. The open-chain acids, in particular, are still called fatty acids, and are usually referred to as the "higher fatty acids" or the "lower fatty acids," depending on whether they have a high or a low carbon content.

Hydrolysis and *saponification* are synonymous terms often employed in organic chemistry, especially in connection with the chemistry of the esters. In the textbooks of inorganic chemistry the statement will often be found that certain salts hydrolyze easily. This means that the salt reacts with water, either cold or when heated,

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$

and the products are a base and an acid. Hydrolysis is the reverse of neutralization, which we defined in section 31.8*a*, and occurs most readily with salts of weak acids or weak bases.

Since the esters can be hydrolyzed without much difficulty, the reaction for the formation of an ester is really reversible:

$$\underset{\text{Acetic acid}}{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH} + \underset{\text{Ethyl alcohol}}{C_2H_5{-}OH} \underset{\text{hydrolysis}}{\overset{\text{esterification}}{\rightleftharpoons}} \underset{\text{Ethyl acetate}}{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OC_2H_5} + H_2O$$

If an excess of water is present and the mixture is boiled, the reaction goes to the left, but in the presence of a dehydrating agent to remove the water from the sphere of action, the reaction goes to the right. The hydrolysis of esters to form the original acid and alcohol

is best accomplished when a small amount of strong acid or alkali is added as a catalyst.

We have already explained that fats are esters. The hydrolysis of fats is one of our major industries. When glyceryl tristearate, the formula of which has been given in the last few pages, is heated with a large amount of water and alkali, it is hydrolyzed or broken down to glycerol and stearic acid. If the alkali used in the hydrolysis of the fat is sodium hydroxide, the sodium salt of stearic acid is formed. We have already explained that this salt is known as a *soap*. In fact, it is one of our common soaps. The hydrolysis of fats is technically termed *saponification* and the same term is now used for all types of hydrolysis of esters, even though no soap is formed.

The first stage of the digestion of fats in the animal body consists in the hydrolysis of the fat to glycerol and the free carboxy acid. It is brought about by the action of enzymes called *lipases*.

In animal and vegetable life, oily substances are often found which are not esters. Since they are not esters, they cannot be broken down by enzymes or hydrolysis into an acid and an alcohol. They are said to be nonsaponifiable. The sterols (section 44.2) and the carotenes (section 37.7) are present in the nonsaponifiable fraction of many oils and fats, such as cod-liver oil.

31. 8c. Formation of Acid Chlorides. The method of preparation of this important class of compounds consists in the replacement of the –OH in the $-C(=O)-OH$ group by a Cl atom:

$$3\ CH_3-C(=O)-OH + PCl_3 \rightarrow 3\ CH_3-C(=O)-Cl + H_3PO_3$$

Acetic acid — Acetyl chloride

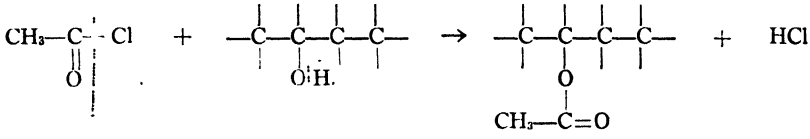
This replacement of –OH by –Cl is exactly the same as that illustrated in section 27.4*a*, when we showed how alcohols can be converted to alkyl chlorides, $CH_3-OH \rightarrow CH_3-Cl$.

Because of their structural similarity to the *alkyl* chlorides these chlorine derivatives of the acids are known as *acyl* chlorides:

$\ldots -CH_2-CH_2-Cl$ (R—Cl) $\qquad \ldots -CH_2-C(=O)-Cl$ (Ac—Cl)

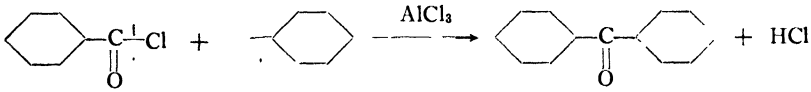
The *acyl group* is the acid molecule with the –OH missing, thus $CH_3-\underset{\underset{O}{\|}}{C}=O$. The group is named by dropping -ic from the name of the acid, and replacing it by -yl. For example, acetic acid gives acetyl chloride, propionic acid gives propionyl chloride, and benzoic acid gives benzoyl chloride.

The acyl chlorides are reactive substances, due to the activity of the halogen atom. A whole chapter might easily be devoted to the study of their usefulness in synthetic chemistry. They are often used to detect an –OH group in organic compounds because of the ease with which they react with this group:



The product is an ester, but is often referred to as an *acetyl substitution product* when acetyl chloride is used. If several –OH groups are present in the molecule, they can usually all be replaced by the acetate radical in this way. When the reaction is used not so much for detecting –OH in a molecule as for introducing the acetyl group in place of an H atom, the process is called *acetylation* (section 39.9).

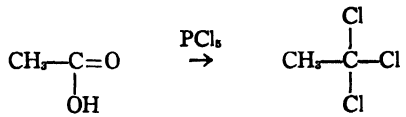
Another interesting application is shown by the following reaction:



Benzoyl chloride Benzene Benzophenone

This is an instance of the Friedel-Crafts reaction (section 20.5). The product is an aromatic ketone.

It is also of interest to point out that if PCl_5 is used instead of PCl_3 in the chlorination of acetic acid, it replaces not only the –OH but also the oxygen in the carboxy group:

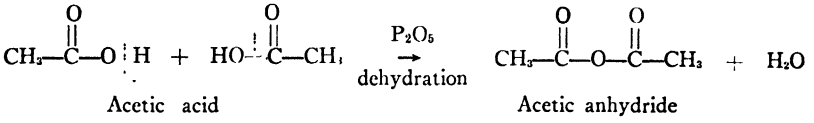


Ethanoic acid
Acetic acid

1, 1, 1-Trichloroethane

This yields a compound with three Cl atoms on the same C atom. This should be compared with the action of the same chlorinating agent on aldehydes and ketones (section 30.5*e*).

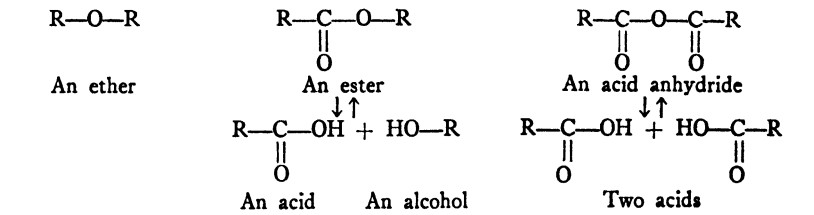
31. 8d. Dehydration to Acid Anhydrides. Carboxy acids can be condensed by the action of strong dehydrating agents. A typical reaction is the following:



The acid anhydrides are of importance in synthesis. They are often useful where the original acids cannot be used because of certain experimental requirements. When warmed with water, the original acid is regenerated.

Mixed anhydrides can be obtained in which two different acyl radicals are joined by the oxygen bridge, such as the anhydride of acetic acid and propionic acid, $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$.

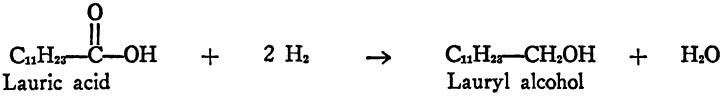
The student should compare the structures of ethers, esters, and anhydrides:



Ethers, it will be recalled, are very stable, but esters and anhydrides can be hydrolyzed by water to their original constituents.

31. 8e. Reduction to Alcohols. In section 30.2 we showed how the C=O group in an aldehyde is readily *reduced*, by addition of hydrogen, to an alcohol. In this chapter we have stressed the relative inertness of the $-\overset{|}{\underset{\cdot}{C}}=O$ group in carboxy acids toward such simple addition reactions (section 31.4*b*). The longer-chain acids can be reduced, however, but the treatment is rather drastic and results

in removal of the =O. The reaction requires high temperature, high pressure, suitable catalysts, and large excess of hydrogen:

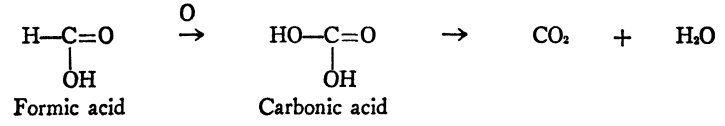


This type of reaction is important industrially because of the usefulness of the long-chain alcohols in the manufacture of detergents (sections 31.11 and 34.3).

31. 9. Representative Carboxy Acids. *Formic acid*, H–C(=O)–OH, is the simplest member of the series of carboxy acids. It is related to methane in that they both contain but one carbon atom; it is also known as methanoic acid. This colorless liquid, corrosive to the skin, occurs in nature in various plants, in bee stings, and in ants.

Formic acid merits a paragraph to itself because of its unusual properties. If the formula of formic acid is examined, it will be seen that it is not only an acid but also an aldehyde, for it contains not only the carboxy group, –C(=O)–OH, but also the aldehyde group, –C(=O)–H.

It therefore has the properties of both types of compounds. It differs from all the other carboxy acids in that it is a reducing agent (section 30.3), that is, it can be easily oxidized:

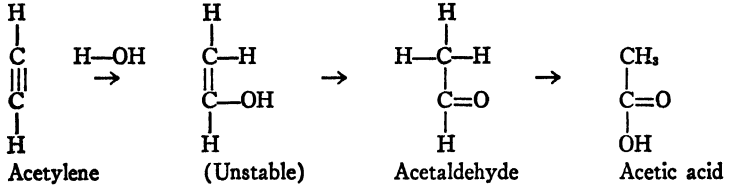


Oxidation converts it to carbonic acid, which decomposes to carbon dioxide and water. Formic acid is also a stronger acid than the succeeding members of its family of compounds.

Acetic acid, CH_3–C(=O)–OH, is the only edible free acid in this series of compounds, about 4 per cent being present in vinegar. Pure, anhydrous acetic acid is called *glacial acetic acid*, because it crystallizes easily in cold weather to form icelike crystals at 16.7°C. The

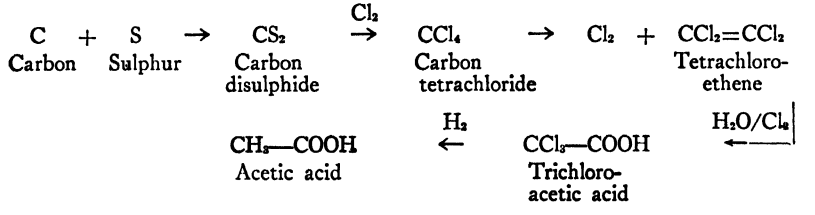
dry acid has a corrosive effect on the skin and is a good solvent for many organic compounds.

Acetic acid is made in large quantities from acetylene by the following reactions:



Water can be added to acetylene through the catalytic effect of mercuric sulphate ($HgSO_4$). The initial product is unstable (see discussions in sections 15.3 and 32.14) and rearranges to yield acetaldehyde, which is easily oxidized to acetic acid.

It was mentioned in section 2.3 that acetic acid was probably the first organic compound synthesized from more elementary substances, and that this synthesis was the first evidence that supernatural powers are not required in such reactions. In 1845, Kolbe succeeded in doing this by the following sequence of reactions, the details of which we shall not discuss:



Crotonic acid, CH_3–CH=CH–COOH, is a carboxy acid derived from butene, a hydrocarbon of the olefin series (table 16.1). Its systematic name is *2-butenoic acid*. The benzene analog of this acid is phenylcrotonic acid, –CH=CH–COOH, commonly known as *cinnamic acid*. It occurs in oil of cinnamon and in various balsams.

Oleic acid is probably the most important of the acids which contain a double bond in the chain. It is derived from the hydrocarbon

octadecene; in other words, there are eighteen carbon atoms in the chain. Experiment has shown that the C=C group is in the middle of the chain, so its formula is CH_3–$(CH_2)_7$–CH=CH–$(CH_2)_7$–COOH.

Oleic acid occurs combined with glycerol as the fat "triolein," similar in structure to the "tristearin" pictured in section 31.8*b*. Triolein (or glyceryl trioleate) is found, together with tristearin, in fats, like lard, and in many vegetable oils. Triolein is liquid, whereas tristearin is solid. Since semisolid fats are in greater demand than oils in the kitchen, the vegetable oils are often converted into fats by hydrogenation (section 15.2). Hydrogen is bubbled through the oil in the presence of a catalyst, and as the H–H molecules add on across the double bonds, the triolein changes into tristearin which is solid. Many cheap oils, like cottonseed oil and peanut oil, are converted to fats by this process and are sold at a higher price.

31. 10. Soaps. In section 31.8*a* soaps were defined as salts of long-chain carboxy acids. The common soap with which everybody is familiar is sodium stearate, the principal ingredient of ordinary bar soap. Its manufacture from fats was briefly described under esters. Many other soaps are used commercially in enormous quantities and in a great many ways. They are often made from the sodium soap by precipitation with compounds of other metals; thus, the aluminum stearate soap is generally made from the sodium soap and aluminum sulphate.

Many of the soaps have lubricating properties; thus, zinc stearate is used in face powders to lubricate the human skin. It is also a water repellent. Calcium, zinc, and magnesium soaps are used as lubricants on metal and leather surfaces. Some soaps can be dispersed in suitable liquids to give "gels." The well-advertised solid alcohol, or *canned heat*, is such a gel in which the semisolid structure is due to a soap. A related gel made by adding aluminum soaps to gasoline was used in tremendous quantities in World War II as a filling in incendiary bombs and was highly effective as a destructive agent. More concentrated mixtures of such soaps in oils yield thick lubricants or "greases."

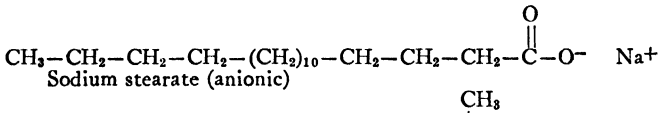
31. 11. Detergents. The cleansing action of ordinary soap (sodium stearate) has been explained as due to its surface activity. Surface-active compounds tend to concentrate at the surface of a solution and the molecules are then forced to align themselves in a

characteristic manner because of their polar nature. Representative surface-active compounds are shown in table 31.5. Figure 31.1 shows how such molecules are arranged in a water surface. The hydrocarbon chain is not water-soluble and tends to escape from the surface, leaving the polar end groups anchored in the water. If there are not too many molecules present, the hydrocarbon chains can move like tall grass in a wind. When the concentration is high, they are packed like the molecules in a crystal. It is apparent that a water solution, with a monomolecular layer of such molecules on its surface, actually presents a hydrocarbon surface to the air. The surface tension is lowered from the normal value of about 72 dynes/cm. to about 25 dynes/cm.

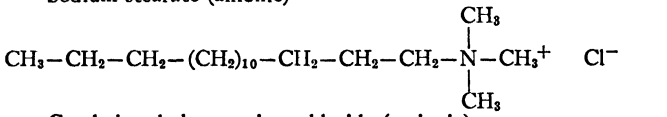
If we place a typically "organic" liquid layer, such as benzene, on a soap solution in water, the polar carboxy group remains anchored to the water layer, but the hydrocarbon chain extends into the benzene layer and anchors that layer. The interfacial tension is greatly reduced. When the mixture is shaken, an emulsion forms, which consists of benzene droplets dispersed in water, the droplets being stabilized by the soap film between the two liquids.

TABLE 31.5. REPRESENTATIVE DETERGENTS

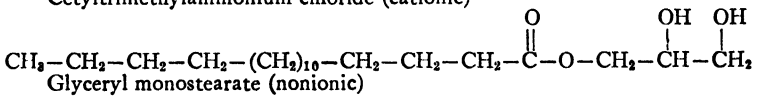
(The effective surface-active, long-chain structure can be either a negative ion, a positive ion, or a nonionic compound)



Sodium stearate (anionic)



Cetyltrimethylammonium chloride (cationic)



Glyceryl monostearate (nonionic)

The "soil" of soiled clothing is understood to consist of solid particles coated with a thin oil film. Removal of such soil makes use of the phenomena just described. A solution of a surface-active agent is added, which necessarily must wet the object. A compound which makes it easy to wet the soiled object, emulsify the oil film,

and keep the particles in suspension until washed away is called a *detergent.* Some surface-active agents merely wet a surface, but have little cleansing action and are not regarded as detergents. These are called wetting agents.

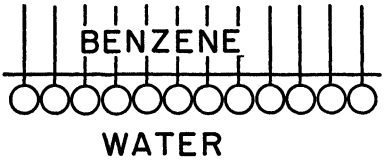
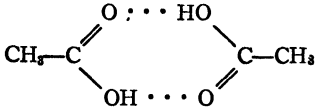


FIGURE 31.1. Distribution of a monomolecular soap film between water and benzene. The small circles are polar groups.

A great many detergents have been made and marketed. They are frequently called soapless soaps. Although ordinary soap is still the best cleanser when used in pure water, it is inefficient if the water is *hard,* that is, contains calcium and magnesium salts. These salts precipitate the corresponding soaps, which are insoluble in water. Of all the detergents, only soap is affected by hard water. This is a very important reason why soap is being replaced by other detergents in many industrial applications.

The cationic type of surface-active compound (table 31.5) is generally highly bactericidal. Since they are relatively nontoxic, they have important applications as cleansers for surgical instruments, dishwashing machines, etc. Some of the nonionic surface-active compounds have such weak polar characteristics that they are used more for wetting than for cleaning in nonaqueous liquids. They are often useful when mixed with other detergents or with soap. (See also ethanolamine and morpholine in section 33.8, and the sulphur compounds in the concluding paragraph of section 34.3.)

31. 12. Hydrogen Bonding. Carboxy acids furnish an excellent illustration of the phenomenon of hydrogen bonds (section 27.7), two molecules of the acid combining through hydrogen bonds to form a *dimer* (compare with the term *isomer,* section 10.5). The dimer, or double molecule, of acetic acid may be written



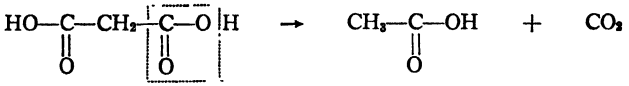
This double molecule is present in the crystalline compound and it is so stable that it holds together even when the acid is vaporized.

31. 13. Polycarboxy, or Polybasic Acids. The acids we have described so far contain only one carboxy group, $-C(=O)-OH$, at the end of a chain of carbon atoms, and, therefore, have only one H atom with acid properties. Since such acids can unite with only one molecule of a base to form a salt, $CH_3-COOH + NaOH \rightarrow CH_3-COONa + H_2O$, they are called monobasic. It is simpler and clearer to call them monocarboxy acids.

In this section, we shall consider a few acids that contain more than one acid group. They are called polycarboxy, or polybasic, acids. They are not usually classified among the "fatty" acids defined in section 31.8*b*.

Oxalic acid, $HO-C(=O)-C(=O)-OH$, is the simplest acid in this group of polycarboxy acids and is dibasic. Its systematic name is ethanedioic acid, which shows its relationship to ethane, CH_3-CH_3. Oxalic acid can be made by the oxidation of glycol (section 27.5) or of glyoxal (section 30.6) and can be obtained from many other substances, such as sugars and cellulose, by oxidizing them with nitric acid. Oxalic acid occurs in many plants, especially of the *oxalis* variety, in the form of its salts. It is a crystalline solid and is poisonous.

Malonic acid, or propanedioic acid, $HO-C(=O)-CH_2-C(=O)-OH$, is of importance because of its extensive use in organic synthesis, since it has properties similar to those of ethyl acetoacetate, as described in section 32.11. When malonic acid is heated above its melting point one of the carboxy groups is decomposed with elminiation of CO_2. This is called *decarboxylation.*

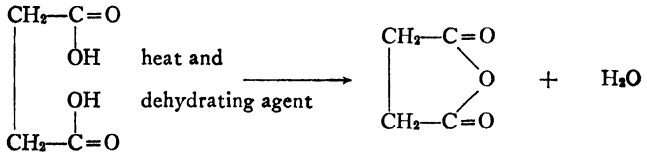


Malonic acid Acetic acid

It is a general rule that two carboxy groups attached to the *same* carbon atom form an unstable system; one of them is easily broken

up as shown. This should be compared with the instability of two OH groups on the same carbon atom, as stated in section 27.4*c*.

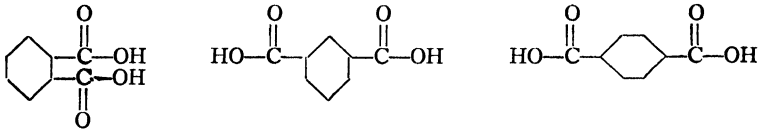
Succinic acid, or butanedioic acid, $HOOCCH_2$–CH_2COOH occurs in amber, the Latin name of which is *succinum*. An interesting property of succinic acid, and of other dibasic acids that contain a chain of at least four carbon atoms, is its ability to form an inner anhydride:



Succinic acid — Succinic anhydride

This behavior is similar to the formation of anhydrides from two molecules of an acid, as described in section 31.8*d*. The anhydride is a ring compound, whereas the original acid is a chain compound. They are both crystalline solids.

Phthalic acid, $HOOC–C_6H_4–COOH$, is a dicarboxy acid in which the two carboxy groups are attached to the benzene ring (section 36.5). There are three acids corresponding to this formula. The three acids differ in the positions of the –COOH groups in the ring; they can be *o*-, *m*-, and *p*- to each other, as shown in section 21.1, where the geography of the benzene ring was explained:



Phthalic acid (See section 36.5) — Isophthalic acid — Terephthalic acid (See section 46.12)

SUGGESTED READING

Luder, W. F., and S. Zuffanti. *Electronic Theory of Acids and Bases*, John Wiley, New York, 1946.

Ralston, A. W., *Fatty Acids and Their Derivatives*, John Wiley, New York, 1948.

Snell, C. T., "Synthetic Detergents and Surface Activity," *J. Chem. Educ.*, 24, 505-511 (1947).

Snell, F. D., "Surface Active Agents," *Ind. Eng. Chem.*, 35,107-117 (1943).

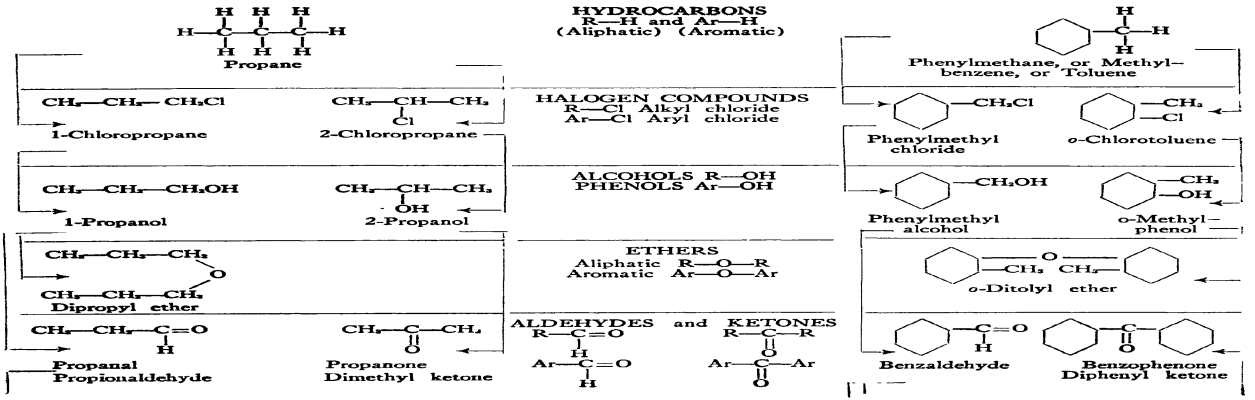
32. MIXED OXYGEN COMPOUNDS

32. 1. Introduction. We have now described the principal simple families of compounds in organic chemistry. We have concentrated our attention on the fact that one particular group in a molecule gives the compound its family properties.

In this chapter, we shall discover what happens to the molecule when it contains two or more characteristic groups. Such substances are called *mixed compounds*. Several examples of these compounds have already been mentioned in this book. For example, we showed that formic acid, $H-\underset{\displaystyle OH}{\overset{\displaystyle |}{C}}=O$, has the usual acid properties of the carboxy group, $-COOH$, but that it differs from other carboxy acids in that it has reducing properties due to the aldehyde group, $-CHO$, present in its structure.

32. 2. Review of Simple Family Types. Before we proceed to a study of the mixed types, let us pause for a moment to review the family relationships of the simple compounds as shown in figure 32.1. As indicated in the chart, the various families of compounds are regarded as derived from *chain* or *ring* structures. Each family is obtained by replacing an H atom in the chain or in the cycle by *one* of the characteristic groups we have studied in the past chapters.

The arrow pointing from one class of compounds to another is used to illustrate how more complex compounds can be developed from simpler ones. The actual manufacture of these various substances seldom follows the outline indicated on the chart. An outline of this kind, however, is of assistance to the beginner in visualiz-



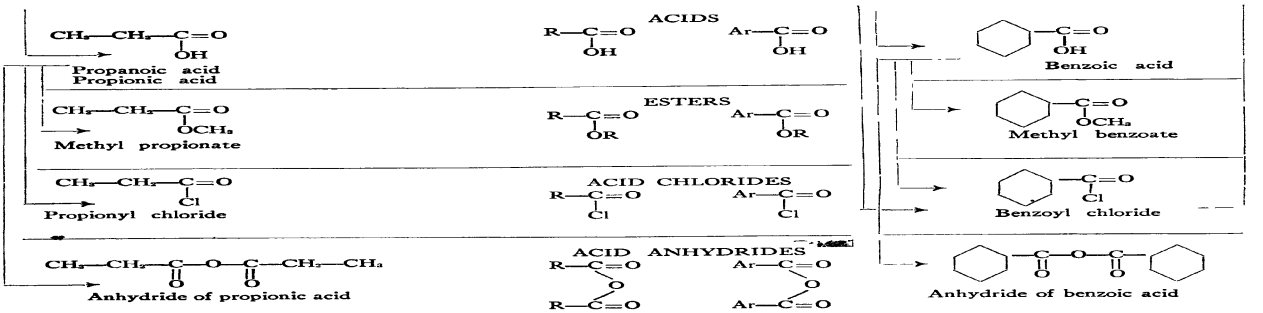


FIGURE 32.1. An outline indicating how the principal characteristic oxygen compounds are related to each other, and are obtainable from open-chain and cyclic hydrocarbons. See sections 24.2 and 24.4 for the meaning of R and Ar.

ing the relationships in organic chemistry. It also serves as a means of classification of organic compounds.

As we have already stated, the properties of each family correspond mainly to the properties of its characteristic group. For example, in the last chapter we found that the properties of acids are the properties of the carboxy group, $-\overset{|}{\underset{H}{C}}=O$, modified by the nature of the chain or ring to which it is attached. If another group, such as –OH or –CHO, happens to be present in the molecule, the compound should have two sets of chemical reactivities.

32. 3. Importance of Mixed Compounds. It would be very pleasant, indeed, if we could say without error that the properties of a molecule are the simple sum of the properties of its two or more characteristic groups. However, a mixed compound is seldom found to live up to this rule.

This is unfortunate for the textbook writer, because, if the additive relation held, he would not have to make a separate study of the properties of mixed compounds.

It is fortunate for the research worker, however, because he finds that a mixture of groups in a molecule often gives him some unusual and very useful properties to work with. It is this last factor which we shall discuss in this chapter.

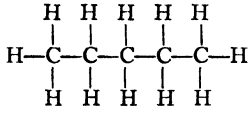
32. 4. Nomenclature. The systematic method of naming carbon compounds has been described in preceding chapters, and the rules already stated cover most of the types of compounds in which the beginner is interested. However, it is appropriate, at this point, to add a few rules of a summary nature.

In section 10.10, we defined what is meant by a functional group and stated that the name of this group appears in the main part of the name of a compound. Thus, for $CH_2Cl–CH_2OH$ we do not say hydroxyethyl chloride, but instead we say chloroethanol, because chlorine is regarded as the substituent in the molecule and the hydroxy group as the functional group.

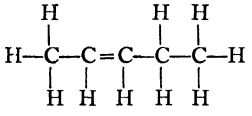
When there are several functional groups in the molecule, the "chief" function is selected for use in the main part of the name. A brief list of functional groups in the order of preference is: carboxy, aldehyde, ketone, alcohol, phenol, ether, etc. As an example,

CH_2OH-CH_2-COOH is 3-hydroxypropanoic acid, the acid function being the chief function with –OH as a lesser function, or substituent. The chain is numbered so as to give the chief function the smaller number.

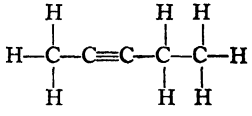
Theoretically, the simplest of the mixed compounds are the olefins and acetylenes which we studied in chapter 15. At that time, we showed how the chain of carbon atoms can be built up of C=C units and C≡C units as well as C–C bonds, to give three families of compounds of which the following are representative:



Pentane
A paraffin



2-Pentene
An olefin

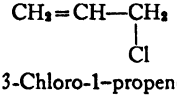


2-Pentyne
An acetylene

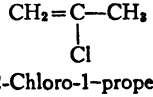
The olefins and acetylenes can be viewed as mixed compounds. The properties of the 2-pentene molecule, for example, are the simple sum of the properties of the *olefin* $-\overset{|}{C}=\overset{|}{C}-$ group as given in section 15.2, and of the *paraffin* grouping $-\overset{|}{C}-\overset{|}{C}-$ as listed in section 10.7.

In common practice, however, the unsaturated hydrocarbons are not considered to be mixed compounds. The C–C–C–C . . . chain is taken to be the fundamental structure in organic chemistry, and $-\overset{|}{C}=\overset{|}{C}-$ is looked on as the characteristic group in the olefins which gives them their family properties. The same is true of the $-C\equiv C-$ group in the acetylene family of hydrocarbons.

32. 5. Olefin-Halogen Compounds. A simple family of mixed compounds was mentioned in section 25.4. From that discussion, it will be apparent that compounds of the following structures,



3-Chloro-1-propene



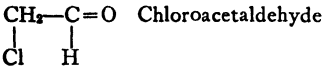
2-Chloro-1-propene

should have markedly different properties because of the different relative positions of the $-\overset{|}{C}=\overset{|}{C}-$ group and the Cl atom. When the chlorine atom is attached to the $-\overset{|}{C}=\overset{|}{C}-$ group it becomes inert and

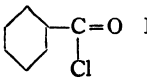
does not show the pronounced activity of the chlorine atom in the $-CH_2Cl$ group.

We see, then, that the properties of an organic grouping cannot be tabulated with any degree of exactness. In preceding chapters, we have endeavored to give the student a general idea of the nature of these groups, but the exact nature of the group depends on its relative position in the molecule with respect to other groups.

In this connection, another important instance should be recalled in which it was shown that the properties of a radical are dependent on the type of molecule in which it is present. In section 30.5*a* we explained that chlorination of an aliphatic aldehyde and of an aromatic aldehyde yields different products:



Chloroacetaldehyde

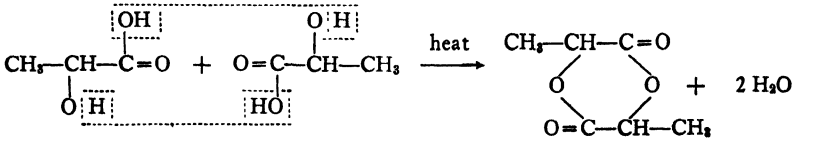


Benzoyl chloride

In the open-chain series, the Cl atom does not enter the aldehyde group but enters the chain. When attached to the nucleus, however, the $-CHO$ group is easily attacked by chlorine; therefore, benzoyl chloride is formed before substitution of H atoms in the ring takes place.

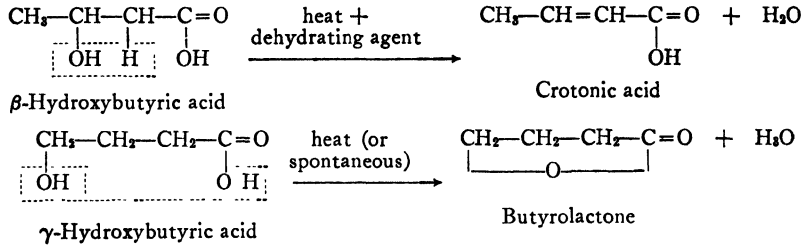
The chemistry of a group, therefore, depends in general on two things: the type of molecule in which it is present, and the relative positions of the other groups in the molecule.

32. 6. Alcohol-Acids. Molecules which are both alcohols and acids constitute a family of mixed compounds very often used for demonstration, because they lend themselves so readily to an explanation of this type of chemistry. The alcohol-acids, in general, show the usual properties of acids and of alcohols, but in addition, they behave in unusual ways, depending on the relative positions of the $-OH$ and $-COOH$ groups:



α-Hydroxypropionic acid
Lactic acid
(2 molecules)

Lactide

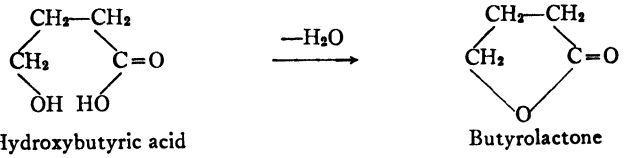


In section 31.8*b* we described the method of formation of an *ester*, from an acid and an alcohol. This should be reviewed by the student. From the formula of lactic acid it is clear that one molecule of the compound *acting as an acid* can react with another molecule of the same compound, *acting as an alcohol*, to form an ester. Heating lactic acid will produce this ester, which is known as *lactide*.

Other α-hydroxy acids behave like lactic acid to form esters of this closed-chain or ring type, which are known, in general, as the lactides. The theory of the ring compounds as described in section 12.6 should be reviewed in this connection. It will be recalled that rings containing four to six atoms are the easiest to form.

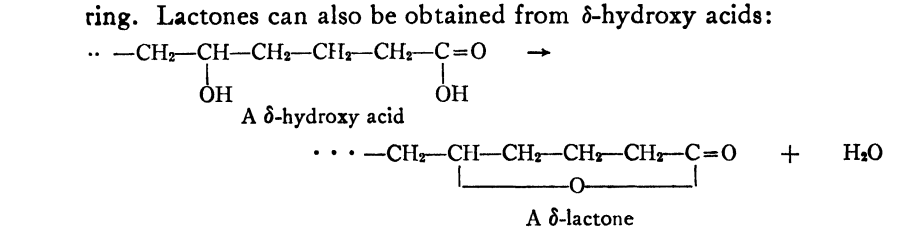
The β-hydroxy acids do not form esters when heated; instead, they lose water as shown in the preceding reactions, to form an olefin-acid. The student should notice that if the β-acid were to form an ester like that of the α-hydroxy acid, it would have to make an eight-membered ring, which is quite difficult.

The γ-hydroxy acids, when heated, form esters *within the same molecule*. If the formula of the γ-acid is written



it will be evident that the acid –COOH group and the alcoholic –OH group, by rotation about the C–C bonds, may come quite close to each other. We have, then, ideal conditions for the formation of what is known as an *inner ester*, or more commonly called a *lactone*. This is another ring structure, but it should be carefully observed that it is different from a lactide.

The lactone obtained from the γ-hydroxy acid is a five-membered ring. Lactones can also be obtained from δ-hydroxy acids:



A δ-hydroxy acid

A δ-lactone

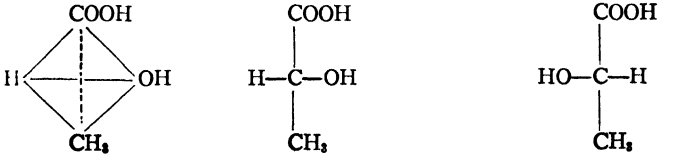
This lactone has a six-membered ring. The five-membered lactone ring is usually distinguished from the six-membered ring by calling one a γ-lactone, and the other a δ-lactone.

Lactones cannot be obtained easily from hydroxy acids in which the –OH group is more distant from the –COOH group than the δ-carbon atom.

The lactone ring is of great importance in the study of carbon compounds (section 36.1); ring compounds consisting of C atoms and O atoms are very common in nature.

32. 7. Some Important Alcohol-Acids. Table 32.1 lists the names and formulas of some other hydroxy acids that are important, but cannot be considered in detail in a book of this size and kind. In this table, those carbon atoms to which four different groups are attached and can, therefore, give the molecule optical activity are marked with an asterisk (*).

Lactic acid is found in sour milk (from fermentation of lactose, as mentioned in section 41.5), in sauerkraut, and in an extract of muscle tissue. It is optically active and can exist in D, L, and DL (that is, *racemic*) modifications. In aqueous solution, the D and L



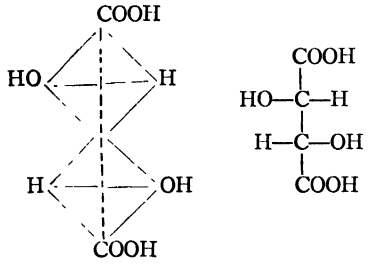
D (*levo*)-Lactic acid

L (*dextro*)-Lactic acid

forms rotate plane-polarized light in directions opposite to those of their family heads shown in figure 22.11. The type of projection formulas used here for the lactic acids should be reviewed in section 22.8*b*. It is of interest to observe that the *dextro*-lactic acid is pro-

duced in flesh by biological processes, whereas the *levo*-lactic acid is produced by bacterial action on milk sugar. The *dextro* compound, that is, L-lactic acid, is also known as *sarcolactic* acid, from the Greek word for flesh.

Tartaric acid has two asymmetric carbon atoms and, because of the symmetry of the molecule, can exist in a *meso* form as well as the D, L, and *racemic* modifications. The L form occurs in nature in various fruits, especially in the grape. The isomeric forms of tartaric



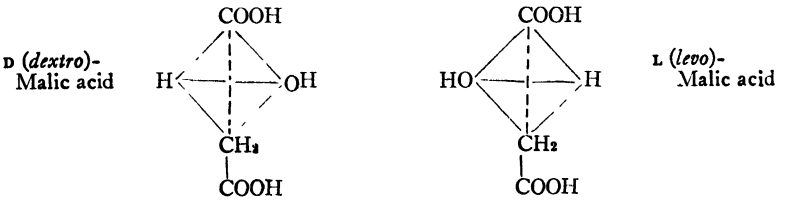
D (*levo*)-Tartaric acid

L (*dextro*)-Tartaric acid

meso-Tartaric acid

acid were discussed in section 22.12 and table 22.1, which should be reviewed. The projection formulas for tartaric acid should be compared with those for 2,3-butanediol in figure 22.13.

Malic acid is found in many fruits and plant products. It was first isolated from unripe apples (Latin *malum*, apple). The optically



active isomers possible are D and L modifications, with an optically inactive *racemic* mixture. The configuration of the D-compound has been proved to be the same as that of D-lactic acid, but the rotation is in the opposite direction. The L isomer, of course, is the mirror image of the D isomer, with OH to the left of the observer when the formula is *projected* in the conventional manner. The L compound is the one which occurs in nature. This isomer in dilute solution in water rotates polarized light to the left (*levo*), but the extent of

rotation decreases until, at a concentration of 34%, it changes to *dextro* and at higher concentrations it is increasingly *dextro*. Malic acid has been used as a reference compound to determine whether other optically active compounds are members of the D or L families (see section 22.8 and the Walden inversion in section 32.15).

Glyceric acid, the formula of which is in table 32.1, has been used as a reference compound for D and L families, as just described for malic acid. When the structure of D-glyceric acid is projected by the conventional procedure the OH on the asymmetric carbon atom will be on the right. The racemic compound (DL-glyceric acid) can be made by careful oxidation of glycerol. (See *glycerose* in section 39.1.)

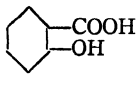
Saccharic acid can be obtained by oxidation of glucose, and its relation to this sugar will be discussed in section 39.9. It has four asymmetric carbon atoms; a comment on the calculation of the number of possible optical isomers will be found in section 39.4.

TABLE 32.1. COMMON NAMES OF SOME IMPORTANT HYDROXY ACIDS

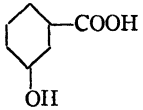
Carbonic acid (Hydroxyformic acid)	HO—COOH
Glycollic acid (Hydroxyacetic acid)	CH_2—COOH | OH
Lactic acid (α-Hydroxypropionic acid)	CH_3—*CH—COOH | OH
Hydracrylic acid (β-Hydroxypropionic acid)	CH_2—CH_2—COOH | OH
Glyceric acid	CH_2—*CH—COOH | | OH OH
Tartaric acid	HOOC—*CH—*CH—COOH | | OH OH
Malic acid	HOOC—CH_2—*CH—COOH | OH
Saccharic acid	HOOC—(*CHOH)$_4$—COOH OH
Citric acid	HOOC—CH_2—C—CH_2—COOH | COOH

Carbonic acid is listed in the table as the hydroxy derivative of formic acid. The solution called carbonic acid is really mostly a solution of carbon dioxide in water: $H_2CO_3 \rightleftarrows CO_2 + H_2O$. There are relatively few molecules of H_2CO_3 or HO–C(=O)–OH in such a solution because of its instability. The rule of instability of two –OH groups on the same carbon atom holds true in this case as in others which have been mentioned (section 27.4*c*).

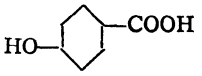
32. 8. Salicylic Acid. It is also of interest to examine a family of compounds in the benzene series:



o-Hydroxybenzoic acid (Salicylic acid)



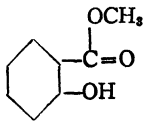
m-Hydroxybenzoic acid



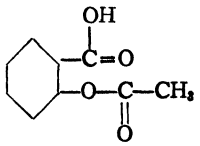
p-Hydroxybenzoic acid

Of these compounds the most important is the *ortho* compound, commonly known as salicylic acid. Salicylic acid can be separated from the other two isomers by boiling it with calcium chloride and ammonia, which precipitates only the *o*- compound as a calcium salt, $C_6H_4(-C(=O)-O-Ca-O)$. It is probable that the –COOH and –OH groups are too far apart in the other two compounds to be able to form such a salt. Salicylic acid is a phenol-acid. The H atoms in both the –COOH and –OH groups are, therefore, acidic, which explains why Ca can replace both these H atoms in salicylic acid.

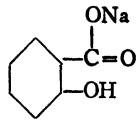
Salicylic acid is used in the preparation of many important substances, such as these:



Oil of wintergreen



Aspirin

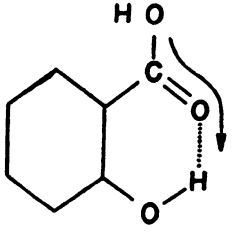


Sodium salicylate

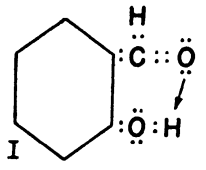
Oil of wintergreen is the methyl alcohol ester of salicylic acid; it is formed by reaction of the –COOH group of salicylic acid with

CH_3OH. Aspirin is the acetic acid ester of salicylic acid; it is formed by reaction of the –OH group of salicylic acid with CH_3–COOH. (Review the formation of esters in section 31.8*b*.)

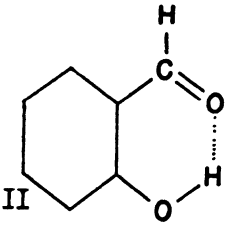
32. 9. Chelation. Salicylic acid, in which the –OH and –COOH groups are *ortho* to each other, is a much stronger acid than either the *meta* or *para* compounds in the same family. This is attributed to the formation of a hydrogen bond (section 31.12) as follows.



o-Hydroxybenzoic acid
Salicylic acid



I



II

o-Hydroxybenzaldehyde

The increased acidity of salicylic acid is due to a loosened potentia hydrogen ion in the carboxy group, caused by an electron displacement in the direction of the arrow, analogous to that described as an inductive effect in section 31.6.

Many *ortho* derivatives in the benzene series (another example of which is shown in structures I and II) have unusual properties as compared with the corresponding *m*- and *p*- compounds, and the cause is often the formation of the hydrogen bond, in which an unused pair of electrons is shared with the H atom. Structure II is the molecule of *o*-hydroxybenzaldehyde as it may ordinarily be pictured; structure I indicates the electronic configuration which makes the formation of the hydrogen bond more apparent. The –OH group in this compound is not as active as in the *m*- and *p*- compounds because of the smothering effect of the hydrogen bond.

Ring structures of the type shown here, in which a bond is formed by the sharing of an unemployed electron pair, are called chelate rings and the process of ring formation, which will be further described in section 32.12, is called *chelation*. The examples described here are stable six-membered rings.

32. 10. Steric Hindrance. In the preceding section, we observed that a ring structure with groups *ortho* to each other often has

unusual properties due to interaction of the groups. This is one more illustration of the effect of the space relationships of groups on their activity. We have shown how a double bond in a molecule can produce *cis* or *trans* isomers with different properties (section 22.3). We also showed how the different space arrangements of the same four groups around a carbon atom can produce *dextro* and *levo* isomers (section 22.8). These are a few of many examples of the great importance of space relations of the various parts of molecules.

A type of molecule which has interested many research chemists is that in which the steric effect is one of hindrance, that is, where certain groups in the molecule interfere with each other due to space limitations. An interesting phenomenon believed to be due to steric hindrance is the fact that two stereoisomeric forms of certain compounds of the structures shown in figure 32.2 can be prepared. These are diphenyl derivatives (section 25.4), containing two different atoms or groups represented by A and B in *ortho* positions in the molecule. Molecules of this type can be obtained in one form which is right-handed and another form which is left-handed toward plane-polarized light. These are good illustrations of substances that are optically active, yet have no asymmetric carbon atoms in the molecule, of the type described in section 22.14. The molecule is asymmetric because A and B prevent free rotation of the two rings, and these rings can therefore be "frozen" into definite positions as indicated by figure 32.2.

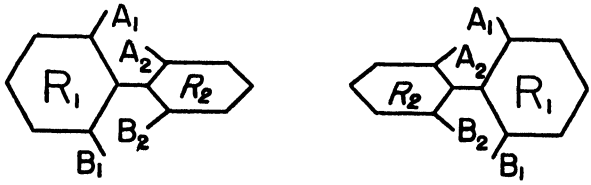


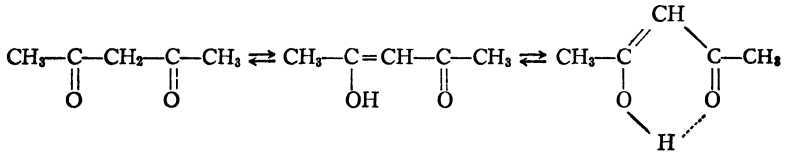
FIGURE 32.2. Mirror-image isomerism due to steric hindrance.

These two modifications are mirror images, and cannot be superimposed on each other. The R_2 ring should be imagined as horizontal, with the R_1 ring vertical; a little study will then show that in the R_2 ring, A_2 can be either on the left or the right with respect to R_1. Much depends on the size of A and B. If they are small,

like the fluorine atom, they do not prevent free rotation of the rings and two isomeric forms are then not possible. At least three of the four A and B positions must be occupied in order to produce stereoisomeric forms.

32. 11. Tautomerism. It has not been our aim in this chapter to give a summary of mixed compounds, because detailed information can be obtained from the larger books on organic chemistry. We have selected a few types of mixed compounds which show in a forceful way that when two or more characteristic groups are present in a molecule the organic chemist must beware of unusual properties. These unusual properties are generally due to the relative positions of the groups in the molecule.

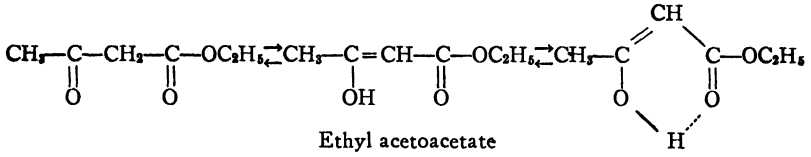
We shall now describe compounds which behave as if more functional groups were present in the molecule than can be accounted for by a single formula. The phenomenon will be illustrated with *acetylacetone*, one of the family of diketones, which behaves like an olefin-alcohol as well as a ketone in accordance with these two structures:



Acetylacetone (Keto form) | Acetylacetone (Enol form) | Acetylacetone (Cyclic enol form)

The word *enol* is coined from *ene*, meaning a compound with the C=C structure, and *ol* for the alcohol group, –OH. The phenomenon of the same compound acting in two different ways is called tautomerism (Greek *tauto*, the same). The extent to which each of these tautomers is present will depend on the solvent. In water solution at ordinary temperatures, the equilibrium composition is 20 per cent *enol* and this is probably in the cyclic form as a result of hydrogen bonding (see sections 32.9 and 32.12).

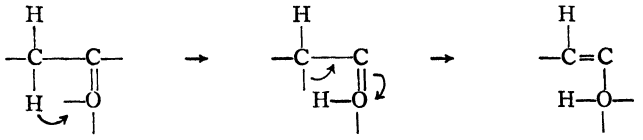
In the case of *ethyl acetoacetate*, the ethyl ester of acetoacetic acid, both the *keto* and *enol* forms have been isolated, but they are unstable when alone and in a relatively short time they revert to an equi-



Ethyl acetoacetate

librium mixture. Tautomeric forms which can be isolated are known as *desmotropes*, but this term is not used much in modern chemistry. Ethyl acetoacetate will be discussed further in section 32.11*a*.

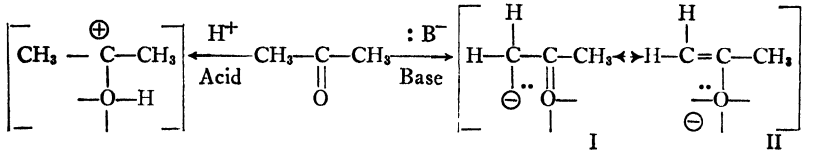
The requirement for *enolization* is that C–H must be *adjacent* to a C=O group. This makes the compound acidic, that is, ionizable. The hydrogen can leave the molecule or migrate to another position in the form of a hydrogen ion (H^+), which is, of course, a proton. The transfer of positive charge (which on paper appears to be the movement of a hydrogen atom) can be illustrated by the following scheme, in which the unshared valence bonds are represented by the procedure used in section 17.3:



Enolization is an example of proton transfer, or *prototropy* (Greek *tropē*, a turning).

Keto and enol structures can be written for acetone, $CH_3{-}\underset{\underset{O}{\|}}{C}{-}CH_3$ and $CH_2{=}\underset{\underset{HO}{|}}{C}{-}CH_3$, the simplest of the ketones, but the enol form cannot be present in more than trace amounts. The two compounds previously described contain a $-CH_2-$ group between two C=O groups; this makes the H atoms more acidic than those in acetone and promotes formation of the enol. Furthermore, the enol structures which are developed from those compounds are stabilized by hydrogen-bonding in the form of six-membered rings.

It is of interest to re-examine the electron structure of acetone which was presented in section 30.5, and to postulate how the molecule will behave in solvents which are made acidic or basic.

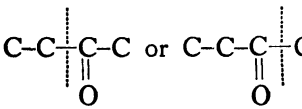


Positive ion Acetone Resonance of the negative ion

An acid represses the tendency of the molecule to lose protons; instead, H^+ ions are added to the molecule. A base facilitates the ionization by removing a proton; the resulting negative ion is a resonance hybrid which shows both *keto* (I) and *enol* (II) structural characteristics. This ease of ionization in bases supplies the reason for the *exchange* process which will be described in section 45.4.

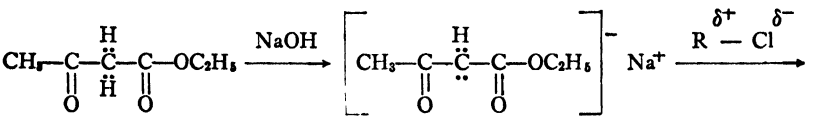
Metallic sodium displaces a hydrogen atom in acetone with formation of a salt $Na^+[CH_2COCH_3]^-$ in which the negative ion is the resonance hybrid shown in the preceding paragraph. Salts of this type will generally be found written with the metal replacing H in the OH group of the enol structure (see section 32.12). Although sodium metal is often used to dry organic solvents (by reacting with the water present), it cannot be employed to dry acetone, a fact which many chemistry students learn from unfortunate experience.

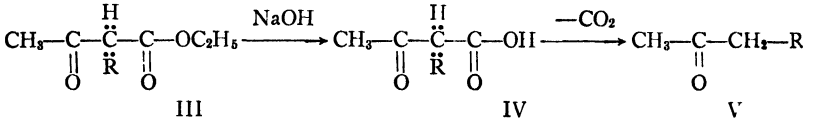
When ketones are oxidized they break at the carbonyl group, thus,



able that in the course of oxidation the *enol* adds two OH groups across the C=C group and then breaks (section 15.3).

32. 11a. Acetoacetic Ester Synthesis. Although in this book we do not stress the laboratory procedures of organic chemistry, it is of interest to follow the outline of a typical synthesis involving the ethyl ester of acetoacetic acid.



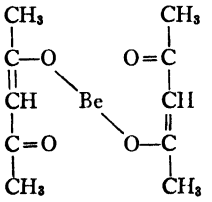


III IV V

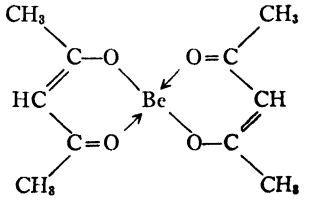
The H atoms in the $-CH_2-$ group of I are mobile and "acidic." In II, one of the wandering H^+ ions from the $-CH_2-$ group has been replaced by Na^+ ion to yield a salt. When this salt solution is treated with an alkyl halide (such as the polar CH_3-Cl molecule), the alkyl radical forms a C–C union with the ester (III). This is synthesis as defined in section 10.2. The Na^+ and Cl^- also become partners. Now the ester is hydrolyzed by means of a weak NaOH solution to IV, to free the carboxy group, which can then be decarboxylated (section 31.13) to produce V.

Since R in this outline can be any one of a large number of organic radicals, it is obvious that this synthesis is a useful step in the development of a wide variety of compounds. The ketone in V can be reacted in many ways as described in chapter 30. Both of the H atoms in the methylene group of acetoacetic ester can be replaced by R groups by the procedure illustrated. Synthesis with malonic ester (section 31.13) is similar to that outlined in this section.

32. 12. Chelate Rings. The properties of the metal derivatives of acetylacetone (section 32.11), because they do not behave like salts, puzzled chemists for a long time, but their structure and behavior were clarified by the electron-valence theory. In structure I is shown the customary formula of the beryllium compound, in which the divalent beryllium atom exercises its normal ionic valence of two (see figure 6.1). It can fill up its octet, however, by accepting



I



II

two pairs of electrons from neighboring oxygen atoms by formation of two dative bonds (section 8.5), as shown in structure II. This is

facilitated by the fact that a six-membered ring is formed, which is generally almost free from strain.

Ring structures of this type, in which a metallic compound with at least one ionic valence bond gives ring closure through dative bonds, are called *chelate* rings. This term is derived from the Greek (*chēlē*, claw) implying the action of a crab's claw, or forceps, and is pronounced *keelate*. The term is (perhaps unfortunately) also employed to describe other types of ring structures, such as those in which hydrogen bonding causes ring closure (section 32.9). The ring structure of the *enol* tautomer of ethyl acetoacetate in section 32.11 is an example of hydrogen bonding rather than true chelation. The use and formation of chelate compounds is being widely exploited in analytical identification, commercial cleansing agents, dye chemistry, pharmacology, etc. Compounds like the beryllium derivative of acetylacetone are soluble in organic solvents and usually can be melted and distilled without difficulty.

32. 13. Co-ordination Number. The Be atom discussed in the preceding section has a principal valence of two as indicated by the two electrons in its valence shell in figure 6.1. Its normal tendency is to acquire stability by losing two electrons and forming two electrovalence bonds in the formation of salts, such as beryllium chloride, $BeCl_2$ (i.e., $Cl^-Be^{++}Cl^-$). As we have just seen, it can also form two covalent bonds by the sharing of electrons.

In addition to its principal valence of two, beryllium is said to have a co-ordination valence of four. This is also called co-ordination number and is defined as the maximum valence an element can show in any of its compounds. In the case of the beryllium compound, the co-ordination number of four was reached by accepting pairs of electrons from other atoms. These two added bonds are usually called dative bonds in this book, but they are also known as co-ordination bonds (section 8.5). The meaning of the term co-ordination number as applied to valence is different from that given in section 8.1 in the discussion of crystal structure.

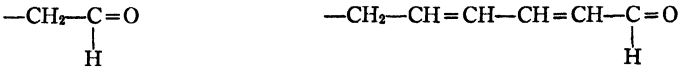
32. 14. Vinylogy. The tautomeric behavior of acetone shown in section 32.11 probably has its counterpart in acetaldehyde. It was indicated when discussing the manufacture of acetic acid (section 31.9) that the intermediate product in the oxidation of acetylene probably has the structure of an *enol*,

Vinyl alcohol (Nonexistent) Acetaldehyde

which is unstable and rearranges practically irreversibly to acetaldehyde (which may be regarded as the *keto* form). The compound that would be called vinyl alcohol does not exist, although more complex open-chain compounds are known, such as Vitamin C (section 44.4), which contain the C=C–OH linkage.

In this book, we have repeatedly shown how the C=C bond acts as a path by which an electron can move through a molecule in such a way that the electron density is simultaneously decreased and increased at two points distant from each other. There is a corresponding alteration in chemical reactivity at those points (figure 21.1 and sections 17.3 and 17.4). This phenomenon depends on the presence of a conjugated system of single and double bonds. In section 28.2, the acidity of phenol was ascribed to such a relay action; this should be reviewed. In vinyl alcohol, a corresponding acidity effect cannot be determined because the compound is unstable. The student should especially review the discussions under vinyl chloride and chlorobenzene in section 25.4 (and in section 32.5).

The relay effect of the C=C group is particularly noticeable when it is present in aldehydes in a conjugate system. In section 30.5*a*, we found that the *alpha* carbon atom in an aldehyde is especially susceptible to attack. This is the C atom next to the –CHO group. For example, the H atoms on the *alpha* carbon are easily replaced by chlorine and in section 30.5*d* it was shown that *condensation* reactions take place readily on the *alpha* carbon. In other words, there is an interaction between $-CH_2-$ and –CHO which makes the $-CH_2-$ reactive. When these groups are separated by one or more –CH=CH– groups



the $-CH_2-$ still retains its characteristic activity. This relay effect is known as *vinylogy*.

32. 15. The Walden Inversion. The classification of optically active compounds in Dee and Ell *configurational* series (section 22.8) is based on whether certain functional groups are on the right or left of an asymmetric carbon atom when the formula is "observed" according to a standard procedure. It will be recalled that the rotational direction of a compound is independent of its Dee or Ell configurational family. In 1893, Walden discovered that by certain reactions it is possible to change a Dee compound into its Ell isomer, and *vice versa*. Because of its historical interest a complete *Walden cycle* is shown in figure 32.3, where the asymmetric carbon atoms are labeled C*.

From figure 32.3., it is apparent that we can start with any one compound in the cycle and by a series of reactions reach its mirror image. Reversals in direction of rotation occur between I and II

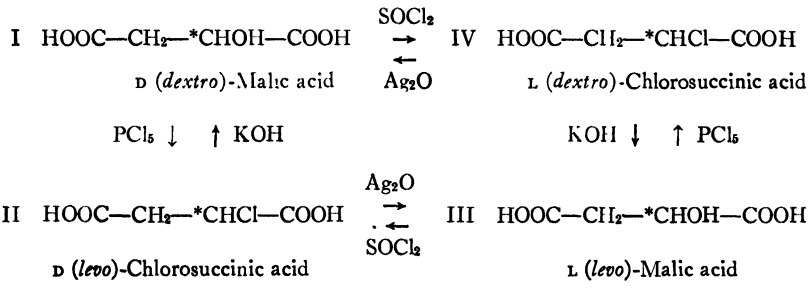


FIGURE 32.3. A Walden inversion cycle.

and between III and IV. These changes have been proved by experiment. It is not so certain that inversions between D and L families occur between I and IV and between II and III, as shown, because it is not yet agreed that *dextro*-chlorosuccinic acid is an L compound. If it is really D, then family inversions take place in this cycle simultaneously with reversals in optical rotation.

The explanation for the inversion steps in this cycle was given in section 22.16, where it was shown to be the result of a *displacement* reaction in which the entering group in an asymmetric molecule takes a position opposite to that of the group it displaces. The reaction is *bimolecular*, taking place through an intermediate transition stage diagrammed in figure 22.24.

Those steps in the cycle in which inversion does not occur are probably *unimolecular*, as shown in figure 22.25; the reagents, reac-

tion conditions, and solvents must operate in such a way as to cause the entering group to occupy the same position in the molecule as was occupied by the displaced group. In other words, the racemization shown in figure 22.25 can be prevented by certain combinations of reagents and conditions. This is known as retention of configuration, as contrasted with inversion.

32. 16. Molecular Rearrangements. We have found in this chapter that the several functional groups in a molecule often interact with each other chemically (section 32.6) or physically (section 32.10); and that in certain molecules the ease of motion of a proton gives rise to a tautomerism (section 32.11) which is equiva-

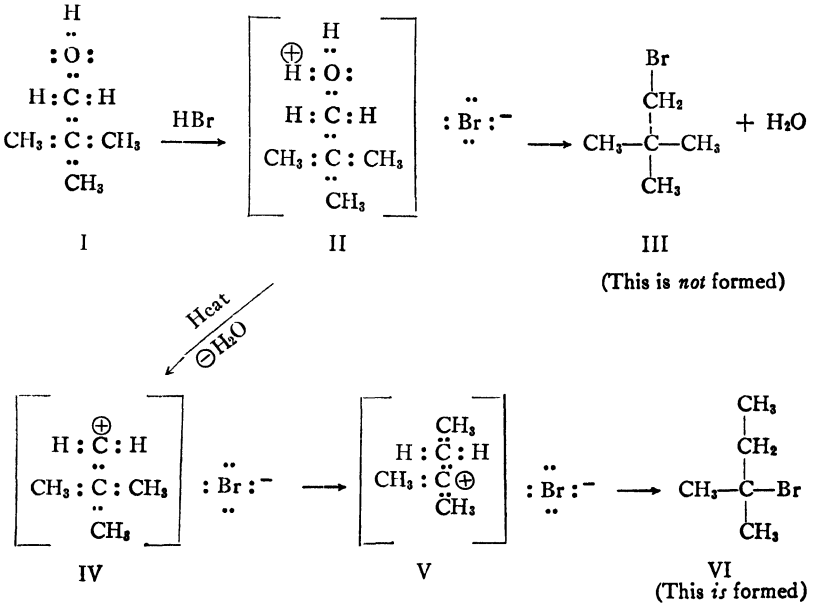


FIGURE 32.4. A molecular rearrangement according to the Whitmore theory.
I. Neopentyl alcohol, or 2,2-dimethyl-1-propanol
III. Neopentyl bromide, or 2,2-dimethyl-1-bromopropane
VI. *tert*-Amyl bromide, or 2-methyl-2-bromobutane

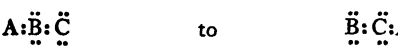
lent to rapid oscillation of the molecule from one structure to another. In this section, we shall refer to structural effects which lead to actual migration of a group from one position in the molecule to another position in which it is more stable.

In section 30.5*e* we described the formation of an oxime as taking place in two steps: a simple addition compound which is first formed is unstable and then breaks down by elimination of a molecule of water. The formation of an unstable intermediate is, in fact, the mechanism by which most reactions take place. In some reactions, these intermediate compounds are sufficiently stable to be isolated and identified (section 27.3).

Our object at this point is to call attention to rearrangements that sometimes take place and that result in products of a wholly unexpected nature. This is illustrated by the reactions in figure 32.4 which indicate how compound I, which, according to preconceived notions should give III, results in compound VI.

Reaction product III would be expected on the basis of the discussion in section 27.3, relating to the replacement of –OH groups by halogen atoms, where it was shown that an oxonium salt, such as II, is the usual unstable intermediate. The oxonium ion of compound II eliminates water as explained in section 27.3 and yields the ion shown in IV. This ion, however, does not add the Br^- ion to give III. Instead, the ion in IV rearranges to V; a methyl radical, *with its electron pair*, moves to the terminal carbon atom to complete its octet. This still leaves a carbon atom with only a sextet, which means the fragment is still an ion with a single positive charge as shown in compound V. Capture of the Br^- ion then takes place to give VI.

The literature of organic chemistry is full of rearrangement reactions, many of which took years to explain. The student will find it of interest to read further in the larger texts on these problems. The electron conception of valence has been very useful in clearing up these difficulties, largely due to the studies of Whitmore, who found that many rearrangements can be represented by the transformation.



(a) (b)

In these structures B and C are atoms, but A may be either a single atom or a large radical. If structure (a) is formed during a reaction it will probably be unstable because it has only six electrons on

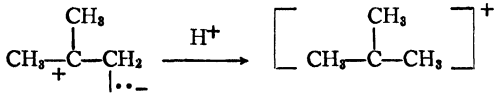
atom C. The radical A then migrates, *with its electron pair*, to atom C to give a more stable (but not necessarily a completely stable) structure. This is illustrated in figure 32.4 by the rearrangement from IV to V, where the ion in V is more stable than that in IV. The reader should review the discussion of *carbonium* ions in section 24.5.

32.17. Alkylate. In the modern petroleum industry, gasolines of high antiknock quality (section 10.8) are made by alkylation of olefin type hydrocarbons. The product is frequently called *alkylate*. The reactions are complex, but have been considerably clarified by the rearrangement interpretation described in the preceding section and by simple assumptions as to the behavior of carbonium ions (section 24.5).

One of the important alkylation reactions is usually written

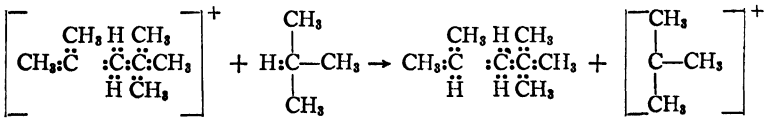
$$\underset{\text{Isobutene}}{(CH_3)_2C{=}CH_2} + \underset{\text{Isobutane}}{HC(CH_3)_3} \longrightarrow \underset{\text{Isooctane (section 10.8)}}{(CH_3)_2CH{-}CH_2{-}C(CH_3)_3}$$

which looks like a simple addition across the double bond, but it is actually not so simple. The reaction is catalyzed by concentrated sulphuric acid, which maintains a constant supply of the *tert*-butyl ion:



Isobutene *tert*-Butyl ion

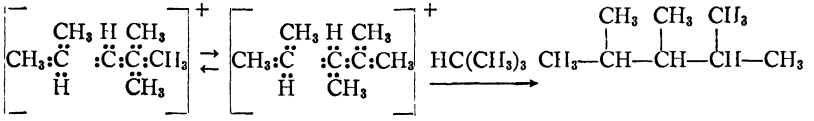
These two substances react with each other to form a more complex ion VII. This ion decomposes a molecule of isobutane by withdrawing an H: unit (the atom and its electron pair); the product is isooctane,



VII Isobutane Isooctane 2,2,4-Trimethylpentane *tert*-Butyl ion

but the by-product is the *tert*-butyl ion, which is made available to react with more isobutene as described before. Complex ion VII

rearranges twice; first an H: unit migrates to give VIII and then a methyl group moves to yield IX. The complex ion IX now extracts



VIII IX 2,3,4-Trimethylpentane

an H: unit from a molecule of isobutane, by the same procedure as shown before for the complex ion VII, and another octane is obtained. It is obvious that other reactions should also take place, and they do, but the principal products are the two octanes.

SUGGESTED READING

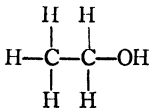
Whitmore, F. C., "Alkylation and Related Processes of Modern Petroleum Practice," *Chem. Eng. News*, **26**, 668-674 (1948).

33. NITROGEN COMPOUNDS

33. 1. Introduction. Up to this point, we have devoted our attention mostly to families of oxygen compounds, that is, carbon compounds in which there is a C–O linkage. This was reviewed in the last chapter, and the student should once more consult figure 32.1 to refresh his memory as to the way the various families of chain and ring compounds are related to each other.

In this chapter we shall consider briefly the organic chemistry of nitrogen, that is, compounds which are characterized by the presence of the C–N bond.

33. 2. Amines. In chapter 27 we showed how the family of alcohols can be looked at in two ways:

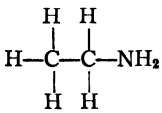


An OH group replacing an H atom in a hydrocarbon

C_2H_5—OH

An alkyl radical replacing an H atom in water, H—O—H

Similarly, amines can be regarded either as derived from an *organic* hydrocarbon, or as derivatives of the *inorganic* substance, ammonia:



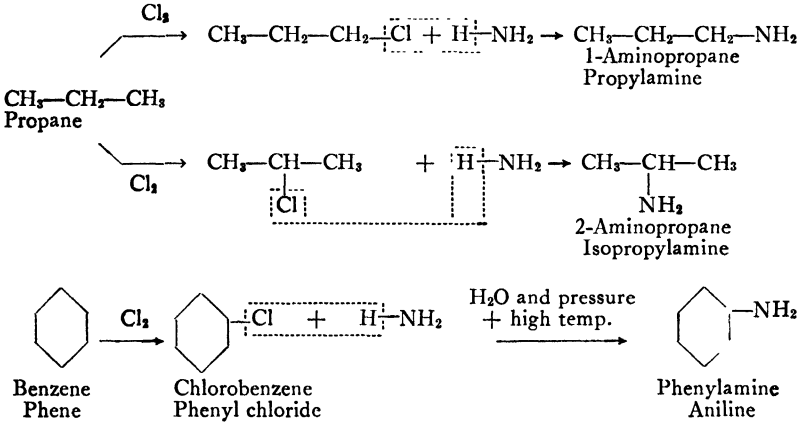
An —NH_2 group replacing an H atom in a hydrocarbon

C_2H_5—NH_2

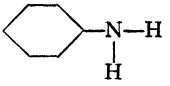
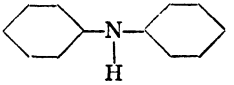
An alkyl radical replacing an H atom in ammonia, NH_3 or H—NH_2

The nature of the amines can readily be understood from the following reactions which show how amines can be prepared from familiar hydrocarbons. The $-NH_2$ group is called the *amino* group.

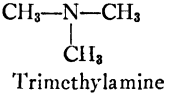
The process is the familiar one of first introducing a reactive halogen atom into the compound and then causing it to react with a substance containing the group in which we are interested:



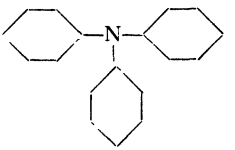
Throughout this book, we have endeavored to show how the various families of compounds can be obtained by such methods as these, that is, by means of simple variations of carbon chains and carbon rings. In the case of amines, however, it is better to pay less attention to the carbon chains and rings, and to regard the amines as derivatives of the *inorganic* part of the molecule. There are three H atoms in ammonia, and all three can be replaced by open-chain or cyclic radicals. Thus, we have

	Aliphatic compounds	*Aromatic compounds*
Primary amines: $R—NH_2$ or $Ar—NH_2$	$CH_3—N(H)—H$	
	Methylamine	Phenylamine or, Aniline
Secondary amines: R_2NH or Ar_2NH	$CH_3—N(H)—CH_3$	
	Dimethylamine	Diphenylamine

Tertiary amines: R_3N or Ar_3N

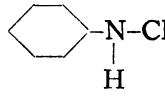


Trimethylamine



Triphenylamine

It is important to notice that this classification of amines as primary, secondary, and tertiary is different from that used in sections 26.1 and 27.3 for alcohols and related carbon compounds. To illustrate this difference, we have intentionally given the structure of 2-aminopropane. It is a *primary amine* because only one radical is attached to the nitrogen atom; it is a *secondary carbon compound*, because that carbon atom attached to the $-NH_2$ group is also attached to two other carbon atoms.

Mixed amines are possible, in which several different radicals are attached to the N atom, as in methylphenylamine,  .

This is also known as N-methylaniline; the prefix N- indicates that the $-CH_3$ group is on the nitrogen atom and not in the ring.

33. 3. Properties of Amines. The aliphatic amines listed in the preceding table occur in herring brine and have a characteristic fishy as well as ammoniacal odor. All three amines are gases, very soluble in water, but the higher open-chain amines are liquids insoluble in water, and are practically odorless.

The aromatic amines are liquids or solids, and usually have characteristic but not fishy odors.

The properties of amines are in many respects similar to the properties of ammonia, and we must, therefore, recall the essential nature of this inorganic substance. Ammonia, NH_3, is a gas lighter than air, easily liquefied and sold commercially in cylinders as liquid ammonia. It is very soluble in water, and its chemical properties can be explained by assuming the following equilibria to exist in solution:

$$\underset{\text{Ammonia}}{NH_3} + H_2O \rightleftarrows \underset{\substack{\text{Ammonium}\\\text{hydroxide}}}{NH_4OH} \rightleftarrows \underset{\substack{\text{Ammonium}\\\text{ion}}}{NH_4^+} + \underset{\substack{\text{hydroxyl}\\\text{ion}}}{OH^-}$$

This solution is the familiar ammonium hydroxide, used when a weak alkali is required.

Perhaps it would be more accurate to call this solution ammonia water, because there are relatively few NH_4OH molecules in solution, most of the dissolved ammonia remaining as NH_3 molecules. In the words of the physical chemist, the dissociation of NH_4OH into molecular NH_3 is more pronounced than the dissociation of NH_4OH into NH_4^+ ions.

The amines, when soluble in water, behave like ammonia:

$$\underset{\text{Methylamine}}{CH_3NH_2} + H_2O \rightleftarrows \underset{\substack{\text{Methylammonium}\\\text{hydroxide}}}{CH_3NH_3OH} \rightleftarrows \underset{\substack{\text{Methylammonium}\\\text{ion}}}{CH_3NH_3^+} + \underset{\substack{\text{Hydroxyl}\\\text{ion}}}{OH^-}$$

The solutions of aliphatic amines, like CH_3NH_2, are more basic than ammonium hydroxide, but solutions of aromatic amines, such as phenylamine, C_6H_5–NH_2, are less basic.

33. 4. The Valence of Nitrogen. Probably the simplest way to explain the chemistry of the amines and of the ammonium compounds is to picture their electronic structures.

The nitrogen atom ($\cdot\ddot{N}\cdot$) has five valence electrons, and the hydrogen atom ($H\cdot$) has only one as shown in section 7.2. The combination of these two elements in ammonia is presumably as follows:

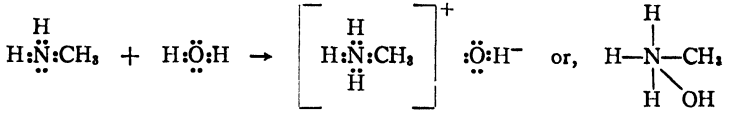
$$3\,H\cdot + \cdot\ddot{N}\cdot \rightarrow H{:}\ddot{N}{:}H \quad (H \text{ above and below } N)$$

In ammonia, there is a potential valence bond left unused on the N atom and the ease with which ammonia forms ammonium compounds is due to this lone pair of electrons. In the formation of an ammonium compound addition takes place to the lone electron pair, as in the following reaction which shows what happens when ammonia is dissolved in water:

$$\underset{\text{Ammonia}}{H{:}\ddot{N}{:}H} + \underset{\text{Water}}{H{:}\ddot{O}{:}H} \rightarrow \underset{\text{Ammonium hydroxide}}{\left[H{:}\ddot{N}{:}H\ (H)\right]^+ {:}\ddot{O}{:}H^-} \quad \text{or,} \quad \underset{\text{(Ordinary formula)}}{H{-}N(H)(H){-}OH}$$

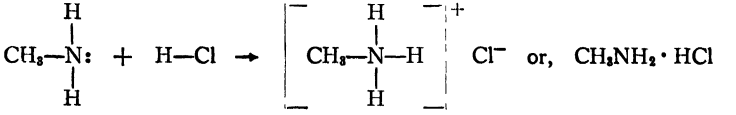
The H^+ ion of the water molecule adds to the electron pair of the N atom, and the NH_3 molecule becomes an NH_4^+ ion with a positive charge of one. In the "ordinary formula" of NH_4OH, it appears that the nitrogen atom has a valence of five. In the electronic formula, it is evident that the fifth valence can only be used by a negative ion, like OH^- or Cl^-, in an electrovalence bond.

The amines form similar hydroxy compounds with basic properties:

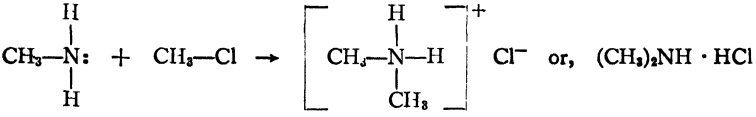


Methylamine — Methylammonium hydroxide

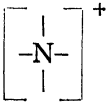
Because of their basic properties, ammonia and amines yield salts quite easily. These salts can be prepared by the addition of either an *acid* or an *alkyl halide*:



(An acid) — Methylammonium chloride — Methylamine hydrochloride



(An alkyl halide) — Dimethylammonium chloride — Dimethylamine hydrochloride

These "substituted" ammonium salts are represented by the general formula  in which the four valences in the bracket usually occupied by hydrogen atoms, as in NH_4Cl, are now taken up by *one or more* hydrocarbon radicals. Aliphatic radicals, like $-CH_3$, produce more stable salts than the original ammonium salts; aromatic radicals, like the phenyl group, result in less stable salts. Triphenylamine, $(C_6H_5)_3N$, for example, is so weak as a base that it does not add acids to form salts.

It should be observed that the salts derived from amines are sometimes named as "double compounds," as illustrated by the hydrochlorides in the equations given previously.

33. 5. Quaternary Ammonium Compounds. By the use of methods based principally on the preceding reactions, it is possible to prepare an entire series of amines and substituted ammonium compounds in which one or all of the hydrogen atoms of NH_3 or of the NH_4^+ ion are replaced by radicals:

$$\begin{array}{llll} NH_3 & + & H_2O & \rightleftarrows & NH_4OH \\ RNH_2 & + & H_2O & \rightleftarrows & RNH_3OH \\ R_2NH & + & H_2O & \rightleftarrows & R_2NH_2OH \\ R_3N & + & H_2O & \rightleftarrows & R_3NHOH \end{array}$$

$$R_3N + R{-}Cl \rightarrow R_4N{-}Cl \xrightarrow{Ag{-}OH} R_4NOH$$

For the series containing $-CH_3$ groups, the relative basic strength of the hydroxy derivatives is shown in table 33.1. These values should be compared with the corresponding ionization constants of organic acids in table 31.4.

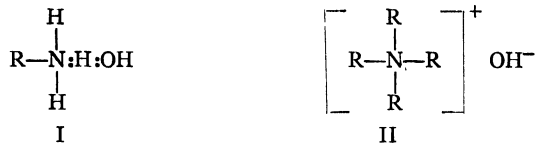
These constants are for the *electrolytic* dissociation, such as $NH_4OH \rightleftarrows NH_4^+ + OH^-$, measured under conditions in which the interfering *molecular* dissociation, $NH_4OH \rightleftarrows NH_3 + H_2O$, mentioned in section 33.3, has presumably been eliminated.

It will be observed that all these bases are weak, except the compound $(CH_3)_4NOH$. Compounds of this type, in which all four hydrogen atoms of the NH_4^+ ion have been replaced by radicals, are known as "*quaternary* ammonium compounds," from the Latin word, *quaternarius*, meaning a group of four.

TABLE 33.1. IONIZATION CONSTANTS (AT 25° C.)

Ammonium hydroxide NH_4OH	0.000 018
Methylammonium hydroxide CH_3NH_3OH	0.000 5
Dimethylammonium hydroxide $(CH_3)_2NH_2OH$	0.000 52
Trimethylammonium hydroxide $(CH_3)_3NHOH$	0.000 074
Tetramethylammonium hydroxide $(CH_3)_4NOH$	about 1.0
Anilinium hydroxide	0.000 000 000 46

The strongly basic character of quaternary ammonium hydroxides is explained by the absence of a hydrogen bridge, thus permitting formation of an ionic compound. If the following structures are compared:

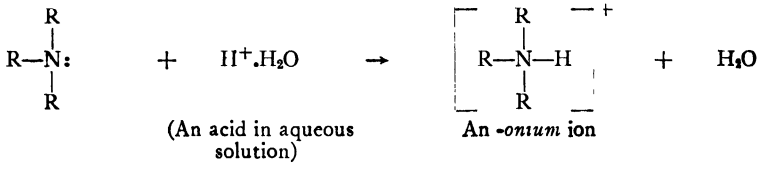


I II

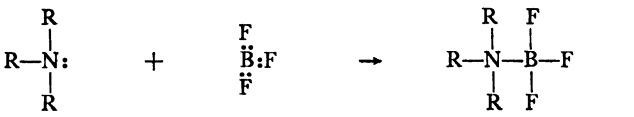
it will be seen that in I, it is possible for the proton of an H atom to act as a bridge between pairs of electrons on the highly electronegative elements, oxygen and nitrogen. This phenomenon was described in section 27.7. This accounts for the low extent of ionic dissociation of structure I as compared with II which does not have this hydrogen bond.

Since the quaternary ammonium compounds cannot dissociate in any way but the electrolytic way, the quaternary ammonium hydroxides, like tetramethylammonium hydroxide, $[(CH_3)_4N]^+ OH^-$, are very strong bases; they dissociate in solution to practically the same extent as sodium hydroxide, $Na^+ OH^-$. Moreover, these hydroxides are hygroscopic solids, similar in appearance to the strong inorganic bases. Analogous arsenic compounds (section 34.8), and phosphorus compounds (section 34.7) have been prepared, and all substances of this general nature are referred to as the *-onium compounds.*

33. 6. Basicity of Amines. In section 31.7, we referred to the electron theory of acids and bases, according to which a base is a substance willing to *donate* an electron pair and an acid is a substance willing to *accept* an electron pair. The basic properties of ammonia and of the amines are illustrated by these two reactions:



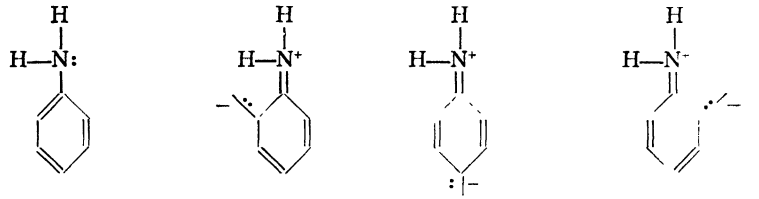
(An acid in aqueous solution) An *-onium* ion



Boron trifluoride (An electron-deficient molecule) A "double compound"

The relative basicity of the amines shown in table 33.1 refers to the relative tendency of the lone electron pair on the N atom to be shared. An aliphatic amine such as CH_3NH_2 is a stronger base than NH_3 because of the electron displacement C $+\!\!\rightarrow$ N. The CH_3 group tends to release electrons (section 21.7); this increases the tendency of electrons to pile up at the N atom, and consequently enhances the ability of the free electron pair to attract a positively charged particle (such as H^+) or an electron-deficient molecule (such as BF_3).

An aromatic amine such as aniline is a weaker base than ammonia. This is due to resonance possibilities, as a result of which the average



Resonance structures of aniline

state of the molecule is one in which the free electron pair is transferred from the N atom into the ring. Substitution reactions at *ortho* and *para* positions in the ring are facilitated (section 21.5), but the electron pair is less available for reactions involving the N atom, and the negative charge on the N atom can be said to be decreased. In other words, the basic tendency of aniline should be much lower than that of NH_3, and this is borne out by the ionization constant given in table 33.1 for aniline (more strictly the constant of anilinium hydroxide).

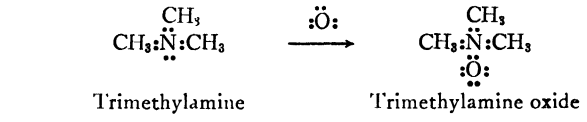
When reactions are carried out with aniline in acid solution, anilinium salts, such as $C_6H_5NH_3^+\,Cl^-$, are formed. Since the anilinium ion does not have the resonance possibilities shown for the free base, there is no transfer of electrons into the ring. Substitution reactions, therefore, do not take place *ortho* and *para* in acid solution, but practically entirely *meta*, and are slower.

Since CH_3NH_2 is more basic than NH_3, one should expect increasing basicity with a larger number of alkyl radicals on the nitrogen. From table 33.1, however, it is seen that $(CH_3)_3N$ is a weaker base than CH_3NH_2. This is now thought to be due to steric hindrance (section 32.10), which can be understood by referring to the structure of the NH_3 molecule in figure 8.6. When there are three CH_3

radicals, instead of small H atoms, on the N atom, the bond angle C–N–C is expanded in order to take care of their mutual repulsion and space requirements. If a fourth group should "sit down" on the free electron pair (see figure 8.6) it will be resented by the three groups already present at the back of the molecule; they would necessarily have to draw closer, approaching the normal bond angle shown in figure 8.6. The tertiary amines, therefore, show less tendency to share the electron pair and their basicity is, consequently, lower than that of primary amines. The steric effect is the more pronounced the larger the alkyl radicals in the tertiary amine.

This steric-hindrance effect at the back of a molecule has been labeled back-strain or *B-strain*, as contrasted with the front-strain or *F-strain* which is the usual concept in steric chemistry. Similarly, internal steric effects which alter the chemical activity of carbon compounds have been termed *I-strain*. An example of *I*-strain is seen in figure 12.16, where the ring structure is internally strained due to mutual carbon-hydrogen repulsions. A further example of *B*-strain is to be found in section 26.1; the readiness with which *tert*-butyl chloride ionizes and hydrolyzes is ascribed to *B*-strain and to the electron-inductive effects discussed in that section.

Willingness to share an electron pair is the reason for the fact that tertiary amines can be oxidized to amine oxides:

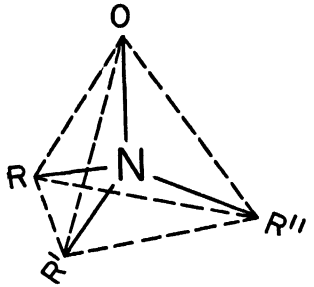


Trimethylamine Trimethylamine oxide

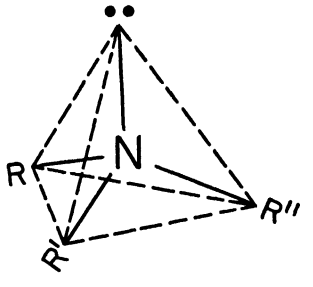
This type of reaction is also given by aromatic amines. The reaction played an important role in the history of the development of the electron theory of valence. According to the old classical valence theory, the oxides were written $R_3N=O$, but the compounds had no properties associated with an N=O bond. The new theory showed that the bond is essentially a single bond, which is in better accord with the properties of the compounds. The formation of the bond is dative (section 8.5). The structure of amine oxides will be discussed further in section 34.7.

Amine oxides in which the three organic radicals are all different can be resolved into optically active forms (see section 22.14). It is

obvious from diagram I that the N atom in such a molecule is asymmetric. In section 34.5 we shall describe sulphur compounds which are optically active and which lead us to look for optical activity in analogous nitrogen compounds like that shown in

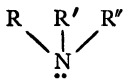


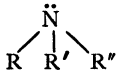
Optically active amine oxide
I



A tertiary amine
II

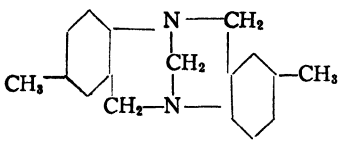
diagram II. These nitrogen compounds, however, are not optically active. The reason is that these molecules are in a constant oscillatory motion like the constant reversing of an umbrella. This intra-





molecular motion in the case of ammonia, NH_3, has been located in its absorption spectrum. It absorbs energy corresponding to a wavelength of 1.25 cm. Because of this constant oscillation (the frequency, according to table 13.2, is 2.4×10^{10} cycles per second for the ammonia molecule), the unshared electron pair is not fixed in position and this precludes the possibility of an asymmetric molecule.

Although the *simple* nitrogen compounds shown in diagram II are not optically active, isolation of optical isomers of a more *complex* trivalent nitrogen compound was accomplished in 1944. The compound resolved into its isomers is known as Troger's base, which is not at all the flat molecule pictured here, but is partially folded along the N–CH_2–N axis. It is evident from its structure



Tröger's base

that in such a molecule the "umbrella action" described in connection with diagram II, and called Walden inversion in section 22.16, cannot take place.

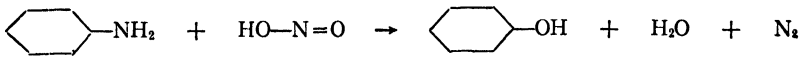
33. 7. 1°, 2°, and 3° Amines. As indicated by the preceding study of the properties of amines, the primary, secondary, and tertiary amines all have the same general characteristics. There are, however, a number of substances with which they react differently These reactions are described in detail in the larger texts, but it is of interest to note here at least one such reagent with which different products are obtained, depending on whether the amine is primary secondary, or tertiary:

$$\underset{\text{Methylamine}}{CH_3{-}NH_2} + \underset{\text{Nitrous acid}}{HO{-}N{=}O} \rightarrow \underset{\text{Methyl alcohol}}{CH_3{-}OH} + N_2 + H_2O$$

$$\underset{\text{Dimethylamine}}{CH_3{-}\overset{\displaystyle H}{\overset{|}{N}}{-}CH_3} + HO{-}N{=}O \rightarrow \underset{\text{Dimethylnitrosoamine}}{CH_3{-}\overset{\displaystyle N{=}O}{\overset{|}{N}}{-}CH_3} + H_2O$$

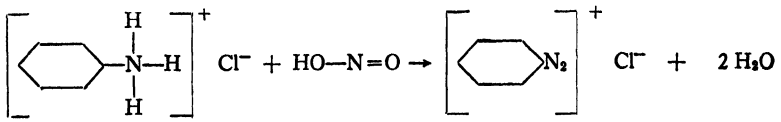
A primary amine with nitrous acid yields an alcohol with evolution of nitrogen, but a secondary amine forms an oily liquid called a nitroso compound. A tertiary amine cannot react with nitrous acid, because of the absence of H atoms on the N atom.

A secondary aromatic amine behaves just like the open-chain compounds when treated with nitrous acid. A primary aromatic amine, however, reacts in two ways with this substance. When the reaction is carried out in *hot* water, it behaves like a primary aliphatic amine:



Aniline Phenol

If the primary aromatic amine is used in a *cold* acid solution, a salt is formed and the reaction takes place as follows:

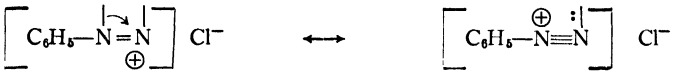


Aniline hydrochloride Benzenediazonium chloride

Several resonance structures are possible for the benzenediazonium ion. They can be represented by:

Two resonance structures of benzenediazonium ion

Each form is shown together with the chloride ion. The crosses are electrons contributed by phenyl and by chlorine to the electron pair valence bonds. It will be seen that the transfer of an electron pair by the scheme outlined in section 17.3, as follows,



gives the N atom attached to the phenyl group a positive character. That is in accord with the thinking which produced the old formula of benzenediazonium chloride given later in this section.

The resonance structures of the ion can be visualized as in figure 33.1, which shows the double bond and triple bond configurations.

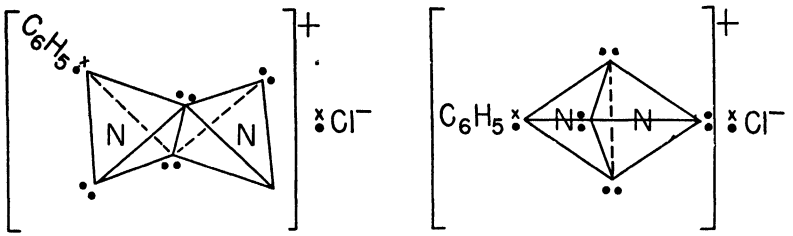


FIGURE 33.1. Resonance in benzenediazonium ion

Before the advent of the electron interpretation of valence, the nature of the diazonium salts was uncertain. They reacted as if they had what is called a *diazonium* structure ($-\overset{|}{N}\equiv N$) or a *diazo* structure ($-N=N-$), depending on the reaction conditions:

Benzenediazonium chloride **Benzenediazo chloride**

It should be remembered, however, that the fifth valence of nitrogen is really an ionic bond (section 33.4) and should not be written N–Cl.

The diazonium compounds are among the most important intermediates used in the dye industry. A compound like aniline is first *diazotized* with nitrous acid, as shown previously, and the "diazo" compound is then coupled in neutral or alkaline solution with many other substances to form the *azo* dyes (for examples, see section 42.10).

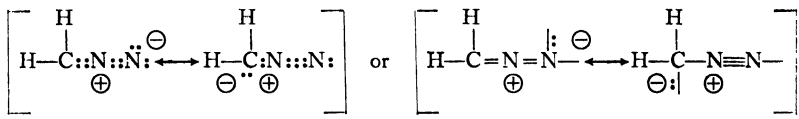
The diazonium compounds are also very useful in synthetic organic chemistry. Many of the standard types of organic compounds can be made from them. For example, if the acid solution of the diazonium salt is warmed in water to about 50°C., a phenol is formed:

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+\,Cl^-} + H{-}OH \rightarrow \underset{\text{Phenol}}{C_6H_5OH} + H^+Cl^- + N_2$$

The *evolution* of nitrogen is a characteristic of this type of reaction, whereas it will be observed that in the formation of the azo dyes (section 42.10), the two nitrogen atoms are used to *couple* the reacting molecules.

If the *azo* compounds described in section 42.10 are compared with the compounds now under discussion, it will be apparent that these are called *diazo* because they have two N atoms (*azote* is the French name of nitrogen) to one hydrocarbon radical, whereas the ratio in azo compounds is one to one.

Before leaving the diazo structure we shall give a brief description of diazomethane, CH_2N_2, a compound of importance in the research laboratory. This substance is apparently a resonance

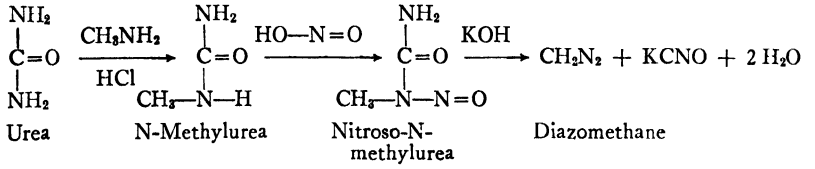


Resonance structures of diazomethane

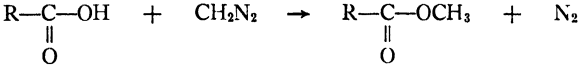
hybrid, shown here in accordance with a few of the schemes which have been used in this book for writing electronic structures.

Diazomethane is a toxic, yellow gas. It is so likely to be explosive in the gaseous state that it is generally employed in ether solution.

One method of preparation of the compound is from urea (section 33.12):



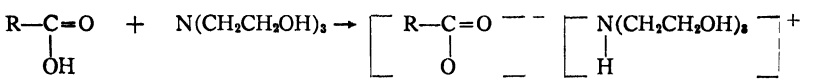
An example of its use in the laboratory is the preparation, in excellent yields, of methyl esters from carboxy acids:



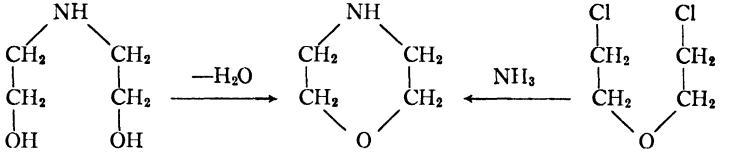
The reaction is run in ether solution, and is complete when the evolution of nitrogen ceases.

33. 8. Representative Amines. The following two compounds, $H_2N-CH_2-CH_2-CH_2-CH_2-NH_2$ Putrescine and $H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$ Cadaverine are found in decaying animal matter, which accounts for their names. They are diamines. They are classed among the ptomaines (section 43.6), but are not poisonous.

Ethanolamine, $\begin{matrix} CH_2-CH_2 \\ | \quad | \\ OH \quad NH_2 \end{matrix}$, is an alcohol-amine, that is, a mixed compound like those described in the last chapter. Ethanolamine and related compounds have many uses. For example, *triethanolamine* $(HOCH_2CH_2)_3N$, combines with fatty acids to form detergents, or soapless soaps (section 31.11). These soaps are almost neutral, and are free from injurious effects on textiles or skin. Their structure is similar to that of the sodium soaps (section 31.10), with the amine in an *onium* radical replacing the sodium ion:



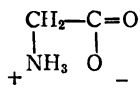
Morpholine is a cyclic mixed compound, and is of considerable commercial importance as a solvent and for the manufacture of detergents (section 31.11). It can be made in several ways:



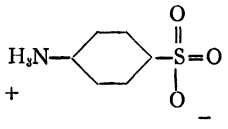
Diethanolamine Morpholine Dichlorethyl ether

Glycine, $\begin{matrix} CH_2 & C=O \\ | & | \\ NH_2 & OH \end{matrix}$, or aminoacetic acid, is the simplest of the amine-acids, another class of mixed compounds. Glycine is closely associated with the chemistry of the proteins (chapter 38).

The family of mixed compounds of which glycine is a simple member presents an unusual characteristic in that the compounds are both acids and bases. There is evidence to show that most compounds of this kind have an uneven distribution of charge due to migration of the hydrogen ion, H^+, which the reader will recall is a proton, from the acid group to the basic group:



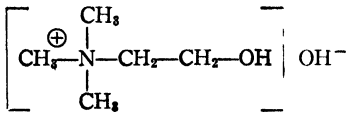
Glycine



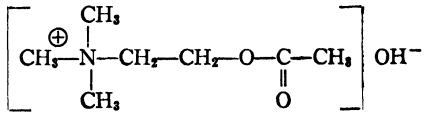
Sulphanilic acid
(see sulphonic acids, section 20.3)

These are neutral molecules, but are called *dipolar ions* (the German word for this is Zwitterionen). Molecules of this type have also been called inner salts. The crystals of these compounds are probably held together by electrostatic action, as in the case of crystals of ionic compounds (figure 8.1).

Choline is both an alcohol and a quaternary ammonium base. Through its alcohol group it forms compounds which are of great importance in life processes; an example is *acetylcholine* (section 44.2).



Choline



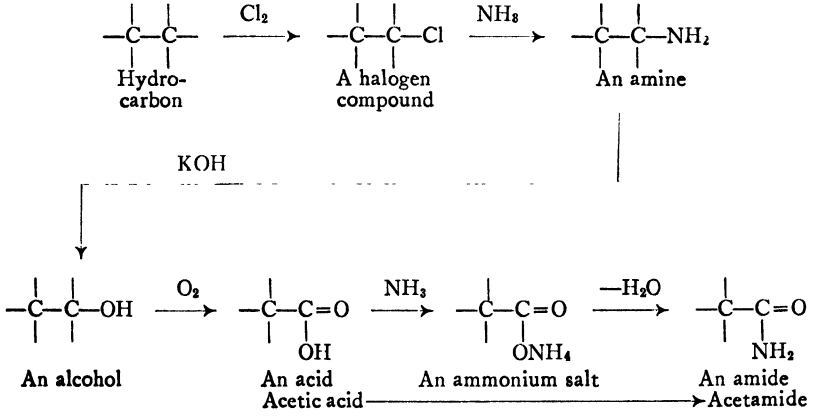
Acetylcholine

The physiological action of choline and its derivatives is due to the positive ion, which is associated with whatever negative ions may be present at the site of activity.

33. 9. Hydrazines. Hydrazine is an inorganic substance directly related to ammonia, and has the composition $H_2N–NH_2$. It forms hydrocarbon derivatives known as *hydrazines*, just as ammonia yields derivatives called *amines*. The best known hydrazine in the laboratory is phenylhydrazine, $C_6H_5NH–NH_2$ (section 40.3), which is used as a reagent for the identification of aldehydes and ketones (section 30.5*e*). Important drugs can also be made from hydrazine. This compound has become industrially important as a result of its usefulness in modern jet engines, in which power is obtained through spontaneous oxidation of hydrazine by active oxidizing agents, such as hydrogen peroxide.

33. 10. Amides. The amides are a series of nitrogen compounds in which the –OH group in the $-\overset{\displaystyle O}{\overset{\|}{C}}-OH$ group of an acid is replaced by the $-NH_2$ group.

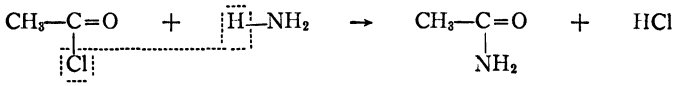
The relation between the amides and the other families of compounds we have studied can be understood from the following series of reactions:



An amide is obtainable from the corresponding acid by heating the ammonium salt of the acid. It is evident from the preceding

formulas that the effect of the heat is to remove a molecule of water from the salt.

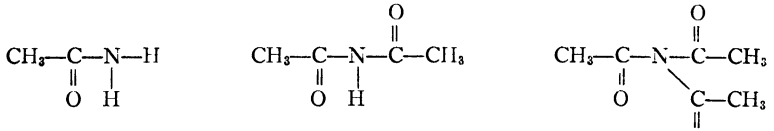
The amides and amines are similar in that both contain $-NH_2$ groups, but amides are derived from acids, whereas amines are derived from hydrocarbons. Like the amines, it is best to regard the amides as structurally derived from the inorganic substance, ammonia. When an acid chloride and ammonia are brought together, they react rapidly as follows:



Acetyl chloride (section 31.8*c*) Acetamide

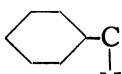
This is analogous to the reaction by which an amine is formed from an alkyl chloride and ammonia (section 33.2).

There are primary, secondary, and tertiary amides. just as there are three classes of amines:



Acetamide Diacetamide Triacetamide

Only the monoamides are important.

33. 11. Properties of Amides. With the exception of the amide of formic acid, $HC(=O)NH_2$, *formamide*, which is a liquid, the amides are crystalline solids. The lower open-chain members are soluble in water but the higher members and the aromatic amides, such as ***benzamide***,  , can be crystallized from hot water.

When studying the amines, such as methylamine, CH_3–NH_2, we showed that they are basic substances, even more basic than their parent ammonia. This was accounted for by the fact that the ***alkyl***

groups are positive and increase the basicity of the molecule (section 33.6).

The *acyl* radicals, such as acetyl $CH_3-\underset{|}{C}=O$, however, are negative in character and they accordingly tend to neutralize the basic nature of the $-NH_2$ group. An amide, $R-\underset{|}{C}=O$, is, therefore, practically a neutral compound, but it does retain some basic properties, as indicated by the following discussion of acetamide.

Acetamide, just like the amines and ammonia, forms salts with strong acids. It is possible to make *acetamide hydrochloride*,

$$CH_3-\underset{|}{C}=O$$
$$NH_2 \cdot HCl$$

showing that acetamide has basic properties. The salt formed is not very stable, however, and is easily hydrolyzed by water. The student should compare the formula of this compound, *acetylammonium chloride*, with that of methylammonium chloride in section 33.4. These two forms of acetamide are tautomeric, as defined in section 32.11, in connection with a similar equilibrium for acetone:

$$\underset{\text{Amido form}}{CH_3-\underset{|}{C}=O} \rightleftarrows \underset{\text{Imido form}}{CH_3-\underset{\|}{C}-OH}$$
$$NH_2 \qquad\qquad NH$$

The most important property of amides is their hydrolysis with water:

$$\underset{\text{Acetamide}}{CH_3-\underset{|}{C}=O} + H-OH \rightarrow \underset{\text{Acetic acid}}{CH_3-\underset{|}{C}=O} + NH_3$$
$$NH_2 \qquad\qquad OH$$

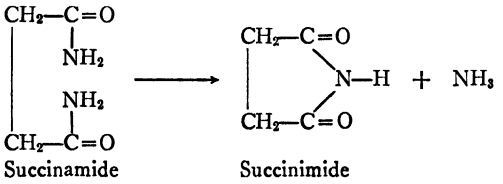
The bond between C and N is broken and the free acid is regenerated. However, the bond between C and N is very stable in amines, for we showed that water solutions of amines are stable, and are similar to ammonium hydroxide in behavior (section 33.3).

33. 12. Other Amides.

Urea, $NH_2-\underset{\|}{C}-NH_2$, is the amide of carbonic acid (section 32.7).
$\qquad\qquad O$

It is a crystalline solid and is the principal waste product of the metabolism of foods in the animal body. It has the general properties of amides, but has many other individual characteristics and uses too numerous to mention in this book. One such application of urea will be given in section 43.4 in the chapter on drugs.

Succinamide, $NH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-NH_2$, is the amide of succinic acid (section 31.13). It is noteworthy for the ease with which it forms an *imide* when heated:



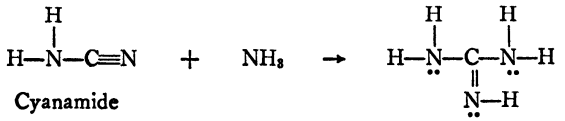
Succinamide Succinimide

The combination =N–H is called the *imido* group when it is part of an acid derivative as in this case, or the *imino* group when part of a secondary amine, as in section 33.2.

The *imido* H atom of succinimide is replaceable by sodium or potassium. With such a metal in the molecule, its usefulness in organic syntheses is greatly increased, since it will easily react with many types of halogen compounds.

Guanidine, $NH_2-\underset{\underset{NH}{\|}}{C}-NH_2$, is the imide of urea. It is a decomposition product of *guanine*, which is a derivative of purine (section 43.5). Guanine is 2-amino-6-oxypurine; it is present in large quantity in the bird excrement, guano.

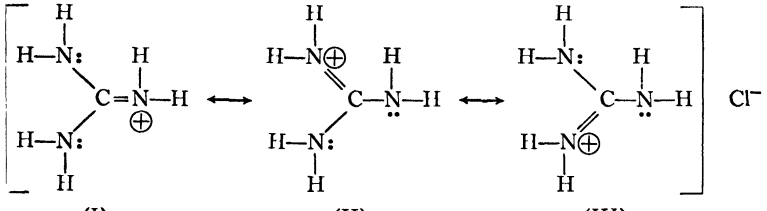
Guanidine can be made by the addition of ammonia to cyanamide:



Cyanamide

Of particular interest in the chemistry of guanidine is that it is a ***very strong base.*** This is explained by the resonance theory as

follows. We learned in section 33.4 that the free electron pair on the N atom is responsible for the basicity of amines, i.e., the tendency to add the protons, H^+, of acids to form salts. Guanidine, however, reacts with only one molecule of an acid instead of the three that its formula may lead us to expect. When guanidine reacts with one molecule of an acid, a highly symmetrical guanidinium ion is formed, in which the guanidine molecule has accepted



(I) (II) (III)

Guanidinium chloride
Guanidine hydrochloride

a proton to yield resonance structure (I). Resonance structures (II) and (III) can be written simply by rearranging the valence bonds; the positive charge originally acquired by one N atom is distributed equally among all three N atoms. Since the three structures are equivalent (X-ray data show that the three $-NH_2$ groups in the ion are symmetrically placed about the C atom), the resonance energy is maximum, as explained in section 18.8.

Because of the great stability of the guanidinium ion, there is no tendency to add more protons, which would result in a less stable structure. The strong basic activity of *guanidine* is explained by the fact that, although it has some resonance energy, it tends to add a proton to give the much more stable *guanidinium ion* with its greater resonance energy.

The nitrate of guanidine is used in the manufacture of explosives. Elimination of a molecule of ammonia from two molecules of guanidine yields *biguanide* (biguanidine), from which certain important compounds can be made (section 43.10).

33. 13. Nitriles. Potassium cyanide, KCN, and also sodium cyanide, NaCN, are common reagents in the laboratory of organic chemistry because they are so useful in the preparation of compounds containing nitrogen. It is a simple matter, using the reactive

halogen compounds, to attach the $-C\equiv N$ group to a hydrocarbon chain structure:

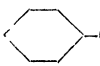
$$\underset{\text{Methyl chloride}}{CH_3{-}Cl} + K^+[:C:::N:]^- \rightarrow \underset{\substack{\text{Methyl cyanide}\\ \text{Methyl nitrile}\\ \text{Acetonitrile}}}{CH_3{-}C\equiv N} + K^+Cl^-$$

These organic cyanides are known as *nitriles.*

The following reactions show how the nitriles can be used to prepare members of the two important families of N compounds which we have already discussed in this chapter, namely, the amines and amides:

$$\underset{\text{Methyl cyanide}}{CH_3{-}C{\equiv}N} + 2\,H{-}H \xrightarrow{\text{hydrogenation}} \underset{\text{Ethylamine}}{CH_3{-}CH_2{-}NH_2}$$

$$\underset{\substack{\text{Acetonitrile}\\ \text{Methyl cyanide}}}{CH_3{-}C{\equiv}N} + 2\,HO{-}H \xrightarrow{\text{hydrolysis}} \underset{\substack{\text{(Unstable, 2 OH}\\ \text{groups on same C)}}}{CH_3{-}\overset{\overset{OH}{|}}{\underset{\underset{NH_2}{|}}{C}}{-}OH} \longrightarrow \underset{\text{Acetamide}}{CH_3{-}\overset{\overset{O}{\|}}{\underset{\underset{NH_2}{|}}{C}}} + H_2O$$

Some common names of the nitriles are obtained from this second type reaction. They are named from the acid to which they can be hydrolyzed. Methyl cyanide is *aceto*nitrile because it hydrolyzes to acetamide, and this, as we have already learned, can easily be hydrolyzed further to acetic acid. Similarly, phenyl cyanide, or *benzo*-nitrile  $-C\equiv N$ is so named because it can be hydrolyzed to benzoic acid (table 31.2).

It should be noticed in both these typical reactions that we believe the activity of the $-C\equiv N$ radical is due to its unsaturation. It adds on other molecules across the triple bond in exactly the same way as shown for acetylene hydrocarbons in section 15.2.

33. 14. Isonitriles. We have seen that the reaction between $CH_3{-}Cl$ and KCN results in the formation of a nitrile. When silver cyanide is used instead of the potassium salt, it is found that an isonitrile is produced:

$$CH_3\text{—}Cl + Ag{:}C{:::}N{:} \rightarrow \underset{\substack{\text{Methyl isocyanide}\\ \text{Methyl isonitrile}\\ \text{Methyl carbylamine}}}{CH_3\text{—}N{=}C} + AgCl$$

The fact that the product is RNC instead of RCN when using silver cyanide instead of potassium cyanide as a reagent has aroused much controversy. The reason apparently lies in the fact that potassium cyanide is an ionic compound, whereas silver cyanide is largely covalent,

$$K^+CN^- \qquad\qquad Ag{:}CN{:}Ag{:}CN{:}Ag{:}CN$$

and exists in the crystal state as a chain of covalently linked atoms of indefinite length. The structure of silver cyanide would indicate the existence of both AgCN and AgNC.

The attack on the CH_3–Cl molecule by ionic potassium cyanide may be visualized as either a frontal attack by K^+ on the chlorine end of the molecule, or an attack from the rear by CN^-, as discussed for a similar system in section 22.16. The attack on the CH_3–Cl molecule by molecular silver cyanide, however, presumably results in an intermediate complex of the nature $Ag{:}CN{:}CH_3{:}Cl$ which breaks down to Ag^+Cl^- and CH_3NC.

It should be understood that these reactions are not clear-cut. The formation of a nitrile is accompanied by the formation of some of the isonitrile, and vice versa.

The isonitriles have very offensive and disagreeable odors, whereas the normal nitriles have strong but fairly agreeable odors. The *iso* compounds are also much more poisonous.

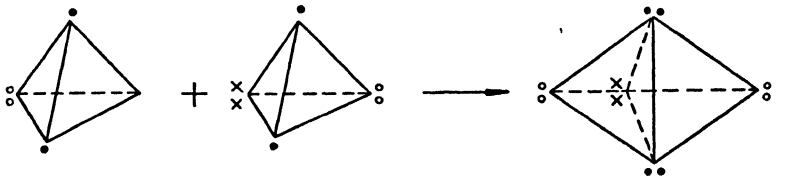
The valence of the carbon atom in the isonitriles was for a long time a matter of dispute. Originally, the argument centered about the acceptance of the formula R–N≡C instead of R–N=C. The first had to be abandoned because if the carbon atom is tetrahedral, as pictured in section 12.2, it cannot be joined to another element by all four of its valences.

The formula R–N=C was the accepted one for many years, on the assumption that carbon can have a valence of two as well as a valence of four. In carbon monoxide, C=O, also, it was thought for a long time that the carbon atom is divalent.

At present, on the basis of the electron theory of valence, and on the strength of a number of physical constants which we cannot go

into here, the divalent carbon atom has also been quite largely abandoned. It is now thought that the formula of an isocyanide is R–N⇉C and of carbon monoxide is C⇇O. The union consists of two *covalence* bonds (section 7.5) and one *dative* valence bond (section 8.5), the carbon atom acting as the acceptor.

In general, the carbon atom is stable only when it shares *four* covalent bonds as in methane (section 8.10). In the few supposed divalent compounds that are known, the carbon atom does the exceptional thing in *sharing only two* of its electrons, and acting as an *acceptor for a lone pair* (section 8.5) from another atom. This may be pictured as in figure 33.2 for the carbon monoxide molecule.



Carbon Oxygen Carbon monoxide

FIGURE 33.2. Electron sharing in carbon monoxide.

In these diagrams, the electrons *shared by* the atoms are blacked in, and the electron pair *accepted from* the oxygen atom is designated by crosses. This structure really has all the characteristics of a triple bond, like that shown for acetylene in section 14.1. In actual practice, the isocyanides and carbon monoxide are usually written with double bonds, for that suffices to indicate their most important chemical properties.

The isonitriles do not hydrolyze to acids of the same carbon content as the normal cyanides do, but yield amines:

$$CH_3{-}CH_2{-}N{=}C + 2\,H{-}OH \rightarrow CH_3{-}CH_2{-}NH_2 + H{-}C(=O){-}OH$$

Ethyl isocyanide — Ethylamine — Formic acid

When a normal cyanide is reduced, a primary amine is obtained but reduction of an isonitrile results in the formation of a secondary amine:

$$CH_3{-}CH_2{-}N{=}C + 2\,H_2 \rightarrow CH_3{-}CH_2{-}\underset{\displaystyle H}{N}{-}CH_3$$

Ethylmethylamine

These two reactions are evidence supporting the belief that the N atom in an isonitrile is attached to the alkyl radical as well as to a C atom (CH_3–N=C); in a normal cyanide it is attached to only one C atom (CH_3–C≡N).

A curious thing in this connection is the fact that organic *cyanates* R–O–C≡N, do not exist, but many *isocyanates* have been prepared of the general formula R–N=C=O. These are derivatives of cyanic acid, HO–C≡N, which must not be confused with hydrocyanic acid, H–C≡N, and is tautomeric with isocyanic acid, H–N=C=O.

Cyanogen, N≡C–C≡N, is a poisonous gas with a characteristic odor resem bling that of bitter almonds. It can be called *oxalo*nitrile because ithydrolyzes to oxalic acid (section 31.13).

Hydrocyanic acid, H–C≡N, is a volatile liquid with an odor like that of cyanogen, and is very poisonous. It is also known as *formo*nitrile because it can be hydrolyzed to formic acid (section 31.9). As a result of considerable research on its physical properties, especially the Raman spectrum, it is believed that hydrocyanic acid contains a small proportion of *isohydrocyanic* acid, that is, H–N=C molecules.

33. 15. Nitro Compounds. The student should review section 20.4, where we discussed in some detail the mechanism of nitration (or nitronation), the difference between *nitro* compounds and *nitrates*, and the resonance structures of the nitro group. Nitro compounds need to be referred to again in order to bring out their relation to the nitrogen compounds described in this chapter.

Nitrobenzene (section 20.4) is an important compound because of its many commercial uses, one of which is reducing to aniline. Aniline (section 33.7), in turn, can be converted to diazonium salts which are useful not only industrially but also in the laboratory. Both nitrobenzene and aniline are liquids and are sufficiently toxic to demand rather careful handling under laboratory conditions. (Also see discussion of TNT in section 21.4.)

Nitromethane, CH_3NO_2, is a liquid that can be made in good yield by nitration of methane under pressure. It has explosive properties which make it useful for jet propulsion engines. Nitromethane is the simplest member of a series of nitro compounds that are currently being made on a large scale by direct nitration of paraffin

hydrocarbons. Other examples are nitroethane and both 1-nitropropane and 2-nitropropane. They are easily reduced to amines with many uses and are also employed in condensation reactions (see under section 33.16).

33. 16. Tautomerism of Nitro Compounds. Those nitroparaffins in which C–H is *adjacent* to the $-NO_2$ group exhibit the phenomenon of tautomerism analogous to that described in section 32.11 in connection with ketones. *Nitro* and *aci* forms are possible similar to the *keto* and *enol* forms mentioned in the earlier chapter. The

Nitro form *Aci* form

(See section 20.4 for this method of writing the NO_2 group.)

aci structures in this series of compounds are relatively more stable than the *enol* structures among the keto compounds; it will be recalled that acetone is normally essentially all *keto* because the molecule contains only one C=O group, and that development of a reasonably stable *enol* depends on C–H (or $-CH_2-$) being joined to two C=O groups.

The nitroparaffins containing *alpha* hydrogen atoms are acidic, a fact which is evident from the ease of enolization to the *aci* form. Water-soluble salts are produced in dilute alkali solutions. When the basic solvent removes a proton (H^+) at the *alpha* carbon atom it gives rise to a negative ion which is stabilized by resonance (structures I and II) similarly to the behavior pictured for acetone in section 32.11. However, when the solution is acidified, the proton does not return to the *alpha* carbon atom (structure I), but becomes attached to the oxygen atom (structure II). The acid solution, there-

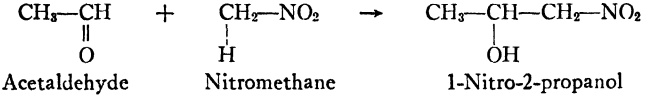
(I) (II)

Resonance structures of the negative ion of a nitroparaffin. The electron pairs are shown as in section 17.3.

fore, at first contains the *aci* form of the nitro compound; this slowly reverts to the *nitro* form as the proton migrates to the more stable position on the carbon atom.

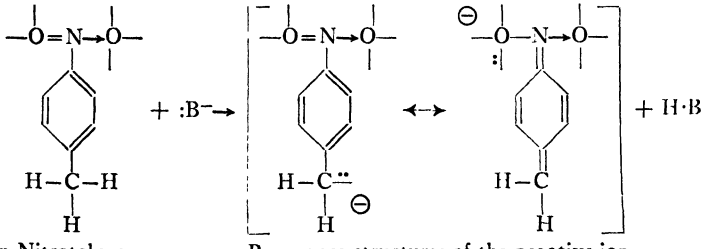
The acidity of nitroparaffins is thus explained by the same reasoning as employed for carboxy acids (section 31.6) and phenols (section 28.2), which should be reviewed. The resonance energy of the negative ion is greater than that of the unionized molecule, and this results in acidity, that is, tendency for the H^+ to remain as such in a solution of the substance.

The nitro group in a nitroparaffin is said to have an activating influence on the *alpha* hydrogen atoms. Such an activating effect is illustrated by a reaction of nitroparaffins which resembles that of aldehydes (section 30.5*d*); when catalyzed by dilute alkali they undergo condensation reactions if an *alpha* H atom is present in the molecule:



Acetaldehyde Nitromethane 1-Nitro-2-propanol

Acid properties of certain aromatic nitro compounds are also explainable on the basis of resonance stabilization of the carbanions which result when a proton is removed by the solvent medium. This is illustrated by the effect of a base ($:B^-$) on p-nitrotoluene, the formulas being written according to the scheme shown in section 17.3:



p-Nitrotoluene Resonance structures of the negative ion

34. COMPOUNDS WITH SULPHUR, PHOSPHORUS, AND OTHER ELEMENTS

SULPHUR

34. 1. Introduction. Sulphur is just below oxygen in the periodic system of the elements and the two elements form analogous series of compounds. The *simpler* sulphur compounds in organic chemistry are studied as being derived from hydrogen sulphide, H_2S, just as the oxygen compounds are related to water, H_2O, on a structural basis.

H—O—H	Water	H—S—H	Hydrogen sulphide
C_2H_5—OH	Ethyl alcohol Ethanol	C_2H_5—SH	Ethyl mercaptan Ethanethiol
C_2H_5—O—C_2H_5	Diethyl ether Diethyl oxide	C_2H_5—S—C_2H_5	Diethyl thioether Diethyl sulphide

The compounds containing sulphur are often given the names of the analogous oxygen compounds, adding the prefix *thio* from the Greek word for sulphur. There are thioalcohols, thioethers, thioaldehydes, thioketones, etc. However, alcohol analogs are more frequently called *thiols*, as illustrated before, or *mercaptans*.

The nomenclature system mentioned for oxygen compounds in section 29.1, in which diethyl ether is called 3-oxapentane, is sometimes also used for sulphur compounds. According to this scheme, diethyl sulphide is 3-thiapentane, and mustard gas (section 34.4) is 1,5-dichloro-3-thiapentane.

34. 2. Thiols. These compounds can be prepared by a method that recalls the preparation of the oxygen alcohols (section 25.2):

$$C_2H_5\text{—Cl} + \underset{\substack{\text{Potassium}\\\text{hydrosulphide}}}{\text{K—SH}} \rightarrow \underset{\substack{\text{Ethyl mercaptan}\\\text{Ethanethiol}}}{C_2H_5\text{—SH}} + KCl$$

The mercaptans are flammable liquids, with a very unpleasant, garlicky odor. They are not poisonous. A mixture of mercaptans is blended with illuminating gas in some cities in order to help the gas companies detect leaks in the mains.

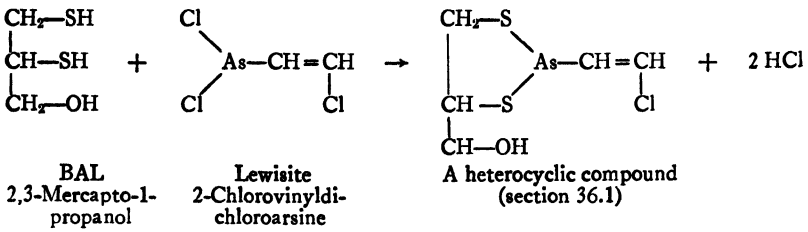
The mercaptans are similar to alcohols in their fundamental chemical properties. For example, they react with sodium:

$$2\,C_2H_5\text{—SH} + 2\,Na \rightarrow 2\,C_2H_5\text{—SNa} + H_2$$

$$C_2H_5\text{—SH} + NaOH \rightarrow \underset{\substack{\text{Sodium thioethylate}\\\text{Sodium ethyl mercaptide}}}{C_2H_5\text{—SNa}} + H_2O$$

Alcohols do not react with sodium hydroxide to form ethylates, because they are too weakly acidic, but mercaptans react as shown. Furthermore, since mercaptans are more acidic than alcohols, the mercaptides are more saltlike than ethylates (section 27.3). The mercaptans get their class name from their ability to form the mercury salt which has the composition $(C_2H_5S)_2Hg$, mercury mercaptide. The name mercaptan is derived from the Latin, *mercurium* (mercury) *captans* (seizing).

A *dithiol* with interesting medicinal properties was developed during World War II by British chemists and was given the name BAL (British Anti-Lewisite). It was originally prepared for use in an ointment to give protection against lewisite (section 43.14) with which it reacts as follows:



BAL
2,3-Mercapto-1-propanol

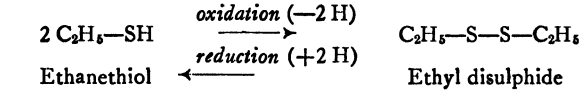
Lewisite
2-Chlorovinyldichloroarsine

A heterocyclic compound (section 36.1)

BAL has given spectacular results in the treatment of heavy metal poisoning, because, as a mercaptan, it reacts readily with salts of lead, mercury, etc., which are sometimes accidentally introduced

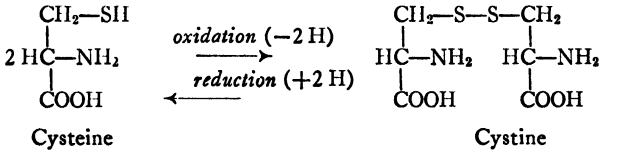
into the body. It must be used with caution, however, because it is rather toxic.

The mercaptans are easily oxidized to disulphides. This takes place even when the mercaptans are exposed to air, but is usually accomplished in the laboratory by means of hydrogen peroxide or



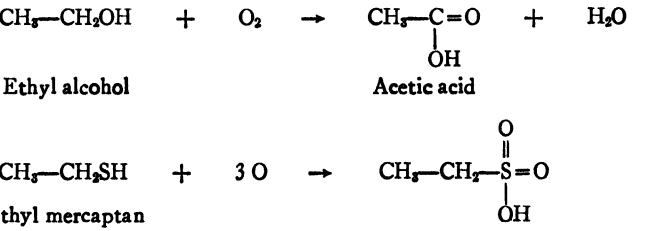
iodine. The reaction is reversible; the disulphide can just as readily be reduced back to the thiol.

A closely related oxidation-reduction system is believed to operate in the animal body. Cystine, one of the α-amino acids in proteins (see table 38.1), is a disulphide which is easily interconvertible with cysteine. Cysteine has not yet been isolated from proteins in the



free state. Presumably because it is so easily oxidized, it is not found in dead tissue. It is thought, however, that the cystine $\rightleftarrows$ cysteine system is of great importance as a catalyst in metabolisms involving oxidation and reduction.

34. 3. Sulphonic Acids. Mercaptans differ from alcohols in their behavior when oxidized. It will be recalled (section 31.2) that a primary alcohol is oxidized to an acid by a process which involves an appreciable amount of bond breaking. A mercaptan also yields an acid, but the oxidation process is simply the *addition* of three atoms of oxygen:



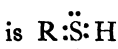
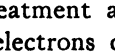
The end products are similar; they are acids, but acetic acid is weak, whereas the sulphonic acid is strong, practically as strong as hydrochloric acid.

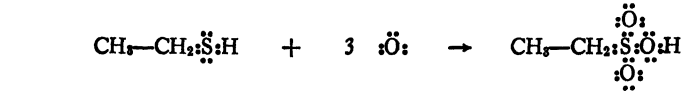
An intermediate type of compound in the oxidation state of sulphur is the series of *sulphinic acids*, in which two atoms of oxygen are added to the molecule. These compounds are made by indirect methods rather than by direct oxidation of mercaptans. Their chemistry is relatively unimportant in an elementary study, but

Ethanesulphinic acid

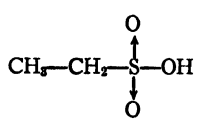
we shall briefly refer to an interesting aspect of their molecular structure in section 34.5.

According to old established procedure in chemistry, that is, "classical" procedure as contrasted with "modern," the valence of an element is calculated from the number of valence bonds that are attached to it in a structural formula. For this reason, it was stated that the valence of the S atom is two in the mercaptans, four in the sulphinic acids, and six in the sulphonic acids. According to the modern electron-valence theory, the valence of an atom is the number of electron pairs with which it is bound to other atoms in the molecule.

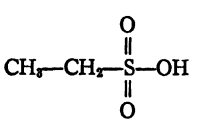
The electronic structure of the sulphur atom is and of a mercaptan is  , where sulphur has a valence of two in the modern treatment as well as in the classical. The two pairs of unshared electrons on the sulphur atom in mercaptans are more easily shared with other elements than are the corresponding electron pairs in alcohols,  . This sharing of electron pairs explains the formation of the sulphonic acids by addition of oxygen:



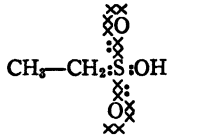
Since two of the oxygen atoms have *accepted* electron pairs to form valence bonds, the product has two *dative* bonds (section 8.5) and the formula of ethanesulphonic acid is, therefore, often found written in the modern literature as in I. Formula II is known as the classical



I



II



IIa

formula. In the modern formula I, the valence of the sulphur atom is four, whereas in the old-fashioned formula II, it is six.

A dative bond is a *single* bond. In the classical formula, the sulphur-oxygen links are *double* bonds and we have shown (see figure 18.5) that such a bond is shorter than a single bond. The actual length of the SO bond can be determined, for example, by spectroscopic methods, but the data are still controversial (see section 34.7).

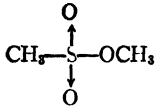
From the numerous examples of resonance given in this book, the student will understand that we should not consider a sulphonic acid from either the classical or modern standpoint exclusively. We can regard the molecule as a resonance hybrid of several plausible structures, in which the atoms retain their relative positions, but the electron bonding is altered.

The crosses in formula II*a* are the electrons of the oxygen atom. It will be seen that the sulphur atom in this structure is surrounded by twelve electrons instead of the octet described in chapter 6. Compounds such as SF_6 are known in which it is obvious that the octet rule does not hold, so that infraction of the octet rule is not a serious objection to the classical structure of II and its modern counterpart in II*a*. In this book, we shall use both modern and classical formulas for the sulphur compounds, but modern practice will generally be followed by writing the structures with single (dative) bonds rather than with double bonds.

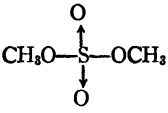
The reader should refer to section 20.3 where we described the preparation of sulphonic acids of the aromatic series by direct sulphonation of the hydrocarbon, as in the preparation of benzenesulphonic acid –SO_2–OH. The sulphonic acids in the open-chain series are not easily made by direct sulphonation of the hydrocarbon except in special cases, but can be prepared by oxidation of the mercaptan as described in this chapter.

The sulphonic acids have the general properties of the carboxy acids listed in chapter 31. They form acid chlorides, salts, esters, and other acid derivatives (see the sulphonamides in section 34.6).

As already explained in section 20.3, the sulphonic acids must be distinguished from sulphates. Organic sulphates do not have a C-S bond:



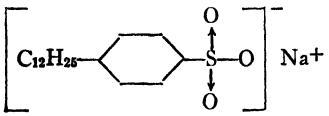
Methyl ester of methanesulphonic acid
Methyl methanesulphonate



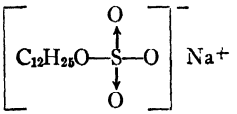
Dimethyl ester of sulphuric acid
Dimethyl sulphate

These two compounds are not isomers. The student should, however, refer back to section 2.2 where related compounds were formulated as derived from sulphurous acid, H_2SO_3 The two compounds in section 2.2 are isomers and are, respectively, diethyl sulphite and the ethyl ester of ethanesulphonic acid.

Sulphonic acids and organic derivatives of sulphuric acid are widely used in commerce, especially in the manufacture of detergents (section 31.11). In fact, these detergents constitute the major part of those currently on the market. They are good lathering agents, useful in shampoos. These detergents are typical:



Sodium dodecylbenzenesulphonate
(An alkarylsulphonic acid derivative)



Lauryl sodium sulphate
Dodecyl sodium sulphate

Triethanolamine salts (section 33.8) are often used instead of the sodium salts.

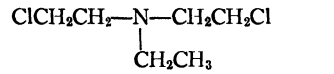
34. 4. Thioethers. The thioethers are similar to ethers (chapter 29) in methods of preparation and most of their chemical properties. A representative member of the series is CH_3–CH_2–S–CH_2–CH_3, known as diethyl thioether, or diethyl sulphide. Like the mercaptans, the thioethers have piercing, disagreeable odors.

Mustard gas, Cl–CH_2–CH_2–S–CH_2–CH_2–Cl, is a symmetrical dichloro-derivative of diethyl sulphide. It is one of the important chemical-warfare agents. It is not a gas, but an oily liquid which

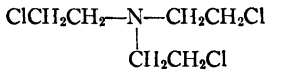
vaporizes very slowly and maintains a toxic concentration in the air for a long time. Both the liquid and the vapor cause serious skin burns. The Cl atoms in this molecule are on the β-carbon atoms; when they are on the α-carbon atoms, that is, next to the sulphur, the molecule is less toxic.

The thioethers are more active than their sister oxygen compounds, both chemically and physiologically. For example, the oxygen compound analogous to mustard gas is dichloroethyl ether, $ClCH_2–CH_2–O–CH_2–CH_2Cl$. It is comparatively nontoxic, and is used in large quantities as a commercial solvent and "dry cleaner."

Another group of compounds analogous to mustard gas are the *nitrogen mustards*, a few important members of which are:



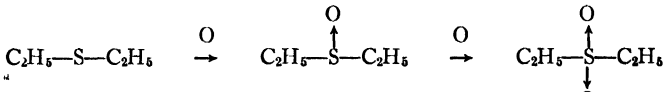
Ethyl-*bis*-(β-chloroethyl)-amine



Tris-(β-chloroethyl)-amine

These are vesicant, like mustard gas (section 43.13).

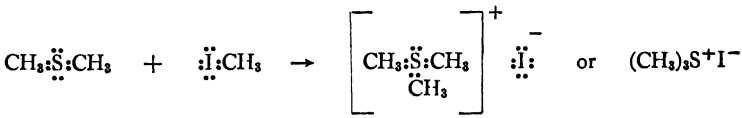
When thioethers are oxidized, oxygen adds directly to the sulphur atom exactly as described earlier in this chapter for mercaptans:



Diethyl thioether — Diethyl sulphoxide — Diethyl sulphone

Each of these oxygens atoms is held by a dative bond. Sulphoxides and sulphones are stable substances and are made by oxidizing thioethers with strong oxidizing agents. By the proper choice of oxidizing agent the oxidation can be stopped at the sulphoxide stage.

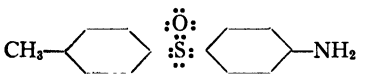
Thioethers are alkyl sulphides, R–S–R, analogous in structure to the amines, $\begin{matrix} R–N–R \\ \quad | \\ \quad R \end{matrix}$. Accordingly, we find that they form *sulphonium* compounds which are analogous to the ammonium compounds (section 33.5):



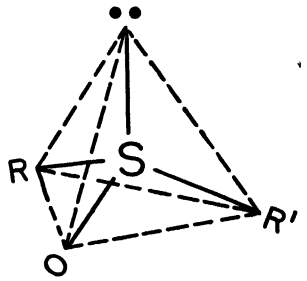
Dimethyl sulphide — Methyl iodide — Trimethylsulphonium iodide

From this product we can prepare trimethylsulphonium hydroxide, $(CH_3)_3S^+OH^-$, a strong base, similar in behavior to sodium hydroxide.

34. 5. Asymmetry of Sulphur Compounds. In section 22.14 we discussed the possibility of optically active compounds in which the asymmetry is not due to the carbon atom. Sulphoxides and sulphonium compounds are of considerable interest in this connection, in that certain of these compounds have been resolved into optically active isomers. An example is the following compound:



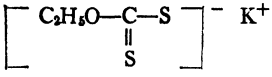
4-Methylphenyl 4′-aminophenyl sulfoxide



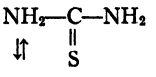
It will be seen that the unshared pair of electrons effectively acts as a group in one corner of the tetrahedron.

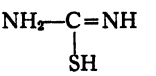
The sulphinic acids, referred to in section 34.3 in this chapter, also have a structural configuration which should lead to optical isomerism, namely, R–S–OH. Such isomers have, in fact, been
↓
O
found for certain of the higher members of this series of acids.

34. 6. Other Sulphur Compounds. We have restricted our study of sulphur compounds almost entirely to those that can be visualized as derived from H–S–H. We should, however, mention at least briefly several other important types of compounds.

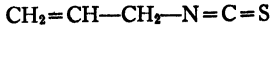


Potassium ethyl xanthate





Thiourea



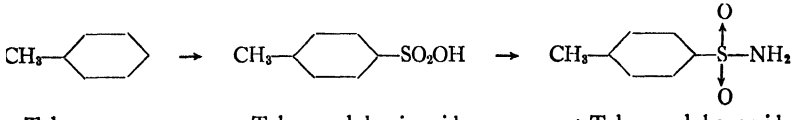
Allyl isothiocyanate
A "mustard oil"

Xanthic acid, C_2H_5O–CS–SH, is an unstable compound; its salts, however, can be made by the reaction between CS_2 and a solution of KOH in alcohol. The salts are yellow (Greek word for yellow is *xanthos*). There is a series of xanthates, represented by RO–CS–SM, where R is a radical and M is a metal. When R is ethyl the prefix ethyl is often left out of the name. Just as ethyl alcohol is simply alcohol, potassium ethyl xanthate is simply potassium xanthate. Xanthates are used in the textile industry as a solvent for cellulose, in the manufacture of rayon, etc. Xanthates are derivatives of dithiocarbonic acid (HO–CS–SH).

Thiourea may be looked on as an amide of thiocarbonic acid (HO–CS–OH). In many of its reactions it apparently tautomerizes (section 32.11) to the enol type of structure shown before, which is known as *isothiourea*. In these compounds the S atom in the C=S group is referred to as *thiono* sulphur, whereas in the —SH group it is *thiol* sulphur.

There is a series of thiocyanates, R–S–C≡N, and a series of isothiocyanates, R–N=C=S. An important example of the second is allyl isothiocyanate, the formula of which was given previously. These *iso* compounds are also known as *mustard oils*, a name which originated from the fact that allyl isothiocyanate can be extracted from a glucoside (section 40.7) in black mustard seed. Allyl isothiocyanate is called oil of mustard; it is mildly vesicant and is used in liniments. Possibly, mustard gas (section 34.4) got its name from an exaggerated notion of the resemblance of its odor to that of oil of mustard.

Sulphonamides are commercially important; this is evident from inspection of the formulas of sulfa drugs in section 43.9. In section 33.11, we mentioned the amide of benzoic acid (benzamide). By sulphonation (section 20.3) of the benzene hydrocarbons, the corresponding sulphonic acids can be made, and these, in turn, can be converted to the sulphonamides:



Toluene *p*-Toluenesulphonic acid *p*-Toluenesulphonamide

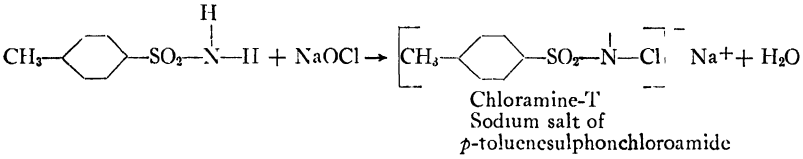
Sulphonation at 100°C. gives mostly the *p*- acid shown here, whereas the reaction at room temperature results mainly in the *o*- compound.

The *o*- acid can be oxidized (which converts the $-CH_3$ to $-COOH$) and then made into saccharin (section 43.16).

p-Toluenesulphonamide is generally prepared by sulphonating toluene with chlorosulphonic acid and ammoniating the p-toluenesul-

$$CH_3{-}C_6H_5 \xrightarrow{HO{-}SO_2{-}Cl} CH_3{-}C_6H_4{-}SO_2Cl \xrightarrow{NH_3} CH_3{-}C_6H_4{-}SO_2NH_2$$

phonyl chloride. A mixture of the *o*- and *p*-isomers is obtained, but the *p*-isomer is easily separated from the *o*-isomer. An interesting property of the amide is the replaceability of the H atoms in the $-NH_2$ group by sodium and by chlorine. When treated with the chlorinating agent, sodium hypochlorite, both replacements take place:

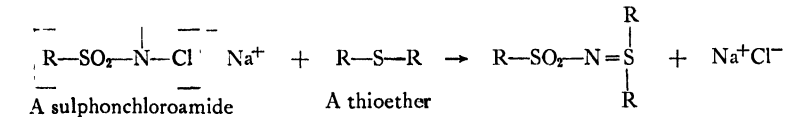


Chloramine-T
Sodium salt of
p-toluenesulphonchloroamide

The product, *chloramine-T*, is a white solid, soluble in water. In dilute solution, it is used as an antiseptic and disinfectant for personal hygiene, the chlorine being liberated on contact with oxidizable substances (bacteria, etc.). This tendency to give up "active" chlorine is characteristic of many compounds with the N–Cl linkage, in which the Cl atom is essentially electropositive like the H atom which it replaces.

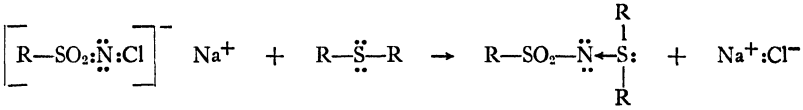
If *p*-toluenesulphonamide is treated with excess chlorine, the product is *dichloramine-T*, $CH_3{-}C_6H_4{-}SO_2NCl_2$. In this compound, both H atoms of the $-NH_2$ group are replaced by Cl atoms. It is a strong antiseptic, only slightly soluble in water, but soluble in organic solvents.

Chloramine-T has been used to destroy mustard gas (section 34.4) by chlorination. The study of this decontamination procedure led to the discovery of a new series of compounds called the *sulphilimines*, the formation of which was written:



A sulphonchloroamide
A thioether
A sulphilimine

The formula of the product, using classical valence bonds, did not seem plausible with the S atom showing a covalence of four. The covalence should more likely be three, as in the sulphoxide described in section 34.5. According to the electron theory of valence, the reaction is:



The sulphilimines are easily crystallized, have sharp melting points and are, therefore, used to identify thioethers and related compounds.

PHOSPHORUS

34. 7. Derivatives of Phosphines. The following closely related elements below nitrogen in group 5 of the periodic table form compounds with the same general structures and properties as the analogous compounds containing nitrogen:

N	P	As	Sb	Bi
Nitrogen	Phosphorus	Arsenic	Antimony (Stibium)	Bismuth
Order of increasing atomic weight ——→				
NH_3	PH_3	AsH_3	SbH_3	(BiH_3)
Ammonia	Phosphine	Arsine	Stibine	Bismuthine (nonexistent)
Order of decreasing stability ——→				

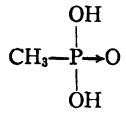
As indicated, the stability of the hydrogen compounds decreases in the order in which the elements occur in the periodic system. Bismuth is so metallic that it does not form a stable hydrogen compound, although some derivatives of the hypothetical bismuthine have been prepared. The carbon derivatives of these compounds are not of sufficient importance to demand a detailed discussion, but the analogies to the nitrogen compounds may be pointed out in some of the series.

The similarity between phosphines and amines may be best shown by a tabulation:

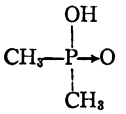
PH_3	CH_3PH_2	$(CH_3)_2PH$	$(CH_3)_3P$	$(CH_3)_4P^+OH^-$
Phosphine	Methyl-phosphine	Dimethyl-phosphine	Trimethyl-phosphine	Tetramethylphos-phonium hydroxide
NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$	$(CH_3)_4N^+OH^-$
Ammonia	Methyl-amine	Dimethyl-amine	Trimethyl-amine	Tetramethylammonium hydroxide

The phosphines resemble the amines not only in structure but also in methods of preparation and general properties. The phosphines have a strong, stupefying odor and a bitter taste.

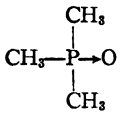
The chief difference between the phosphines and amines is in their reactivity toward oxygen. Nitrogen and its compounds are not easily oxidized, but phosphorus is quite easily oxidized and this property is communicated to its compounds. The phosphines rapidly absorb oxygen from the air with the formation of oxides and are spontaneously flammable. Representative oxygenated compounds have these structures:



Methanephosphonic acid

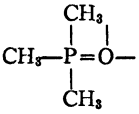


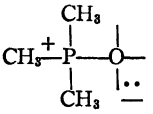
Dimethylphosphinic acid



Trimethylphosphine oxide

Trimethylphosphine oxide is structurally related to trimethylamine oxide (section 33.6) and to dimethyl sulphoxide (section 34.4). Its chemical properties, naturally, are more closely related to those of the nitrogen compound. According to the resonance theory, structures such as these can be written for trimethylphosphine oxide:





The molecule presumably has neither a completely P=O nor a completely P→O link, but has an intermediate character. The extent of ionic character will vary with the nature of the groups attached to phosphorus, and since we know that CH_3 has electron-release properties, we should expect the three methyl groups to promote formation of the structure with greater electron density at the oxygen end of the PO bond.

Ionic behavior of trimethylphosphine oxide is evidenced by the fact that it is an electron-donor; it reacts with BF_3 (see section 8.5)

to form the double compound $(CH_3)_3PO{:}BF_3$, although the resulting compound is much less stable than the corresponding nitrogen compound, $(CH_3)_3NO{:}BF_3$. The greater activity of the nitrogen compound in this type of reaction is to be expected from the data in table 34.1, in which the theoretical interatomic distances are

TABLE 34.1. INTERATOMIC DISTANCES IN CERTAIN OXIDE GROUPS
(*Distances in Angstrom units*)

Type of oxide link, based on these data	*Experimental interatomic distance*			*Calculated interatomic distance*			
				Single bond*		Double bond*	
$(CH_3)_3N\rightarrow O$	N,O	1.36		N 0.70 / O 0.66	1.36	0.61 / 0.57	1.18
$(CH_3)_2S=O$	S,O	1.44		S 1.04 / O 0.66	1.64	0.95 / 0.57	1.52
$Cl_3P=O$	P,O	1.58		P 1.10 / O 0.66	1.76	1.00 / 0.57	1.57

*Calculated by the method described in section 18.7.

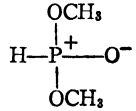
calculated for the NO, SO, and PO bonds from atomic radii by the method described in section 18.7. The table gives data on Cl_3PO, because corresponding data for $(CH_3)_3PO$ were not available. The negligibly weak ionic character of the chlorine compound is to be attributed to the electronegativity of the Cl atom, which would tend to increase electron density at the phosphorus end of the PO bond.

The remarks on the SO bond in section 34.3 should be reviewed in the light of this discussion. Considerable research is being done on the nature of this link and of the OSO links in sulphones, with respect to the influence of the groups attached to sulphur; most of this work is being carried out with benzene derivatives because greater effects are produced by resonance with the ring structures.

In connection with the organic chemistry of phosphorous acid, $P(OH)_3$, it is of interest to observe that the acid is dibasic and probably is best represented by structure I, but that the organic

Phosphorous acid
I

Trimethyl phosphite
II



Dimethyl hydrogen phosphite
III

derivatives can have either a covalence of three as in structure II, or a covalence of four as in structure III.

The chemistry of phosphorus took on considerable importance about 30 years ago when it was found that phosphorus metabolism is important in the animal body (section 44.5). Phosphorus chemistry has been increasingly important since World War II as a result of German investigations in the fields of insecticides (section 43.15) and chemical warfare.

ARSENIC

34. 8. Derivatives of Arsine. The arsines are similar to amines and phosphines, but the arsenic compounds are generally less stable:

AsH_3	$H-As(H)-CH_3$	$CH_3-As(H)-CH_3$	$(CH_3)_3As$	$(CH_3)_4As^+OH^-$
Arsine	Methylarsine	Dimethylarsine	Trimethylarsine	Tetramethylarsonium hydroxide

Like the phosphines, the arsines are readily attacked by atmospheric oxygen with the formation of oxides and acids. The most important oxygen compound is that derived from the secondary arsine and known as *cacodyl oxide*. This is a liquid with a stupefying odor. Many cacodyl compounds can be obtained from this oxide, and are

$(CH_3)_2As-O-As(CH_3)_2$	CH_3-As-	$CH_3-As(CH_3)-Cl$
Cacodyl oxide	The *cacodyl* radical	Cacodyl chloride

regarded as combinations of the cacodyl radical and other elements. An example is cacodyl chloride.

Cacodyl, itself, $(CH_3)_2As-As(CH_3)_2$, is a flammable liquid with a horribly nauseous odor. The generic name of the cacodyl compounds was given to them by their discoverer from the Greek word for "stinking." They are all poisonous. The cacodyl compounds are historically important in having been among the first substances studied which were shown to contain a radical, $(CH_3)_2As-$, which passes unchanged from one compound to another (section 9.6).

Cacodylic acid, $CH_3-As(CH_3)(\rightarrow O)-OH$, is a crystalline substance, soluble in water. Its salts are used medicinally in the treatment of anemia.

ORGANOMETALLIC COMPOUNDS

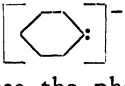
34. 9. Carbon Compounds and the Periodic System. Hydrocarbon derivatives of elements other than those of the nitrogen family and the sulphur family are also possible. A list of such compounds, containing elements from groups 1 to 7 of the periodic system, is shown in table 34.2.

TABLE 34.2. HYDROCARBON DERIVATIVES OF THE ELEMENTS ACCORDING TO THE PERIODIC SYSTEM

Group:	I	II	III	IV	V	VI	VII
	CH_3Na	$(CH_3)_2Mg$	$(CH_3)_3Al$	$(CH_3)_4C$	$(CH_3)_3N$	$(CH_3)_2O$	CH_3F
	CH_3K	$(CH_3)_2Zn$	$(CH_3)_3B$	$(CH_3)_4Si$	$(CH_3)_3P$	$(CH_3)_2S$	CH_3Cl
		$(CH_3)_2Hg$		$(CH_3)_4Ge$			CH_3Br
				$(CH_3)_4Sn$			
				$(CH_3)_4Pb$			
	← *Organometallic compounds* →				*Amines, etc.*	*Ethers, etc.*	*Halogen compounds*

The compounds to the right of the dotted line are types we have already studied in this book, that is, halogen compounds, ethers, amines, etc. Some of these compounds occur in nature.

The compounds to the left of the dotted line are the *organometallic* compounds. They are defined as compounds in which the C atom of an organic radical is directly linked to metal. Such substances never occur in nature.

Because the elements on the left of the periodic chart are metallic or electropositive in character, they do not, as a rule, form stable compounds with those hydrocarbon radicals which are also electropositive, such as CH_3. The further left we go in the table, the less stable are the organometallic derivatives. For example, methylsodium, $[CH_3:]^- Na^+$, is very unstable and one of the most reactive substances known; it burns spontaneously when exposed to the air. This has been mentioned in an early chapter in section 9.6. The electronic structure of methylsodium is interesting, and should be reviewed. Phenylsodium,  Na^+, however, is more stable than methylsodium because the phenyl radical is more electronegative than the methyl radical.

Many organometallic compounds have been made and some of them are of great use in modern life. One such compound is tetraethyllead, the principal constituent of the "ethyl fluid" added to gasoline to improve its qualities as a motor fuel. More complex examples of useful organometallic compounds are salvarsan and mercurochrome (section 43.8).

34. 10. The Grignard Reagents. By far the most valuable of the organometallic compounds is the family of substances known as the Grignard reagents. These were first prepared in 1899 by Barbier, but the credit for investigating their possibilities and uses is due to Grignard.

The preparation of a Grignard reagent can be written

$$Mg + R{-}X \rightarrow R{-}Mg{-}X$$

where R stands for practically any radical, X represents chlorine, bromine or iodine, and Mg is magnesium.

The actual laboratory manipulation is not so simple, because of the great reactivity of these substances. It consists in placing clean magnesium ribbon in carefully dried ether, and then adding the halogen compound. The reaction takes place as follows:

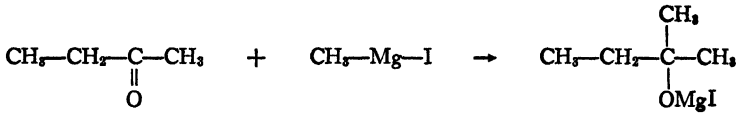
$$\underset{\text{Ethyl iodide}}{CH_3{-}CH_2{-}I} + Mg \rightarrow \underset{\substack{\text{Ethyl magnesium iodide}\\ \text{(A Grignard reagent)}}}{CH_3{-}CH_2{-}Mg{-}I}$$

The ingredients must be kept dry and in an inert atmosphere. With water, the Grignard reagent reacts in this way:

$$CH_3{-}CH_2{-}Mg{-}I + HO{-}H \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + \underset{\substack{\text{Basic}\\ \text{magnesium}\\ \text{iodide}}}{HO{-}Mg{-}I}$$

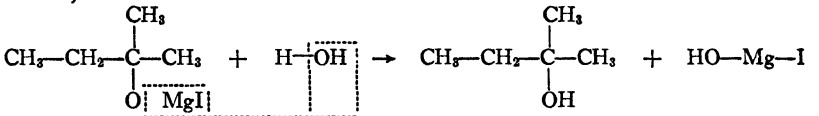
a *pure* hydrocarbon being formed. This is a good general method for preparing hydrocarbons, provided the proper Grignard reagent can be made in the first place.

No attempt is made to isolate the Grignard reagent. It is made in the ether solution when required and then mixed with other substances to create the desired products. For example, to prepare a tertiary alcohol (section 27.3), we can mix a ketone with a Grignard reagent,



2-Butanone
(A ketone)

and the initial complex substance formed is then decomposed with water,

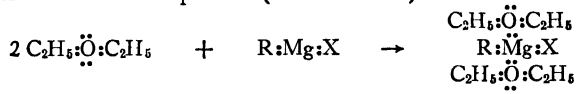


2-Methyl-2-butanol
(A tertiary alcohol)

Similarly, an aldehyde with a Grignard reagent yields a secondary alcohol.

By proper choice of the Grignard reagent and the molecule to which we add it, nearly all the fundamental types of structures known to organic chemistry can be prepared. The value of the Grignard reagents can be judged from the fact that the Nobel prize in chemistry was awarded to Grignard in 1912.

Ether plays an important part in the Grignard synthesis, because it can act as a base to the reagent, that is, it supplies electron pairs to form an oxonium compound (section 29.2):

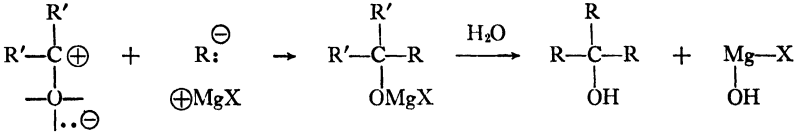


In this dietherate, the magnesium atom builds up a complete octet of electrons. It has been demonstrated, however, that the etherate is in equilibrium with other substances, as follows:

$R^{\bullet}$ $^{\bullet}MgX$	$R:^{-}$ ^{+}MgX	R_2Mg	MgX_2
Free radicals	Ions	Organomagnesium compound	Magnesium halide

These dissociation products account for the many types of reactions possible with the Grignard reagents, too numerous to be considered in this elementary study. In general, the Grignard reagent in ether will be attacked by a reactant which is more basic than ether to the reagent and will displace it; the importance of ether is that it is

basic enough to dissolve the reagent, but not so basic that it cannot be displaced. Although the nature of the intermediate complexes formed prior to ion formation is conjectural, on the electronic basis, the ketone reactant, described before, may be expected to displace the ether and behave as follows:



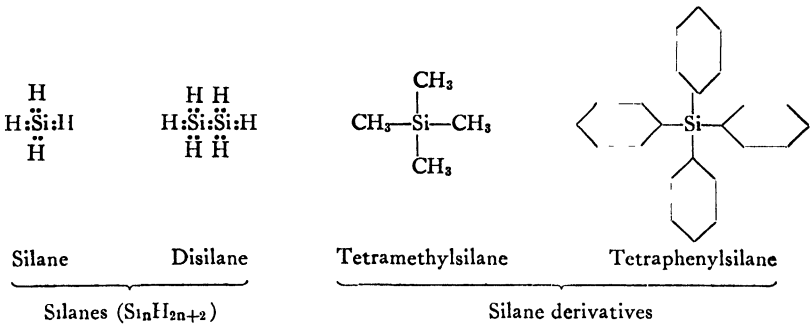
If a solvent more basic than ether is used (for example, pyridine), the reaction is slower and may give different products.

34. 11. Organosilicon Compounds. Just as oxygen is the most plentiful of the electronegative elements in the crust of the earth, silicon is the most plentiful of the electropositive elements. The two elements together constitute about 76 per cent of the earth's crust.

Although the organic chemistry of silicon (that is, preparation and study of compounds with the C–Si bond) had its origins in the middle of the last century, this family of compounds remained essentially laboratory curiosities until about 1940. During World War II, it was discovered that certain of the organosilicon compounds have important commercial uses, and they are now being made in large quantities.

Silicon, of all the elements, most resembles carbon. It is just below carbon in the periodic table of the elements. Like carbon, it forms compounds in which it has a valence of *four*, but unlike carbon, it also exhibits a valence of *six*, as it does in a fluosilicate, such as Na_2SiF_6, where the negative ion is $(SiF_6)^{=}$. This is due to the fact that silicon has a much larger atomic volume than the carbon atom (figure 6.2) and can attain a co-ordination number of six (section 8.1), especially when co-ordinated with a negative ion like F^-, which is quite small.

34. 11a. Silanes. Silicon forms silanes which are analogous to the paraffin hydrocarbons (table 10.2), and both aliphatic and aromatic derivatives of the silanes can be prepared.

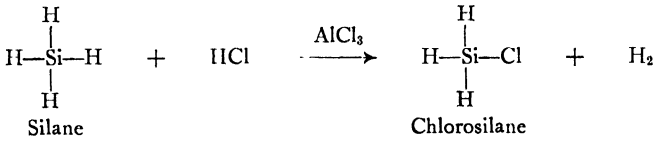


These two silanes are gases which are stable to heat, but are oxidized so readily that they ignite in air. When the Si–H bond is absent, as in the two derivatives shown here, this easy oxidation is no longer possible. In fact, the C–Si bond is more stable than C–C, and tetraphenylsilicon (tetraphenylsilane) is a solid which, when melted, can be distilled at 530°C. without decomposition. This is unusual stability for an organic compound.

Silanes with a Si–Si chain longer than six atoms have never been prepared, whereas in paraffin hydrocarbons C–C chains as long as seventy atoms are known (section 10.4). A method of preparation of silanes consists of treating a metallic silicide with an acid, which results in a mixture of products for which no simple reaction can be written.

$$MgSi \xrightarrow{HCl} SiH_4 + Si_2H_6 + MgCl_2 + SiCl_4, \text{ etc.}$$

Halogen derivatives of the silanes are not prepared by direct action of the halogen because of the violence of the reaction, but can be made by use of the halogen acid if assisted by a catalyst:

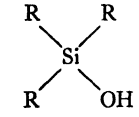


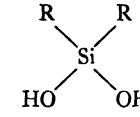
By this procedure, the more completely halogenated compounds can also be prepared, such as SiH_2Cl_2 *dichlorosilane*, and $SiHCl_3$ *trichlorosilane*. These compounds are useful in syntheses, just as

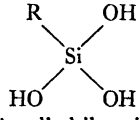
are the corresponding carbon compounds (section 9.4). For example, they can be methylated by means of the Grignard reagents:

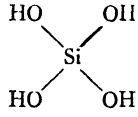
$$\underset{\text{Chlorosilane}}{SiH_3Cl} + CH_3MgCl \rightarrow \underset{\text{Methylsilane}}{SiH_3{-}CH_3} + MgCl_2$$

34. 11b. Silicones. Compounds obtained by hydrolysis of halogenated silanes are of great commercial importance. Typical halogen compounds are R_3SiCl, R_2SiCl_2, $RSiCl_3$, and $SiCl_4$. These give rise to the following hydroxy compounds when treated with water:

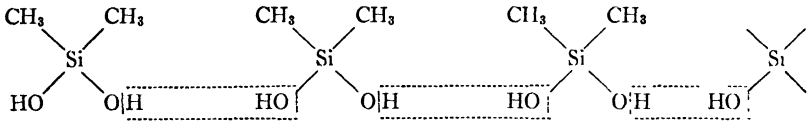

A trialkylsilanol


A dialkylsilandiol

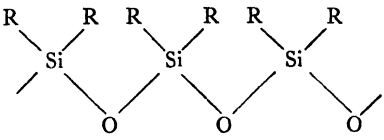

An alkylsilantriol


Orthosilicic acid

Orthosilicic acid forms esters, such as tetraethyl silicate, of some importance, but these compounds contain no C–Si bond and we shall not discuss them. The other types of compounds listed are used in large quantities to make *silicone resins* (section 46.9*a*) due to the ease with which they condense to form large polymeric molecules. The alkyl compounds are less stable (more easily condensed) than the aryl compounds where R is a phenyl group. For example, *diphenylsilandiol* $(C_6H_5)_2Si(OH)_2$ can be obtained as a simple crystalline compound, whereas the *dimethyl* compound condenses with itself as follows:



If a sheet of filter paper is held for a second in the vapor of dimethyldichlorosilane, hydrolysis takes place on the surface of the paper due to the water vapor normally present. The hydrolysis product reacts as just illustrated and the product which then coats the paper has the structure


A silicone

The paper, which is normally easily wetted, is now waterproof. The oxygen atoms in the chain are attached to polar groups in the paper, so that the paper presents a hydrocarbon surface, analogous to that illustrated in figure 31.1, which repels water.

SUGGESTED READING

American Chemical Society Committee on Nomenclature, Spelling and Pronunciation, "Organic Compounds Containing Phosphorus," and "Organosilicon Compounds," *Chem. Eng. News*, 30, 4515-4522 (1952).

Rochow, E. G., *An Introduction to the Chemistry of the Silicones*, 2nd Ed., John Wiley, New York, 1951.

PART 4
Special Topics in Organic Chemistry

In Chapter 1, we showed how organic chemistry originated about 150 years ago as the result of the discovery that the carbon atom is so closely associated with life.

Although it was easy enough to show that "the element carbon stands out as the central luminary in the great mystery of life" (see motto page), it was not so easy to demonstrate *why* it is so important. It took years of persistent endeavor to work out the principles governing the architecture of carbon compounds which we have described in part 2 and part 3 of this book. Now that these principles are well understood, progress is being made rapidly in the study of large classes of compounds that are of interest because they are an essential part of living nature.

In part 4, we shall point out as briefly as possible the fundamental characteristics of proteins, dyes, sugars, etc., substances of so great importance physiologically and industrially. It will be apparent to the student that the structures of these more complex molecules are not at all terrifying, provided we have a thorough knowledge of the various kinds of structural groups described in part 3.

In a book of this size we cannot go into great detail, but we can, even in a small space, make an instructive survey of these interesting fields. For example, in chapter 31 we defined soaps, fats, and waxes in a few pages, although there is an encyclopedia on fats consisting of three large volumes.

35. STRUCTURES OF COMPLEX COMPOUNDS

35. 1. Introduction. In this elementary book we have not used the standard system of teaching organic chemistry. In many cases, we have given the structure of a compound without any proof and then explained its chemistry, whereas the more orthodox procedure is to prove the structure of a substance before explaining its chemistry.

Now, we shall attempt to make up for this deficiency by touching briefly on various chemical and physical methods often used by the research worker in the determination of structure.

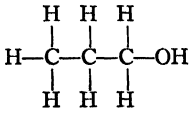
Unraveling the secrets of molecular structure is one of the great interests of the organic chemist. This he does in three steps. First, he decomposes the molecule into recognizable fragments. After finding out the nature of these fragments, he puts them together on paper to give the possible structure of the complex molecule. Lastly, he tries to duplicate the original complex in the laboratory by a synthetic method.

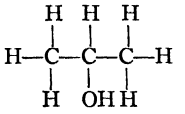
For example, distillation of rubber yields a fragment which has been recognized as isoprene (section 37.6). Research done on isoprene indicates that it is truly the building unit of the rubber molecule. It remains to determine how these units are linked together in the natural substance.

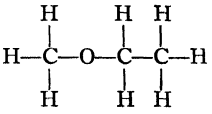
35. 2. Structure from Chemical Properties. The determination of the various structural groupings in a molecule requires a

good working knowledge of the principles we have met in part 3 of this book. The application of these chemical principles may be illustrated by the following simple example.

Assume that a liquid substance is found by a qualitative analysis to contain only the elements carbon, hydrogen, and oxygen and that a quantitative analysis shows the composition to be C_3H_8O. Since carbon always has a valence of four ($-\overset{|}{\underset{|}{C}}-$), the possibilities narrow down to these three structures:


1-Propanol


2-Propanol


Methyl ethyl ether

The alcohols and ethers are different in their chemical properties and only a few simple tests are necessary to prove the structure of the unknown substance. If metallic sodium dissolves in the liquid with evolution of hydrogen (section 27.3) and if the substance reacts with acetyl chloride to form an ester (section 31.8*c*), the substance is an alcohol. If, on treatment with concentrated HI, the substance breaks down as shown in section 29.2, it is an ether.

If we find the substance is an alcohol, then, by oxidizing it, we can determine whether it is 1-propanol or 2-propanol. On oxidation, the primary alcohol would yield an aldehyde, whereas the secondary alcohol would result in a ketone (section 27.4*c*).

35. 3. Structure from Physical Properties. To solve the simple problem described in the preceding section, we really need nothing more than a few physical properties. The different structural possibilities are easily worked out on paper, and the physical properties of each of these possible compounds can then be compared with accepted values given in the handbooks of chemistry. The physical properties usually employed for identification are odor, melting point, boiling point, density, refractive index, etc. The two alcohols and the ether which we have just discussed can easily be differentiated by their boiling points.

35. 3a. Refractive Index. Physical properties are used not only for identification, but also for proving the structures of substances.

In section 39.6 will be found the structures of two isomeric sugars. In one case, two neighboring —OH groups are on the same side of the ring; this is called the α-sugar. In the β-sugar, these same two —OH groups are on opposite sides of the ring. When two —OH groups are adjacent the compound always has a slightly higher refractive index than when they are opposite each other. Refractive index measurements have, therefore, been used to prove the structures.

The effect of structure on refractive index is also illustrated by these compounds:

$CH_2=CH-CH_2-CH_2-CH=CH_2$ Diallyl

$CH_3-CH=CH-CH=CH-CH_3$ Isodiallyl

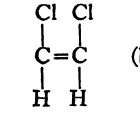
The *iso* compound has a higher refractive index, which leads to the conclusion that the double bonds are conjugated (section 18.1). Conjugated systems of double bonds commonly give rise to such an *optical exaltation.* The student should refer to the allyl group (section 25.4) for the nomenclature of these compounds.

Refractive-index data are often found listed in terms of *molar refraction*, R_M, which is calculated from the refractive index n, the density d, and the molecular weight M by the following expression:

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

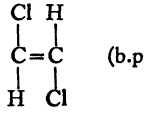
The value depends on the wavelength of light used (which is usually the D-line of the sodium spectrum).

35. 3b. Dipole Moment. Measurements of certain physical characteristics have, in some cases, even changed our notions as to the identity of compounds that had long been thought of as definitely known. The following *cis*, *trans* isomers analogous to those described in section 22.3,



(b.p. 60.2°)

cis-Dichloroethene



(b.p. 48.3°)

trans-Dichloroethene

are now known to have the boiling points as indicated, but up to comparatively recently it was thought that *trans*-dichloroethene boils

at 60.2°C. and the *cis* compound at 48.3°C. The error was recognized when the dipole moments (section 8.3) were measured. The dipole moment of the *trans* compound is zero and that of the *cis* isomer is relatively high according to the theory of dipole moments. The boiling points, shown with the structures, correspond to these respective dipole moments.

35. 3c. Absorption Spectrum. This is one of the physical phenomena widely used in the study of molecular structures. Many molecules have vibrating groups or atoms which absorb in the infrared, as described in section 13.14. Catalogs of these absorption spectra are of great value when investigating the nature of the groupings in a compound of unknown structure. The student should also refer to the opening paragraphs of chapter 42 for a discussion of absorption spectra of colored compounds.

In the structure of ergosterol (section 44.2), the positions of the double bonds were long in doubt and some investigators resorted to the use of absorption-spectra measurements of ergosterol and related compounds of known structure in their attempts to solve the problem. Closely related to absorption phenomena is the Raman effect (section 13.15). Many interesting facts on the structure of organic compounds have come to light as a result of the study of Raman effects. For example, the C=C bond produces twice the shift of the C–C bond, and the C≡C shift is three times as great. It is evident that the Raman effect is a structural effect.

35. 3d. The Parachor. The last physical method of structure determination we shall describe is the measurement of the parachor, often known as Sugden's parachor, after its discoverer. In its simplest form the equation for the parachor is

$$P = V\gamma^{1/4}$$

where V is the molecular volume and γ is the surface tension of the substance. The molecular volume means the molecular weight divided by the density.

The parachor is in general a completely *additive* property. It is a function of (1) the kinds of atoms in the molecule, (2) the number of each kind of atom, and (3) the structural arrangement of the atoms.

The parachor, P, for CH_3–CH_3 is 110.5, whereas for CH_3–CH_2–CH_3 it is 150.8. The difference is the value of P for –CH_2 and is

40.3. The value of P for $-CH_2-$ has been obtained from many series of compounds, such as C_3H_6O and C_4H_8O, $C_2H_4O_2$ and $C_3H_6O_2$, etc. The average value of the parachor for $-CH_2-$ from all these determinations is $P = 39.0$.

The value of P for the H atom is 17.1, and the same value is obtained from measurement with liquid hydrogen as from difference measurements in organic compounds.

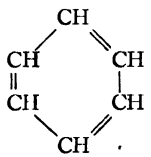
Since the parachor of $-CH_2-$ is 39.0 and of two H atoms is 34.2, the parachor of the carbon atom is 4.8.

A few atomic parachors and structural parachors, sufficient to serve as illustrations, are as follows:

Atomic Parachors		*Structural Parachors*	
Carbon	4.8	Double bond	23.2
Hydrogen	17.1	Triple bond	46.6
Nitrogen	12.5	5-Membered ring	8.5
Oxygen	20.0	6-Membered ring	6.1

An interesting application of the parachor is its use in confirming the Kekule structure of benzene. According to accepted theory, there are the following atoms and structural arrangements in benzene:

6 H atoms	= 102.6
6 C atoms	= 28.8
3 Double bonds	= 69.6
6-Membered ring	= 6.1
	207.1



The actual parachor value for benzene, obtained experimentally, is 206.2, indicating that our conception of the benzene ring as a special case of an alternate ring of single and double bonds is consistent.

35. 4. Synthetic Methods. In this book, we have laid little stress on the synthesis of organic compounds, because we have tried to keep the reader's attention on just one topic — the architecture of compounds.

When it was necessary to show how one type of structure can be developed from another, we indicated how synthetic processes are sometimes employed. In such instances, however, the synthetic method that we used in these pages may not be a popular method in the laboratory. For example, the Wurtz synthesis which we made

so much use of in chapter 10 does not occupy as important a position in laboratory practice as it does in the lecture room.

The reader will find it instructive to review the various synthetic methods and chemical operations, such as substitution, hydrolysis, esterification, etc., which can be found by consulting the index. For more thorough treatment of these topics, the larger textbooks and laboratory manuals of organic chemistry should be consulted.

SUGGESTED READING

Barnes, R. B., U. Liddel, and V. Z. Williams, "Infrared Spectroscopy," *Ind. Eng. Chem., Anal. Ed.*, 15, 659-709 (1943).

Glasstone, S., *Textbook of Physical Chemistry*, 2nd Ed., Chapter VIII, Van Nostrand, New York, 1946.

Hibben, J. A., *The Raman Effect and Its Chemical Applications*, Reinhold, New York, 1939.

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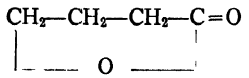
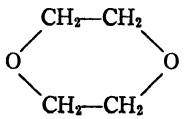
36. HETEROCYCLES AND CONDENSED CYCLES

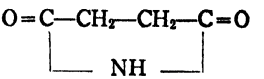
36. 1. Heterocyclic Compounds. In part 3 of this book we met a number of ring compounds containing in the ring other atoms besides the usual carbon atoms. As examples we may recall the following compounds:



Butyro*lactone*
(section 32.6)



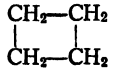
Dioxane
(section 29.4)



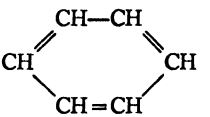
Succin*imide*
(section 33.12)

These are called heterocyclic rings because there are several different kinds of atoms in the ring (from the Greek *heteros*, meaning other).

Heterocyclic rings are to be distinguished from the homocyclic rings in which all the atoms are the same (from the Greek *homos*, meaning one and the same). The following compounds are familiar examples of homocycles:



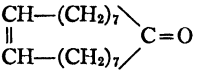
Cyclobutane



Benzene

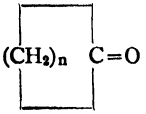
Before proceeding, it is of interest to note that many heterocyclic compounds have recently been prepared in which the rings are quite large. Up to recent years, no ring of more than six carbon atoms had been found in living nature, as discussed in section 12.8. In

1926, however, it was shown that the odorous substance *civetone*, obtained from the civet cat, is a ring compound which has the composition $C_{17}H_{30}O$, and the structure

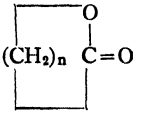


This is a *homo*cyclic compound and is an unsaturated ketone.

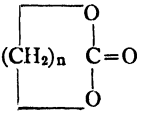
As a result of this discovery related compounds containing up to about thirty carbon atoms in the ring have been prepared. Since such compounds are of importance to the perfumer, research has led to the preparation of other large rings and many compounds of the following types are now known:



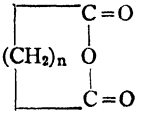
(Homocyclic)
A ketone
(section 30.1)



(Heterocyclic)
A lactone
(section 32.6)



(Heterocyclic)
A carbonate
(section 32.7)

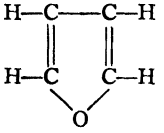


(Heterocyclic)
An anhydride
(section 31.13)

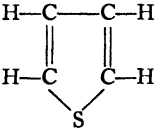
The musk odor, which is especially desired, depends on the presence of the C=O group, and is most pronounced in a ring of about fifteen carbon atoms.

The heterocyclic compounds described in the preceding paragraphs are members of the *aliphatic* series of compounds. In other words, they are simply closed chains. We shall devote most of this chapter to a study of compounds which are not only heterocyclic in character but are also *aromatic*. These compounds have the peculiar properties of the benzene ring (section 36.3) and are the compounds people usually refer to when they speak of heterocyclic compounds.

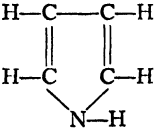
36. 2. Five-Membered Heterocycles. The most important heterocyclic compounds with five atoms in the ring are these three:



Furan



Thiophene



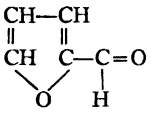
Pyrrole

According to these structures, the compounds appear to be unsaturated, because of the C=C bonds and should, therefore, resemble the olefins quite closely. They do undergo addition reactions, but not as readily as the olefins. In their chemical behavior, they are

more like benzene. For example, thiophene is always present to the extent of about 0.5 per cent in the benzene obtained from coal tar, but its presence was not suspected until 1883, because it behaves so much like benzene. It will be remembered that one name for benzene is phene (section 19.4), and this sulphur compound was accordingly called *thio*phene when it was discovered.

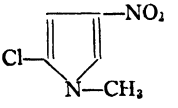
Pyrrole is by far the most important of the five-membered heterocycles. The pyrrole ring occurs in many complex compounds found in living nature. Such substances are the chlorophyll of leaves, the coloring matter of the blood, the nicotine of tobacco, and the decomposition products of the proteins.

The furan ring is present in the structure of certain types of sugars (section 39.7). An important commercial substance containing the furan ring is furfural or furfuraldehyde. This is a liquid with many uses and is obtained, on a large scale, by the distillation of corncobs and cornstalks with dilute acids. It may also be prepared by the dehydration of pentose sugars (section 39.2). Its structure is given, together with the general method of naming derivatives of five-membered rings:



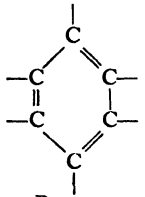
Furfural

Scheme for naming derivatives of five-membered rings

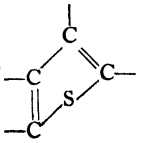


1-Methyl-2-chloro-4-nitropyrrole

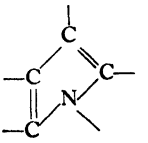
Because the five-membered heterocycles described in this section are similar to benzene in their aromatic properties, their structures will sometimes be found written as follows to show more clearly the resemblance to benzene:



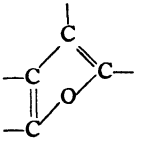
Benzene



Thiophene



Pyrrole

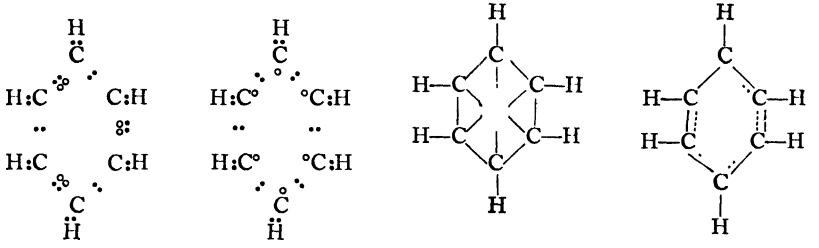


Furan

This kind of graphic formula indicates that the –S– bridge, for example, can replace the $-\overset{|}{C}=\overset{|}{C}-$ group in the benzene ring without causing any serious upset in the aromatic properties. This "steric"

theory of aromaticity is now superseded by the theory to be described in the following section.

36. 3. Sextet Theory of Aromatic Character. Modern electron theory ascribes the aromatic nature of the five-membered rings (and of the benzene ring) to a *sextet* of electrons peculiar to these structures. The student should first review the benzene ring, for which the usual Kekulé formula is given in the introductory paragraphs to this chapter. Other methods of writing benzene are shown in structures I to IV, the proper understanding of which requires a



I — Showing three pairs of π electrons (small circles).

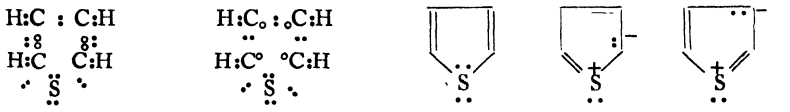
II — Showing six "uncoupled" π electrons (small circles).

III — A centric formula.

IV — Thiele formula.

Formulas for benzene

review of the nature of π electrons in section 17.3 and of the Thiele formula in section 19.2. If the π electrons are uncoupled (structure II), they may undergo interaction in the molecule through carbon atoms opposite each other as in structure III, or the interaction may be peripheral through adjacent carbon atoms as in structure IV.



V — Thiophene

VI

VII VIII IX — Some resonance structures of thiophene

The symmetrical structures shown in III and IV were invented long before the electron conception of valence.

If we similarly write a five-membered heterocycle on the electron basis as shown in structures V and VI, we find that in VI there is a

sextet of electrons available to the ring for interactions. Four of these electrons (small circles) are the π electrons on the four carbon atoms. Two of the electrons (dots) are from the *hetero* atom, in this case the sulphur atom. All the five-membered heterocyclic compounds mentioned in section 36.2 have such a sextet of electrons.

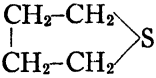
A good pictorial representation of these compounds is given in figure 19.3, which shows that the six mobile π electrons of the benzene ring occupy a π orbital which consists of two parallel doughnuts in which these electrons can circulate around the ring. This π-type of orbital of benzene is retained in the thiophene molecule because the sulphur atom can contribute a pair of π electrons, which share a π orbital with the four π electrons from the carbon atoms in the ring. This will be clear if we examine the distribution of the six electrons in the valence shell of the $\cdot\ddot{S}\cdot$ atom, which is identical with that of the oxygen atom (section 7.8); this distribution is s^2, p_x^2, p_y, p_z.

We can disregard the pair of s electrons. The p_y and p_z electrons pair with electrons of carbon atoms to give the *sigma* type bonds, C–S–C. The pair of p_x electrons is in an orbital at right angles to the ring (compare the CO_2 structure in figure 18.4). That orbital can, therefore, assume a position in which it overlaps with the corresponding orbitals of the adjacent carbon atoms. The *pi* molecular orbital which results is an extension of that formed by the four carbon atoms and completes the doughnuts as in figure 19.3. The orbital now holds four π electrons from the four carbon atoms, and two π electrons from the single sulphur atom. The aromatic properties of the benzene ring, in so far as they are due to a sextet of electrons, are, therefore, retained in the thiophene molecule.

A characteristic of these aromatic rings is that they are flat; all the atoms are in the same plane as in benzene, not staggered as in figure 12.15. This is a consequence of resonance. It is important to recall that the benzene-ring system is stabilized by resonance, and in section 19.3, we calculated the resonance energy to be 36 kg. cal. Resonance implies a realignment of atoms during an electronic vibration cycle, which is of the order of 10^{-13} second as pointed out in section 18.5. This does not give the atoms time to get out of a planar arrangement; in other words, a molecule like benzene, which is in resonance, is necessarily flat (see figure 36.1). When a valence link between two atoms has double-bond character, this link is said

to be coplanar and the atoms directly attached to it are in the same plane. Resonance stabilization, as well as a sextet of electrons, must be considered a necessary factor in "aromatic" behavior.

A few of the possible resonance structures which can be written for a heterocycle like thiophene are shown in VII, VIII, and IX, where it will be seen that an electron pair from the *hetero* atom can distribute itself over the entire ring. (The scheme for working out such diagrams was described in section 21.5.) As a result of this contribution of an electron pair to the aromatic sextet of the ring, thiophene is not capable of forming sulphonium salts (section 34.4), whereas such salts can easily be made from the saturated compound,



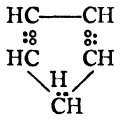
, for which resonance structures are not possible.

The ease with which the *hetero* atom contributes to the aromatic ring sextet is a measure of the aromatic stabilization conferred on the ring by resonance. The estimated resonance energies are listed in table 36.1.

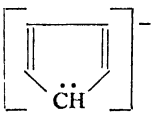
TABLE 36.1. RESONANCE ENERGIES OF HETEROCYCLIC COMPOUNDS

	kg. cal./mole
(Benzene)	36
Thiophene	31
Pyrrole	22.5
Furan	21.5
Pyridine	43

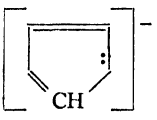
In connection with the aromatic sextet of the five-membered heterocycles, it is of interest to look into the properties of the related homocyclic compound, cyclopentadiene (formula X). This compound does not have aromatic properties (see section 36.8) and has but a very small resonance energy. An important characteristic is its acidity; one of the H atoms in the CH_2 group can be replaced by a



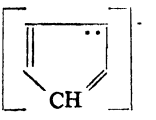
X



XI



XII



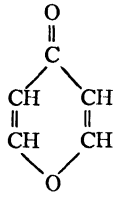
XIII

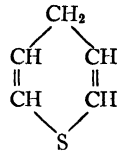
Cyclopentadiene Some resonance structures of the negative ion of cyclopentadiene

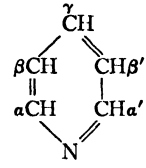
metal, such as potassium. If an H^+ ion leaves the molecule, an electron pair is exposed; this completes the sextet and the *negative*

ion, therefore, has aromatic stability. A number of resonance structures for the ion can be worked out, but only a few are given here (XI, XII, and XIII). The stability of the ion due to this resonance is responsible for the acidity of the compound, for the same reasons as given under phenol (section 28.2) and under acetic acid (section 31.6). Alternatively, acidity of cyclopentadiene (tendency to ionize) can be attributed to the demand set up by the ring structure for a pair of electrons to complete the aromatic sextet.

36. 4. Six-Membered Heterocycles. The cyclic compounds shown in the following with six atoms in the ring contain the same *hetero* atoms as the corresponding five-membered rings which we have just described. The student should work out their electronic formulas and observe that they all have a *sextet* of electrons in the ring. A method of naming the substitution products is shown in the formula


γ-Pyrone


Penthiophene


Pyridine

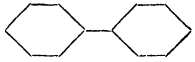
of pyridine. Another system is to number the atoms in the ring, starting with the *hetero* atom, as described for the five-membered ring in section 36.2. Thus, 2-chloro-5-nitropyridine is the same thing as α-chloro-β′-nitropyridine.

Pyridine is a colorless liquid, miscible with water. It has a characteristic, unpleasant odor. When greatly diluted, the odor is that of stale tobacco smoke. It is one of the chief constituents of bone oil. Pyridine is an unusually stable substance, more stable in fact than benzene itself. Substitution in the pyridine ring takes place less readily than in the benzene ring. The pyridine ring occurs in many complex substances in nature, such as nicotine and other alkaloids (section 43.6). The structure of pyrimidine should also be referred to, in section 43.5.

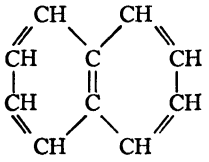
The pyrone ring is found in certain types of sugars (section 39.7) and in some of the compounds present in the coloring matter of flowers. γ-Pyrone itself is interesting because of its tendency to form salts. This is supposedly due to the ability of the oxygen atom

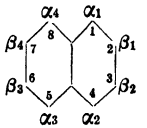
in the C=O group to form *oxonium* compounds, similar to those described in sections 27.3 and 29.2.

α- and β-Pyrones are also known. Penthiophene is unimportant.

36. 5. Condensed Cycles. In section 25.4 we showed how two cyclic structures may be linked in this manner,  , to form what may be called a *polycylic* compound.

Many polycyclic compounds are known, however, in which the rings are joined in a much closer type of union. These are called condensed cycles. An important example is naphthalene; it will be seen that naphthalene is also *homo*cylic in that the rings contain only carbon atoms.



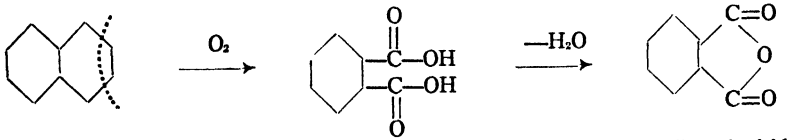


Naphthalene

Naphthalene, $C_{10}H_8$, is present in quite large quantities (5–10%) in coal tar. It is a colorless, crystalline solid, and has a characteristic odor resembling that of coal tar itself. It is used in large quantities in making dyes (section 42.10) and lampblack, and as an insecticide.

The chemistry of naphthalene is similar to that of benzene. There are eight hydrogen atoms in naphthalene which can be replaced by other atoms or groups, and for reference, their positions are designated, as shown, by either numbers or Greek letters. Thus, α_1 α_4-dichloronaphthalene is the same thing as 1, 8-dichloronaphthalene. Ten isomers of such a *di*-substitution product of naphthalene are possible according to our structure theory and for the dichloro compounds they are all known.

When naphthalene is oxidized, one ring is destroyed:

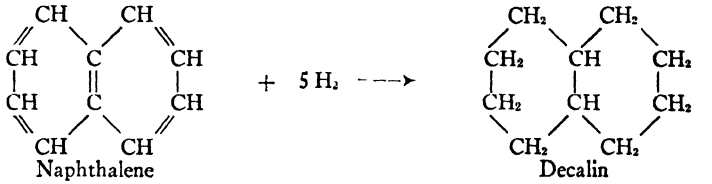


Naphthalene Phthalic acid Phthalic anhydride

The phthalic acid formed is a compound with the two COOH groups *ortho* to each other. This has been proved by its chemical behavior.

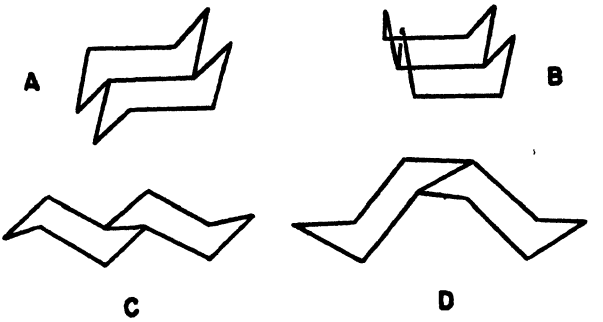
It is also a proof that the two rings in naphthalene are joined to each other through the *o*- carbon atoms. Phthalic anhydride is an important intermediate in synthetic chemistry (section 42.11).

Naphthalene can be reduced to a completely saturated compound, just as benzene can be reduced to cyclohexane (section 19.2):



Naphthalene Decalin

This decahydronaphthalene, commonly called decalin, is the object of considerable interest in connection with the theory of ring structures. It was suggested in 1891 by Sachse, and again in 1922 by Mohr, that decalin should exist in two isomeric forms if the rings of carbon atoms are staggered as shown in figures 12.14 and 12.15. The Sachse-Mohr configurations are shown in (A), which was built from *trans*-cyclohexane rings to represent *trans*-decalin, and in (B), built from *cis*-cyclohexane rings to represent *cis*-decalin.

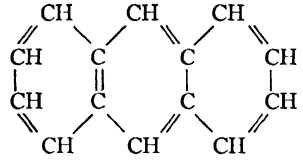


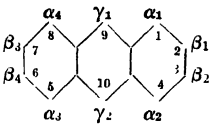
Two different decalins have actually been made. If naphthalene is hydrogenated in glacial acetic acid, a form is obtained which boils at 193°C. and is called *cis*-decalin, whereas hydrogenation of naphthalene in the gas state yields a modification labeled *trans*-decalin that boils at 185°C. The structures of the decalins have been studied with modern experimental methods, including electron diffraction patterns in the vapor phase, light scattering in the liquid phase, and calorimetric measurements as described in section 13.11. A recently recommended configuration for *trans*-decalin is (C) and

for *cis*-decalin is (D), with some evidence that below 50°C. the *cis* form is (B). Other structural configurations which can be assembled from atom models have also received consideration.

As for naphthalene itself, it is probable that the two rings are perfectly plane, as in the case of benzene (section 19.6).

Anthracene, $C_{14}H_{10}$, is a three-ring cyclic compound. Like naphthalene, it consists of *condensed* cycles. Anthracene is present to a small extent (0.5 per cent) in coal tar. The name is derived from the Greek word, *anthrax*, for coal. It is a colorless, crystalline compound, with a blue fluorescence.

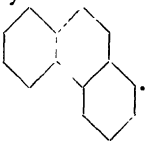




Anthracene

There are ten replaceable H atoms in anthracene, so that possibility of isomerism of substitution products is extensive. There are three possible isomers of chloroanthracene, in which α-, β-, or γ-hydrogen atoms are replaced, and all three are known.

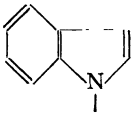
In general, anthracene is more reactive than benzene. It is especially sensitive to oxidizing agents, the sensitive positions being the carbon atoms 9 and 10, which are oxidized to C=O groups. The oxidation product is anthraquinone, the structure of which is to be found in section 42.9 in the formulas of a few common dyes.

An important isomer of anthracene is phenanthrene,  .

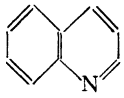
This ring system is found in certain alkaloids such as morphine (section 43.6).

36. 6. Condensed Heterocycles. In the preceding section, we described condensed cycles which consist of two or more benzene rings. In nature, a great many compounds are found which consist of several rings of different kinds. The names and outline structures of some important substances of this type are shown in the following examples. With the name of each of these compounds will be found the names of the two cycles which are present in the structure. All these examples are compounds in which one of the rings is *heterocyclic*.

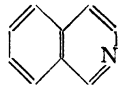
Indole is the parent substance of many compounds of physiological interest, especially among the proteins, and is closely related to indigo (section 42.12). *Chromone*, as its name implies (Greek *chroma*, color), is an ingredient of the coloring matter of flowers in combination with



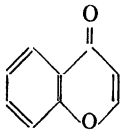
Indole
(Benzene
+ pyrrole)



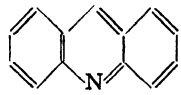
Quinoline
(Benzene
+ pyridine)



Isoquinoline
(Benzene
+ pyridine)



Chromone
(Benzene + γ-pyrone)



Acridine
(Benzene + pyridine)

sugars and phloroglucinol (section 28.5). *Quinoline* and its isomer, *isoquinoline*, occur to a small extent in coal tar and bone oil. They are the principal constituents of the molecules of many alkaloids (section 43.6). *Acridine* is present in crude anthracene. Many important dyes are made from it.

36. 7. Cyclooctatetraene. In this chapter (section 36.3), we explained the aromatic behavior of benzene as due to interaction of a sextet of π electrons in the ring. For a long time, it was thought that aromatic nature was due to the conjugate system of double and single bonds in a ring. This theory could have been tested by studying the properties of cyclooctatetraene (see figure 36.2) which contains such a conjugate system in an eight-membered ring. However, the synthesis of this compound was so difficult that quantities sufficient for thorough study did not become available until very recently (the result of a German discovery that it can be made from acetylene by polymerization with a catalyst under pressure). The properties of cyclooctatetraene are now known to be not aromatic but olefinic, indicating that the conjugate system does not necessarily confer benzenoid behavior on the ring.

It is obvious that the ring system in cyclooctatetraene contains eight π electrons rather than the six believed to be responsible for aromatic behavior. Furthermore, spectral studies of the molecule have shown that the eight-membered ring is not flat. Most organic

chemists favor the "tub" structure shown in figure 36.2, which was built from models that employ conventional single and double bonds. Another configuration which has been seriously considered as a result of spectral analysis is the "crown," in which the arrangement of single and double bonds resembles that of the single bonds in the *trans* cyclohexane ring (figure 12.15). However, such a cyclooctatetraene structure cannot be assembled from the conventional atom models without introducing a very large strain into the ring.

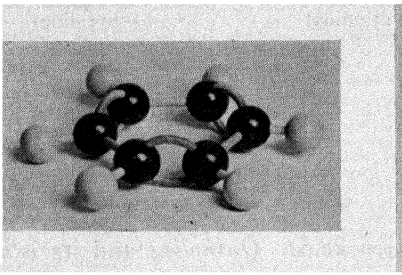


FIGURE 36.1. Cyclohexatriene, C_6H_6 Benzene.

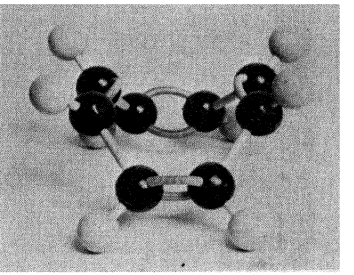
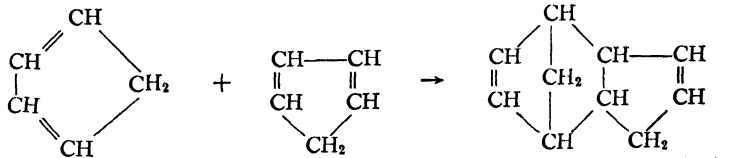


FIGURE 36.2. Cyclooctatetraene, C_8H_8 "Tub" form.

The molecule pictured in figure 36.2 does not permit the resonance phenomenon responsible for aromatic nature, which requires a *flat* structure like that in figure 36.1.

36. 8. Cyclopentadiene is a compound of commercial importance and in section 36.3 it was shown to be of much theoretical interest in connection with problems discussed in this chapter. It is a homocycle related to the heterocycles described in section 36.2. It does not present a sextet of electrons to the ring and is, therefore, not aromatic. On the contrary, cyclopentadiene is a typical olefin; an



1,3-Cyclopentadiene (C_5H_6) (2 molecules)

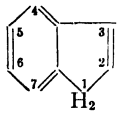
Dicyclopentadiene ($C_{10}H_{12}$)

example of this behavior is the ease with which it combines with itself by the 1,4-addition mechanism (section 18.1).

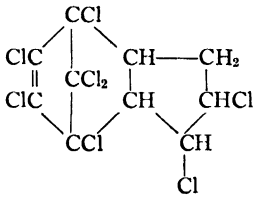
This is an illustration of the Diels-Alder synthesis, which is widely

used for the preparation of polycyclic compounds containing six-membered rings.

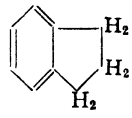
This series of compounds offers a useful lesson in nomenclature, for their *chemical* names bear little relation to the compounds from which they are made. Dicyclopentadiene is considered to be derived from a parent hydrocarbon known as *indene* (found in coal tar), the carbon atoms of which are numbered as shown here. On this basis, dicyclopentadiene is 4,7-methano-4,7-dihydroindene. The name can be modified by using "*endo*methylene" instead of "methano," the term *endo* (within) being employed to indicate the presence of the bridge between two atoms in the ring (in this case, carbon atoms 4 and 7).



Indene



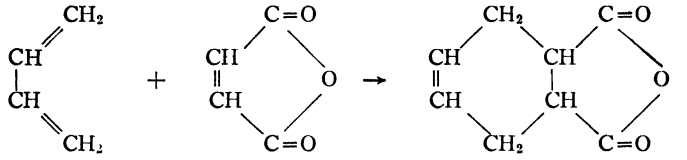
Chlordan



Indan
2,3-Dihydroindene

Chlordan is an important insecticide made from cyclopentadiene. by first combining, through the Diels-Alder reaction, one molecule which has been completely chlorinated from C_5H_6 to C_5Cl_6, with a second molecule which has not been treated. The addition compound is then further chlorinated to $C_{10}H_6Cl_8$ which was originally called Compound 1068. The chlorine in this last step replaces an H atom at the 1 position, eliminating a molecule of HCl which then adds to the 2,3 double bond. Chlordan is generally called a derivative of indan; the chemical name of chlordan is then 1,2,4,5,6,7,8,8-octachloro-4,7-methano-3a,4,7,7a-tetrahydroindan. It has also been named as a derivative of 2,3,3a,4,7,7a-hexahydroindene.

The Diels-Alder synthesis is so general for molecules with a conjugate olefinic system that this synthesis is often used to determine if such a structure is present in a compound. One of the favorite reagents is maleic anhydride, which adds on conjugate systems very readily. The student should compare maleic anhydride with succinic acid (section 31.13) and with malic acid (table 32.1). It is also of interest to observe that the presence of an active conjugate system



1,3-Butadiene (section 18.1) Maleic anhydride Tetrahydrophthalic anhydride

in the middle ring of anthracene (section 36.5) can be proved by its reaction with maleic anhydride; the student should try to work out the structure of the addition product. Diels and Alder received the Nobel prize in chemistry in 1950. Their names became part of our language when two powerful insecticides known as *dieldrin* and *aldrin*, related chemically to chlordan, were introduced commercially.

SUGGESTED READING

Elderfield, R. C., *Heterocyclic Compounds*, first volume of series, John Wiley, New York, 1950.

Hartough, H. D., "The Chemical Nature of Thiophene and Its Derivatives," *J. Chem. Educ.*, **27**, 500 (1950).

37. THE ROLE OF ISOPRENE IN NATURE

37. 1. The Isoprene Skeleton. Isoprene is related to 1,3-butadiene, a compound to which we have already given some attention because of its characteristic arrangement of single and double bonds (section 18.1). The composition of isoprene is C_5H_8, its structure is $CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2$, and its systematic name is 2-methyl-1,3-butadiene. It is a liquid which boils at 34° C., and it may be prepared by the dry distillation of India rubber, or by passing turpentine through a red-hot tube.

Nature has used the isoprene skeleton, $C-\underset{\displaystyle C}{\overset{|}{C}}-C-C$, in the design of an enormous number of compounds of vital importance to man. She has used it to build molecules that are essential constituents of rubber, of the green pigments in leaves, of the yellow pigments in carrots and other vegetables, of the red pigments in tomatoes, of the yellow coloring matter in egg yolks, of some essential oils used as perfumes, and of many other substances in plant and animal life.

In this chapter, we shall describe the structures of some important groups of compounds occurring in nature which illustrate the character of "isoprene chemistry."

37. 2. Terpenes. The terpenes are widely distributed in nature, as shown by the substances listed in table 37.1.

These substances may appear to be very complex at first glance, and, in fact, we must admit that they are complex. However, the

structure of terpenes becomes a comparatively simple thing to understand as soon as we see their relationship to isoprene as indicated in figure 37.1. In these models the carbon atoms of the isoprene

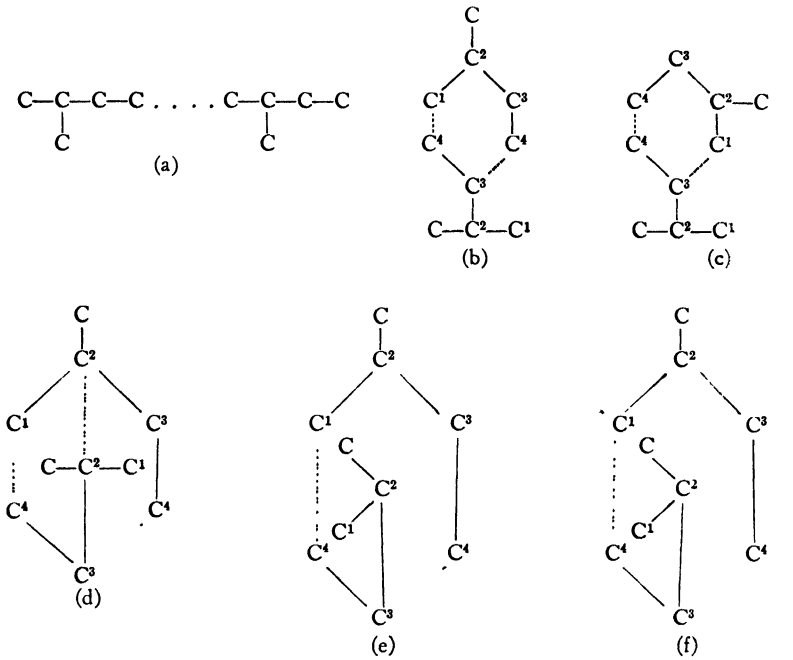
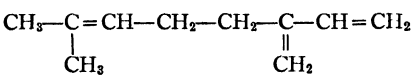


FIGURE 37.1. Outline structures of terpenes.

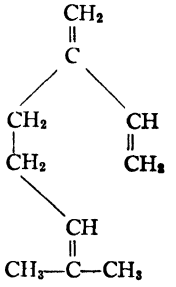
skeleton are numbered thus, C^1–C^2(–C)–C^3–C^4, for reference; the fifth carbon atom does not need a number. In each case, we have shown how *two* isoprene skeletons can be combined to form a chain or a ring compound. Model (a) is the simple union of two isoprene structures in *open-chain* formation. Models (b) and (c) represent the outline structures of the *monocyclic* terpenes. The last three models show the nature of the *bicyclic* terpenes.

Although the terpenes occur in two structural styles, namely, open-chain and closed-chain, the two types are probably closely related. This structural relationship can be illustrated by writing the formula of myrcene, an open-chain terpene, in the following ways:



Myrcene, $C_{10}H_{16}$
(Occurs in oil of bay)

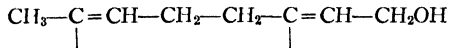
or



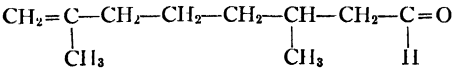
In many cases, this chain-type compound can be converted to a cyclic terpene by reactions involving the simple closure of the ring.

Terpenes consist of two condensed molecules of isoprene, the composition of which is C_5H_8. Terpenes may, therefore, be defined as unsaturated hydrocarbons of the composition $C_{10}H_{16}$. It must be emphasized that the cyclic terpenes, as well as the straight-chain terpenes, are typical olefin compounds and have the general properties of compounds containing C=C bonds. They are not aromatic in character, like the compounds of the benzene series.

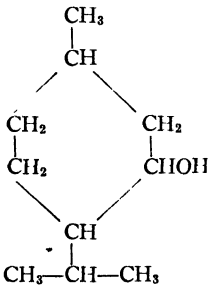
TABLE 37.1. TERPENES, $C_{10}H_{16}$, AND RELATED COMPOUNDS



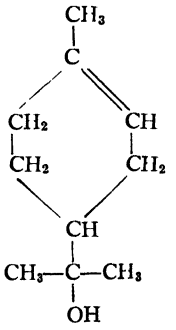
Geraniol, $C_{10}H_{18}O$
Chief constituent of Indian geranium oil.



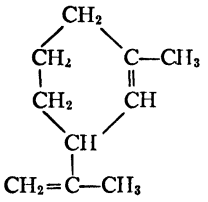
Citronellal, $C_{10}H_{18}O$
In oil of citronella and lemon-grass oil.



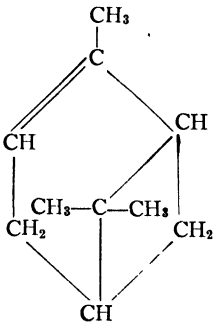
Menthol, $C_{10}H_{20}O$
In oil of peppermint.



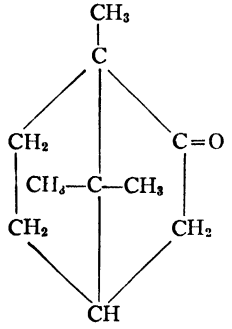
Terpineol, $C_{10}H_{18}O$
In oil of orange.



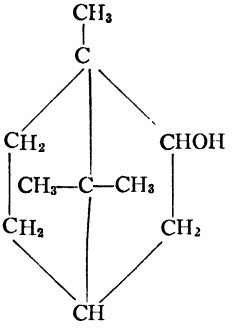
Sylvestrene, $C_{10}H_{16}$
Chief constituent of Swedish and Russian oil of turpentine.



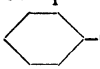
Pinene, $C_{10}H_{16}$
Chief constituent of most varieties of oil of turpentine.



Camphor, $C_{10}H_{16}O$
From Japanese camphor tree. Also made from pinene.



Borneol, $C_{10}H_{18}O$
Called Borneo camphor. From Borneo camphor tree. Has peppery odor.

37. 3. Essential Oils. Most plants contain volatile oils in their leaves, blossoms, fruits, and tissues. These oils can usually be extracted by simple methods. They are often called *ethereal* oils; they are also called *essential* oils, not because they are necessary but because they are volatile *essences*. Some essential oils are fairly simple compounds. For example, the oil of rose contains phenylethyl alcohol,  -CH_2-CH_2-OH, and the oil of wintergreen is methyl salicylate (section 32.8).

The terpenes are an important family of these essential oils. Their name is due to the fact that the most familiar members are present in oil of turpentine.

37. 4. Camphors. Most of the compounds in table 37.1 are oxygen derivatives and are technically known as camphors. They all contain

two isoprene units and, therefore, ten carbon atoms, but the hydrogen and oxygen content varies considerably.

The class name of *camphors* is being slowly abandoned and all the compounds in this group are known as terpenes, regardless of whether they are purely hydrocarbons of the composition $C_{10}H_{16}$ or oxygen derivatives. The name *camphor* is reserved for that one oxygen compound, whose graphic formula is given in table 37.1, and whose composition is $C_{10}H_{16}O$.

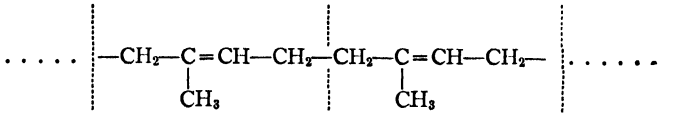
37. 5. The Terpene Unit. The composition of terpene is $C_{10}H_{16}$. Some hydrocarbons are known which have the composition $C_{15}H_{24}$; these are called sesquiterpenes to indicate that they are one and one-half times as large as the terpene molecule. Also, there are complex terpenes in nature built up of many terpene units; they are referred to as the polyterpenes.

We can tabulate all these compounds as follows, based on the number of terpene ($C_{10}H_{16}$) units in the molecule, but we must remember that this unit itself consists of two molecules of isoprene, C_5H_8. Hydrocarbons of the composition C_5H_8, analogous to isoprene, are known as hemiterpenes, meaning one-half as large as a terpene.

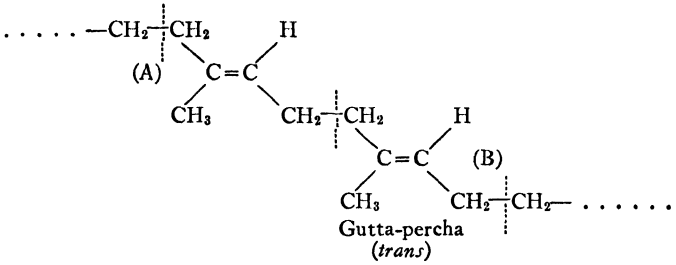
Multiple of C_5H_8, *or* $(C_5H_8)_n$		*Example*
Hemiterpenes,	where n = 1	Isoprene
Terpenes,	where n = 2	Myrcene (open-chain) Sylvestrene (closed-chain)
Sesquiterpenes,	where n = 3	Not discussed in this book.
Polyterpenes,	where n = more than 3	Rubber

37. 6. Rubber. The bark of some tropical plants, when cut, exudes a white milk called latex. When the latex is coagulated, crude rubber is obtained. This crude rubber used to be known as caoutchouc, meaning in Indian a "tree which weeps." The latex of certain of these plants contains a substance which differs somewhat from rubber and is known as gutta-percha. Both rubber and gutta-percha have the empirical composition $(C_5H_8)_n$, where n is a very large number. They are both polyterpenes.

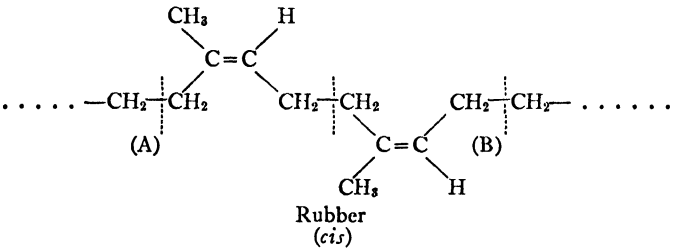
These polyterpenes are structures built up of isoprene units, $CH_2=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=CH_2$, in which double bond rearrangement occurs as described in section 18.2 when the isoprene molecules unite end to end:



Considerable study has been given to these structures and it is currently believed that gutta-percha (which is only slightly elastic) has the *trans* configuration shown in the accompanying formulas, whereas rubber (which is quite elastic) has the *cis* configuration.



Gutta-percha
(*trans*)



Rubber
(*cis*)

The two different arrangements are called *cis* and *trans* because of the positions of the $-CH_2-CH_2-$ groups. In the rubber molecule, it will be seen that they are placed on the same side of the $\overset{|}{C}=\overset{|}{C}$ groups, whereas in gutta-percha they are on opposite sides. There is evidence that freedom of rotation around the single bonds is much greater in the rubber molecule, resulting in greater flexibility.

If the double bonds in these conventionally printed formulas are regarded as *perpendicular* to the plane of the printed page all the carbon atoms in the chain would necessarily be *in* the plane of the page, that is, coplanar (see figure 15.1). The length AB (identity period) calculated from such a model for rubber is a little longer than that obtained from X-ray measurements, indicating that the

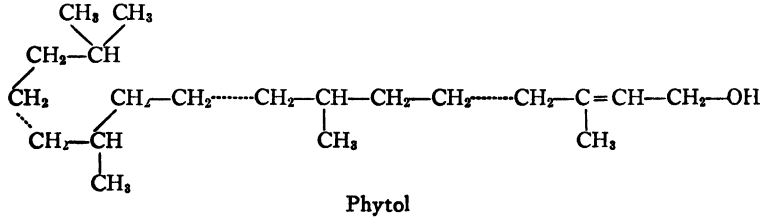
chain actually is somewhat crumpled, that is, zigzag nonplanar. Examination of the zigzag model of the *cis* form shows that the methyl groups permit freedom of rotation in the $-CH_2-CH_2-$ connecting groups.

Gutta-percha in its α form is hard and tough, but undergoes a transition at about 70°C. to a softer β form which resembles rubber in its pliability. Both forms are *trans*, but the α form has an identity period which corresponds to a structure in which the carbon atoms are all coplanar, whereas in the β form the identity period is shorter and the carbon atoms in the chain are, therefore, zigzag nonplanar as in rubber.

A rubberlike substance can be made from isoprene by polymerization. The product has the same composition as natural rubber, but lacks some of its important properties. The du Pont Company has developed an excellent rubber from chloroprene, $CH_2=\underset{\displaystyle Cl}{\overset{|}{C}}-CH=CH_2$. Chloroprene polymerizes about seven hundred times as fast as isoprene; the trade name of the rubberlike substance obtained from it is *Neoprene*. Neoprene does not have the same composition as natural rubber, but is superior to it for certain purposes in that it is chemically more stable.

The substance which the layman knows as rubber is the product obtained by heating natural rubber with sulphur under pressure. This process is known as vulcanization. Neoprene does not need the addition of sulphur when it is vulcanized, although for certain purposes it is helpful (see section 46.11).

37. 7. Some Plant Pigments. Chlorophyll, the green coloring matter of leaves, is the most important of the plant pigments. One of the principal constituents of the chlorophyll molecule is an alcohol called *phytol*. Phytol, $C_{20}H_{39}-OH$, is a straight-chain, unsaturated alcohol, built up from the skeletons of four isoprene molecules:



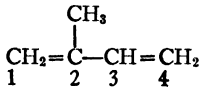
Phytol

The name phytol means *plant alcohol*, from the Greek word *phyton* for plant and *-ol* for alcohol. Phytochemistry is plant chemistry.

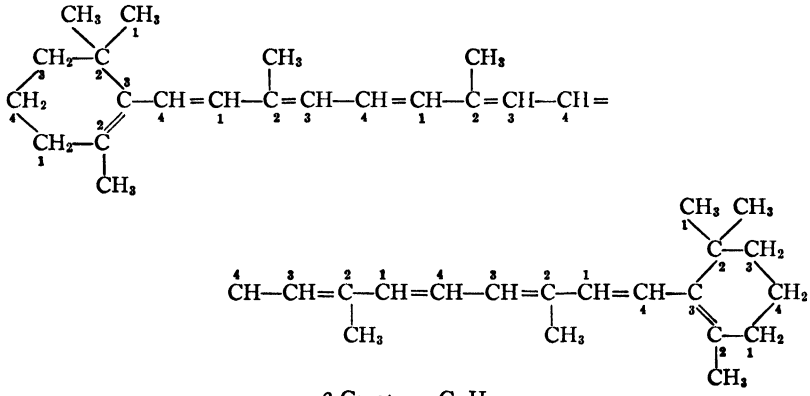
The dotted bonds in this formula for phytol are actually single bonds, but we have used the dots to accentuate the method of linkage of four isoprene units to build this important plant product. The cyclic form at one end of the chain is another liberty we have taken with phytol in order to show more clearly how it is related to the compounds described in the following paragraphs.

The green pigment chlorophyll is usually accompanied in plants by yellow pigments known as *xanthophyll* ($C_{40}H_{56}O_2$) and *carotene* ($C_{40}H_{56}$). Xanthophyll occurs not only in green leaves, but also in yellow petals of some plants, and it is one of the coloring agents of egg yolk (the prefix *xantho* is from the Greek *xanthos*, meaning yellow). Carotene is obtained from carrots and other vegetables, from palm oil and from spinach. *Lycopene*, which has the same molecular formula as carotene ($C_{40}H_{56}$), is the red pigment of tomatoes.

Carotene, lycopene, and xanthophyll are each built up of eight isoprene skeletons, which means practically two phytol molecules. The eight isoprene units are plainly indicated in the way the formula of carotene is written, numbering the isoprene carbon atoms as follows:



Isoprene, C_5H_8

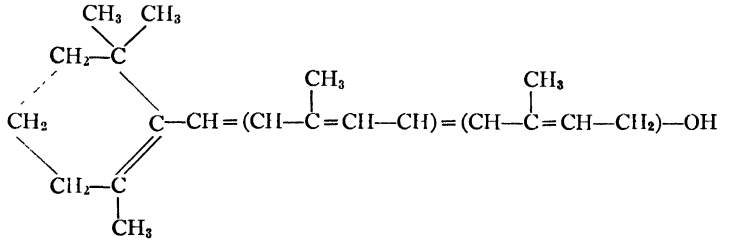


β-Carotene, $C_{40}H_{56}$

Carotene exists in a number of distinct modifications; the structure we have just written is that of β-carotene. In α-carotene, the double bond position in one of the rings is not the same as in β-carotene, and in γ-carotene, one ring is similar to those in β-carotene, but the other end of the molecule is open. Xanthophyll is a dihydroxy derivative of α-carotene, and lycopene does not have a closed ring at either end of the molecule.

When studying the structures of these complex, long-chain molecules, it should be remembered that the chains are *not straight.* They zigzag as illustrated in chapter 12 and many isomeric forms are possible due to *cis*, *trans* isomerism, such as is shown for rubber and gutta-percha in section 37.6.

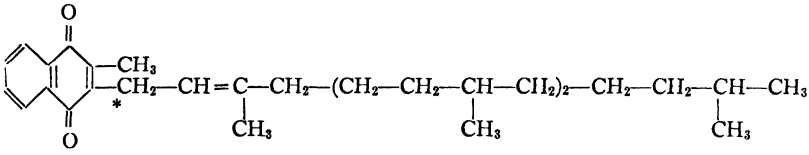
37. 8. Vitamin A. The carotenes have a powerful physiological action, producing a rapid increase in the hemoglobin content of the blood. The vitamin A activity of plants is parallel to their carotene content, and there is ample evidence that vitamin A is obtained from β-carotene by splitting the molecule exactly in the center. The composition of vitamin A is $C_{20}H_{29}$–OH.



Vitamin A (Compare with structure of phytol)

Animals feeding on foods containing β-carotene probably store up vitamin A (in the liver) by breaking down the carotene molecule. Oils obtained from fish livers are especially potent in vitamin A. It is a fat-soluble vitamin (section 44.4).

37. 9. Vitamin K. This is the antibleeding vitamin, the presence of which is essential in the diet in order to insure the normal clotting of the blood. Vitamin K_1 is produced by green leaves, and the closely related vitamin K_2 is produced by certain bacteria. An animal source of the vitamin is hog liver. The K_1 factor has been synthesized; it is still another isoprene, or phytol, derivative. Its chemical name is 2-methyl-3-phytyl-1,4-naphthoquinone:



By referring to phytol (section 37.7), we find that the phytol molecule has been linked to the ring structure through the $—CH_2OH$ end of the molecule, at the position marked by an asterisk (*).

Vitamin K_2 has the same general structure as K_1, but has more double bonds in the side chain. It is slightly less active.

SUGGESTED READING

Bunn, C. W., "Molecular Movements in Rubberlike Polymers," *Proc. Roy. Soc.*, **180**, 82–99 (1942).

Simonsen, J. L., *The Terpenes* (two volumes), Cambridge University Press, New York, 1947–1949.

"Symposium on Organic Chemistry of Plant Synthesis," *J. Chem. Educ.*, **26**, 628–665 (1949).

Treloar, L. R. G., *The Physics of Rubber Elasticity*, Oxford University Press, New York, 1949.

38. PROTEINS

38. 1. Introduction. Animal and plant cells contain three important types of compounds, namely, fats, carbohydrates, and proteins. Of these, the most important from a physiological point of view and certainly the most complex type from the chemical standpoint are the proteins.

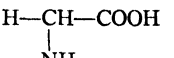
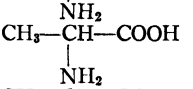
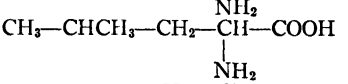
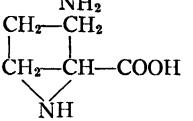
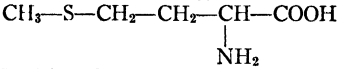
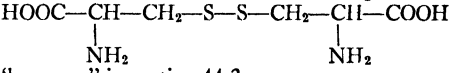
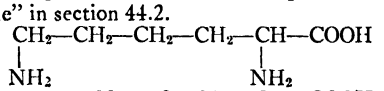
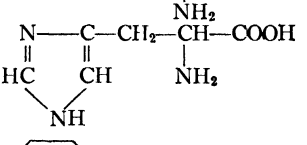
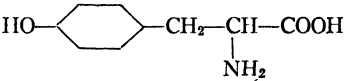
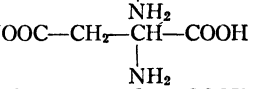
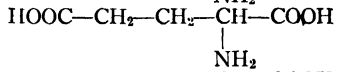
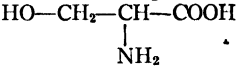
The nature of the fats (section 31.8*b*) and of the carbohydrates (chapter 39) is now definitely established, but we are still far from an exact knowledge of the structure of a single protein molecule.

The great importance of the proteins lies in the fact that they are indispensable to animal life, whereas animals can live for a long time without fats and carbohydrates in the diet. The word *protein*, from the Greek *proteios*, meaning "to be the first," indicates its first importance to the structure of living cells.

38. 2. The Amino Acids in Proteins. Our present knowledge of the structure of proteins has been obtained largely by breaking them down to recognizable fragments. The breaking-down method is either a hydrolysis in dilute acid or dilute alkali, or a hydrolysis by means of enzymes. The decomposition products are almost entirely α-amino acids and these are regarded as the building blocks of the protein molecule.

α-Amino acids are mixed compounds (section 32.1) in which the characteristic groups on the carbon skeleton are $-NH_2$ (or $=NH$) and $-\overset{|}{C}=O$ (OH). Some representative members of this family of compounds are shown in table 38.1. These examples are obtainable by the hydrolysis of naturally occurring proteins.

TABLE 38.1. α-AMINO ACIDS OBTAINED FROM PROTEINS*

Glycine	α-Aminoacetic acid	
Alanine	α-Aminopropionic acid	
Leucine	α-Aminoisocaproic acid	
Proline	α-Pyrrolidinecarboxylic acid	
Methionine	α-Amino-γ-methylthiol-butyric acid	
Cystine (See section 34.2)	Di-(α-amino-β-thio-propionic acid)	
Thyroxine	See the structure of this "hormone" in section 44.2.	
Lysine	α,ε-Diaminocaproic acid	
Histidine	α-Amino-β-imidazole-propionic acid	
Tyrosine	α-Amino-β-(p-hydroxy-phenyl)-propionic acid	
Aspartic acid	Aminosuccinic acid	
Glutamic acid	α-Aminoglutaric acid	
Serine**	α-Amino-β-hydroxy-propionic acid	

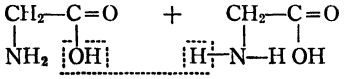
*About twenty such acids are obtainable from proteins (section 38.3).

**This compound serves as a basis for configuration in the D- and L-families of α-amino acids (section 38.6 and section 39.5).

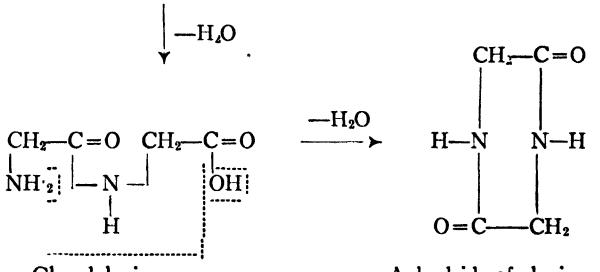
The method of naming the amino acids is similar to that of the other classes of mixed compounds which we have studied (section 32.4). The position of the $-NH_2$ group is indicated by a Greek letter which shows how far it is from the $-COOH$ group. The important fact about proteins is that, on hydrolysis, they yield α-amino acids almost exclusively; that is, the $-NH_2$ group is on the carbon atom next to the COOH group. Lysine, one of the amino

acids listed in the table, contains two $-NH_2$ groups, one on the *alpha* carbon atom and the other on the *epsilon* carbon atom.

The chemistry of the amino acids is entirely analogous to the chemistry of the hydroxy acids as given in section 32.6. The hydroxy acids should be reviewed before proceeding to the following discussion. Like the hydroxy acids, the *alpha*, *beta*, and *gamma* amino acids behave differently when heated, in accordance with the position of the NH_2 group in the molecule.

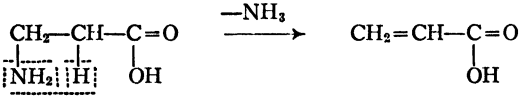


Glycine (two molecules)
An α-amino acid



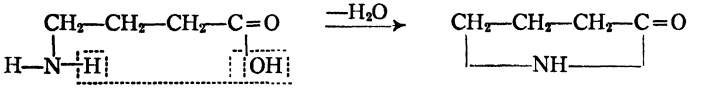
Glycylglycine
A "dipeptide"

Anhydride of glycine
(Compare with lactide in section 32.6)



β-Aminopropionic acid

Propenoic acid

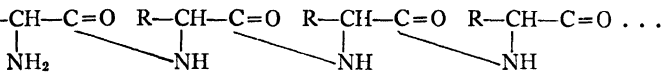


γ-Aminobutyric acid

Butyrolactam (Compare with the lactones in section 32.6)

38. 3. Polypeptides. From the standpoint of the subject matter of this chapter, that is, the structure of the proteins, our principal interest is in the behavior of the α-amino acids as illustrated by glycine. The condensation of two molecules of glycine, when heated, to form a "dipeptide" is of great interest to the protein chemist,

because he believes that this is also the method employed in nature in building the complex protein molecule. Most of the laboratory work on the problem of the structure of proteins has been done from the point of view that they are built up of many α-amino acid skeletons as in glycylglycine. Molecules of this type, composed of a large number of amino acids, are known in general as *polypeptides*. The general form of a polypeptide is



Note that two adjacent amino acids condense by elimination of H_2O from the $-NH_2$ and $-COOH$.

Emil Fischer, who did the pioneer work on the protein problem, prepared a polypeptide containing eighteen amino acid units, and later one of his students made one with nineteen units. It had a molecular weight of 1326. This polypeptide resembles the initial decomposition products of proteins (called proteoses and peptones), but the molecular weights of proteins themselves are supposed to range from 15,000 to some indefinitely higher figure.

The octadecapeptide prepared by Fischer contained fifteen glycine skeletons and three leucine skeletons. It is evident that there are many arrangements possible when these two kinds of molecules are put together in one chain. The number of theoretically possible proteins in nature, assuming they are built like polypeptides, is thus enormous, when we consider that nature has about twenty such amino acids at her disposal.

Of the amino acids now known in proteins, it has been found that ten are essential in the diet of healthy animals. For example, lysine is found in most proteins, but is absent from the proteins of corn meal. Animals fed exclusively on corn-meal protein ration soon have their eyesight impaired, even though the rest of the diet is not changed. It is reasonable to assume that animals require lysine for building up their own tissue and cannot manufacture lysine themselves. In other words, certain amino acids in proteins are as essential to health as the vitamins we shall describe in section 44.4. The common names of the *alpha*-amino acids are listed in table 38.2, roughly in the order in which their presence in proteins was recognized or proved by isolation through hydrolysis. Leucine was isolated in 1818, and threonine in 1935.

In the opening paragraph of this chapter it was said that no protein structure has yet been solved. Progress, however, is rapid in this field. In the period 1950–1952, it was announced that the sequence of the amino acids in the insulin molecule has been worked out. Insulin is a hormone (section 44.2). A brief summary of the problem of protein structure will be found in section 46.4.

TABLE 38.2. THE AMINO ACIDS IN PROTEINS

Leucine*	3,5-Diiodotyrosine
Glycine	Cystine
Tyrosine	Tryptophane*
Serine	Proline
Aspartic acid	Cysteine
Glutamic acid	Hydroxyproline
Alanine	Isoleucine*
Phenylalanine*	Valine*
Lysine*	Thyroxine
Arginine*	Methionine*
Histidine*	Threonine*

*These are the amino acids generally said to be indispensable for healthy animal life. Actually, this means that they have been found to be essential in the diet of young growing rats. It is also claimed that eight of the same ten substances are indispensable for man [W. C. Rose, *Chem. Eng. News*, *30*, 2385-2388, (1952)]; the two compounds said to be dispensable for man are arginine and histidine.

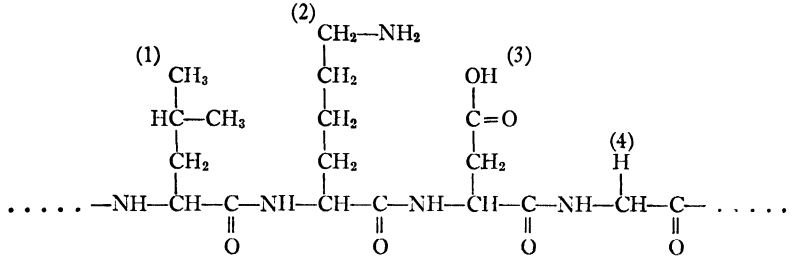
38. 4. Classification and Composition of Proteins. The elements which may be found in a protein are C, H, O, N, S, P, and perhaps a metal. The composition of the proteins obtained from various sources is approximately the same; the nitrogen content, for example, varies over the small range of 14 to 19 per cent.

Most proteins are soluble only in water, but they form colloidal solutions rather than true solutions. They are all optically active in solution; this is also true of the polypeptides and amino acids, with the exception of glycine.

A few proteins, such as the albumin from the white of an egg, have been prepared in crystalline form. In general, however, they are amorphous substances with no definite melting point, and are easily charred when heated. When in solution, they are easily coagulated by heat, as in the familiar case of poached eggs.

The proteins were originally classified according to some of their physical properties, such as reaction to heat, or solubility in certain salt solutions. An attempt at a chemical classification of the proteins has been made by the Society of Biological Chemists and their classification is the one which is followed at present. The complete classification can be found in the larger textbooks.

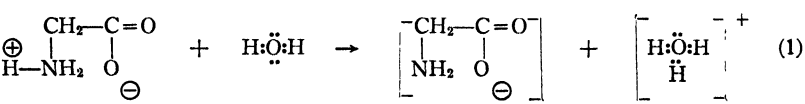
From the general structure of a polypeptide shown in this chapter in section 38.3, it will be seen that the variations among polypeptides (and proteins) are due to the nature of the R groups in the molecule. Let us assume a hypothetical molecule that has three different R side chains. The amino acids (see table 38.1) incorporated in this



molecule are (1) leucine, which yields a *neutral* side chain essentially a paraffin hydrocarbon; (2) lysine, which gives the molecule *basic* characteristics because of the free $-NH_2$ group; and (3) aspartic acid, which introduces a free –COOH group and, therefore, confers *acid* properties on the molecule. A glycine residue (4) is also built into this hypothetical molecule; obviously it does not furnish a side chain but just another H atom.

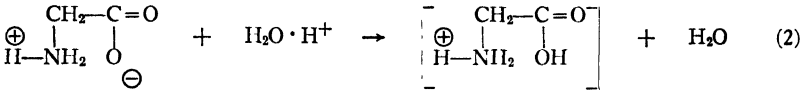
In some proteins the R side chains contain sulphur atoms (see cystine and methionine in table 38.1). Iodine is also present in certain proteins (see thyroxine in section 44.2). A single protein molecule may contain a number of different side chains, which accounts for the complexity of its chemical behavior. Protein structures will be discussed again in the chapter on giant molecules (section 46.4)

38. 5. The Isoelectric Point. This is one of the more important properties of amino acids and proteins. It can be understood by referring back to the discussion of glycine as a *zwitterion* (section 33.8). Glycine is amphoteric; it can react with either acids or bases.



(1)

Glycine reacts as an acid with a base.



Glycine reacts as a base with an acid.

It may be appropriate to review sections 31.5 and 31.6 if the meaning of acids and bases is not clear.

A zwitterion does not have equal activities as an acid and as a base. In water solution, glycine reacts more by (1) than by (2), that is, it gives up protons more readily than it accepts them. Consequently, the pH of a glycine solution in pure water is a little below 7, slightly acid. (It will be recalled that the neutral point for water is pH 7; when the pH is below 7 it is acid, and above 7 it is alkaline.) If an acid, such as HCl is added to glycine solution in water, the formation of negative ions by reaction (1) will be repressed and at pH 6, reactions (1) and (2) will be balanced in that equal numbers of positively and negatively charged ions will be present. This is the isoelectric point for glycine. At this pH not only are the positive and negative charges equal in number, but the total number of charged particles is at a minimum.

On the alkaline side of the isoelectric point (above pH 6) glycine forms negative ions which migrate to the positive pole in an electrolysis cell; on the acid side (below pH 6) it forms positive ions which migrate to the negative pole. At the isoelectric point there is no migration to either pole because the *net* charge is zero.

On the alkaline side of the isoelectric point, glycine, *and proteins*, react with bases; on the acid side they react with acids.

At the isoelectric point, the molecules of a protein in solution are in a favorable condition to coagulate and precipitate, since at that pH the number of positive charges on a protein surface (that is, in the R groups shown in section 38.4) is equal to the number of negative charges and electrostatic repulsion between molecules is consequently minimized.

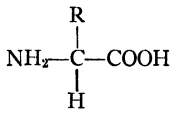
Proteins can often be separated from each other and purified by this principle of adjusting their solutions to the pH values corresponding to their characteristic isoelectric points. Thus, lysine in table 38.1 is seen to have an extra NH_2 group in its molecule, which gives it stronger basic than acidic properties; it has an isoelectric point of pH 9.7. Its normal tendency in pure water is to add H^+

ions to form lysine ions with a positive charge. In order to repress this tendency and balance it with the formation of negative lysine ions equal in number to the positive ions, it is necessary to make the solution alkaline to the extent of pH 9.7. Aspartic acid, with its additional –COOH group, is more acidic than basic and the pH must be lowered to 2.8 to reach the isoelectric point. Proteins containing these amino acids have roughly analogous isoelectric points.

Isoelectric precipitation is favored by the presence in a protein molecule of amino acids like alanine or leucine (table 38.1) which furnish purely hydrocarbon groups with little polarity to the R side chains shown in the typical structure in section 38.4. The precipitation is more difficult when the protein molecule contains amino acids which are basic, like lysine and histidine or acidic, like aspartic acid and tyrosine.

Precipitation at the isoelectric point is the basis for the commercial isolation and purification of insulin.

38. 6. Optical Activity of Amino Acids. The α-carbon atom in all of the α-amino acids (except glycine) is asymmetric, which, of



course, leads to optical activity (section 22.7). The α-amino acids (except glycine) isolated from proteins by hydrolysis and discussed in this chapter are all optically active. There has been some confusion in the past on the nomenclature of the amino acids, because the direction of rotation of the plane of polarized light was determined by various experimenters under various conditions (in neutral aqueous solution, in acid solution, in alkaline solution, etc.) and the same compound might be *dextro* under one set of conditions but *levo* under another set. According to current "official" rules, the direction of rotation does not appear in the name of an amino acid. When a prefix is employed (as in D-leucine or L-leucine) it indicates whether the α-carbon atom belongs to a D- or L-family, according to a convention which will be explained in the next chapter (section 39.5 and figure 39.6), at which time the use of serine to determine what constitutes a right-hand or left-hand carbon atom will also be described. Whether or not the compound rotates light to the right

or to the left may, of course, be stated by an author by use of the usual *dextro* or *levo*, provided the information is not incorporated in the name of the compound.

The α-amino acids in table 38.2, all derived from naturally occurring proteins, belong (except glycine) to the L-family of amino acids, that is, they all have a left-handed α-carbon atom. The official rules permit use of the names without prefixes in such a list, because it is well understood from their source to which family they belong, that is, the L-family.

SUGGESTED READING

American Chemical Society Nomenclature Committee, "Nomenclature of Natural Amino Acids and Related Substances," *Chem. Eng. News*, **25**, 1364–1367 (1947).

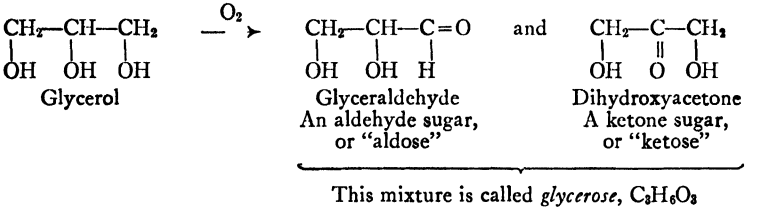
Haurowitz, F., *Chemistry and Biology of Proteins*, Academic Press, New York, 1950.

39. SIMPLE CARBOHYDRATES

39. 1. Definition of a Sugar. Carbohydrates are the principal constituents of plants. Sugars are the simple types of carbohydrates. Sugars are also presumably the building blocks used by plant cells for the manufacture of more complex carbohydrates, like starch and cellulose, which will be described in a following chapter.

In this chapter, we shall consider only the simple sugars. Unfortunately, the average student of chemistry is afraid of a large molecule; therefore, the simple sugars may not appear simple to him until we view them carefully. However, if we pay more attention to their *structure* than to their *size*, the sugars described in this chapter will not fail to live up to their title of "simple sugars."

All simple sugars contain –OH groups, and in the sugar molecule there must also be either a $-\overset{|}{\underset{H}{C}}=O$ group or a $C-\overset{\|}{\underset{O}{C}}-C$ group. We can illustrate these two kinds of sugars as follows:



It will be seen that the sugars are closely related to the polyatomic alcohols.

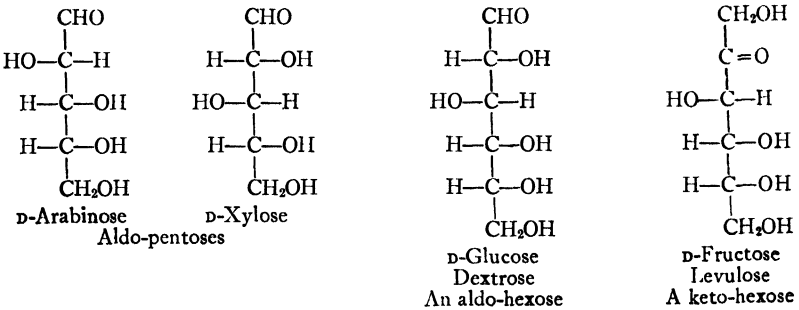
A sugar is a mixed compound (chapter 32): either an aldehyde-alcohol or a ketone-alcohol. In either case, there are two different groups (–OH and $-\overset{\displaystyle H}{\overset{|}{C}}=O$) or (–OH and $-\overset{\displaystyle }{\overset{|}{C}}=O$) on a chain of carbon atoms.

39. 2. General Character of Sugars. The only difficulty in learning the chemistry of the sugars is the fact that there are so many sugars.

This difficulty can easily be eliminated if we keep in mind the following general principles:

1. The names of all sugars end in -ose, as illustrated by glycerose.
2. There are two series of sugars — the aldehyde sugars known as aldoses, and the ketone sugars known as ketoses.
3. The sugars vary in the length of the carbon chain. A C_3 sugar, such as glycerose, is called a triose, a C_4 sugar a tetrose, a C_5 sugar a pentose, a C_6 sugar a hexose, etc.
4. The general formula of a simple sugar is $(CH_2O)_n$. For example, in the case of glycerose, n = 3; in other words, it is a triose. An exception, however, will be mentioned in section 41.10.

The simple sugars of both theoretical and commercial importance shown in figure 39.1 are examples of pentoses ($C_5H_{10}O_5$), and hexoses ($C_6H_{12}O_6$).



(For the meaning of the prefix D- in these names, see section 39.5)

FIGURE 39.1. Representative pentoses and hexoses.

D-*Arabinose* is obtained by boiling gum arabic with dilute acids (section 41.9), which accounts for its name. D-*Xylose*, named from the Greek word *xylon* (meaning *wood*) may be obtained by boiling wood gum, straw, or jute with dilute acids.

D-*Glucose* occurs widely distributed in nature in fruits and in honey. It is known as grape sugar; it is also called dextrose, because it is a right-handed molecule with respect to plane-polarized light. On a commercial scale it is made by hydrolysis of starch or cellulose. It is the sugar of the blood.

D-*Fructose* is usually found associated with glucose, in fruits and in honey. It has long been known as fruit sugar; it is also called levulose because it is a left-handed molecule with respect to plane-polarized light. It is obtainable in large quantities from certain complex carbohydrates (section 41.9).

From now on, we shall devote our attention principally to the C_6 sugars, that is, the hexoses. Not only are these the most important simple sugars, but they are also typical of all the sugars.

39. 3. Open-Chain Isomerism in Sugar Chemistry. Before we can hope to understand the chemistry of the sugars we must be in position to understand their space arrangements. We shall first describe the model invented by Emil Fischer (1891) who did the classical pioneer work in the determination of the structures of the sugars. The Fischer system consists of so-called *projection formulas* shown in (*a*) and (*c*) of figure 39.2. In (*a*), four of the carbon atoms of the sugar molecule are tetrahedra (section 12.2), with their back edges in line and resting on the printed page. This is an abnormal way for

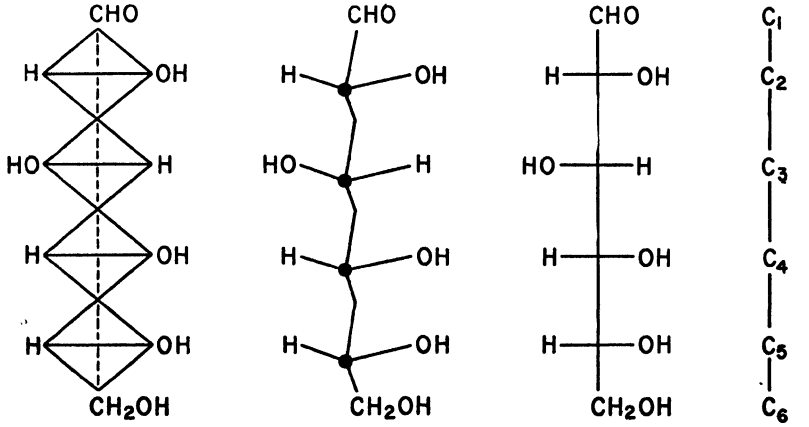


FIGURE 39.2. Projection formula of D-glucose.

us to look at a carbon-to-carbon link; as indicated in (*b*), which is the same structure but showing the tetrahedral valence angles, the carbon-carbon bonds are joined at an angle instead of in the customary straight line which is illustrated in figure 12.5. The projection formula is, however, purely a *convention*, which is useful for tracing the relations among the sugars. A more orthodox convention will be described in section 39.6.

The Fischer type of formula commonly used is that in (*c*) of figure 39.2. The functional group (section 10.10) in an *aldose* like D-glucose is always written at the top and assigned the 1 position in the molecule. The terminal $-CH_2OH$ group, containing the 6 carbon atom, is at the bottom. If the sugar is a *ketose*, like D-fructose which is depicted in figure 39.1, the C atoms in the chain are numbered from that end which gives the functional $-\overset{|}{C}=O$ group the smallest possible number. In D-fructose, the functional group is in the 2 position.

With the aid of figure 39.2 (*c*), we can more easily perceive why there are so many different sugars. If we arrange H atoms and –OH groups on the skeleton in all possible ways, sixteen different isomeric arrangements of the *aldehyde* hexoses will be found possible. The structures of eight of these hexoses are indicated in figure 39.3, where we successively change the positions of the –OH groups to the left-hand side of the chain, and progressively increase the number of –OH groups on that side. For each of these compounds there

CHO	CHO	CHO	CHO
H | OH	HO | H	H | OH	H | OH
H | OH	H | OH	HO | H	H | OH
H | OH	H | OH	H | OH	HO | H
H | OH	H | OH	H | OH	H | OH
CH_2OH	CH_2OH	CH_2OH	CH_2OH
D-Allose	D-Altrose	D-Glucose	D-Gulose
CHO	CHO	CHO	CHO
H | OH	HO | H	H | OH	HO | H
H | OH	HO | H	HO | H	H | OH
H | OH	H | OH	HO | H	HO | H
HO | H	H | OH	H | OH	H | OH
CH_2OH	CH_2OH	CH_2OH	CH_2OH
L-Talose	D-Mannose	D-Galactose	D-Idose

(In the space models of these sugars, shown in model II of figure 39.7, the atoms on the *left* of the chain are on *top* of the ring.

FIGURE 39.3. Illustrating the scheme for working out the possible *aldo*hexoses.

is a mirror-image isomer in which the H and OH positions are reversed, as shown for D-glucose and L-glucose in figure 39.4. There are, accordingly, sixteen possible aldohexoses in the glucose family.

All sixteen isomers of glucose have been identified. Three of these sixteen sugars are found in nature; their names are D-glucose, D-mannose, and D-galactose (see the glycosides in section 40.8).

Similarly, by the structure theory, we can show that there are eight possible six-carbon sugars in the *ketone* series, but only five of these are known at present. The two that occur in nature have the *keto* group on carbon atom 2. They are D-fructose, the structure of which is shown in figure 39.1, and L-sorbose, which will be referred to in section 39.9.

39. 4. Optical Isomerism in Sugar Chemistry. In chapter 22, we found that a carbon atom to which four different groups are attached is asymmetric and leads to optical activity, that is, the compound will rotate plane-polarized light to the right (*dextro*) or left (*levo*), depending on the space arrangement of these groups around the asymmetric carbon atom. For this reason, we can write *dextro* and *levo* forms of glucose, which are mirror images of each other, as in figure 39.4.

The student may say to himself that these two glucose structures are the same because we can rotate the groups around the C—C bonds and make the structures look exactly alike. That can be done with the flat chain formulas, but it cannot be done with space models. If we number the C atoms in the glucose molecule, as in figure 39.2, and consider the C_3 atom, it will be seen there are four different groups on it, namely, H, OH, CHOH—CHO, and CHOH—CHOH—CH_2OH. This C_3 atom is, therefore, similar to that shown in figure 22.4 and there can be two mirror-image arrangements of the groups attached to it.

It is a simple matter to calculate the number of possible optical isomers of a substance if we know how many asymmetric carbon atoms there are in the molecule. In glucose, for example, there are four asymmetric carbon atoms, marked with an asterisk, thus: $HOCH_2-\overset{|}{\underset{|}{C^*}}-\overset{|}{\underset{|}{C^*}}-\overset{|}{\underset{|}{C^*}}-\overset{|}{\underset{|}{C^*}}-CHO$. An inspection of the formula of glucose will reveal there are four different groups attached to each of these carbon atoms. To calculate the number of possible isomers we make use of the expression 2^n, where n is the number of

asymmetric carbon atoms. For glucose, $n = 4$, so that there are 2^4 or 16 isomers. This agrees with the number of isomers of glucose which we have already determined should be possible by assuming that the structure of a carbon chain is that shown in figure 39.2, and by working out all the possible arrangements of H and OH on the chain. The formula we used for calculating the number of possible optical isomers holds only when the two end groups are different. If the terminal groups are the same, as in saccharic acid (section 39.9), the possible number of isomers will be less than 2^n, but the correction factor can be calculated.

It will be recalled that mirror-image isomers are said to be enantiomorphous; D-glucose and L-glucose (figure 39.4) are, therefore, called *enantiomorphs* or *enantiomers*. All the sugars in figure 39.3 are isomeric and are optically active, but they are not mirror images. Thus, D-glucose is not the enantiomer of D-galactose; such optically active isomers were defined in section 22.11 as *diastereoisomers*.

39. 5. Dee and Ell Families of Sugars. The "father of sugar chemistry" arbitrarily decided on the D and L families by employing the conventions illustrated in figure 39.2. He chose saccharic acid (see its formula in section 39.9) as primary reference compound, placed the carbon tetrahedra on paper in such a way as to put most of the –OH groups on the right hand side of the backbone, and called this D-saccharic acid, the structure which rotates the plane of plane-polarized light to the right. Then he called D-glucose the compound which yields D-saccharic acid by oxidation, and wrote the structure of D-glucose as in figure 39.2 with the –CHO group at the top. The left-handed mirror image, L-glucose, the structure of which is obtained by *projection* like that in figure 39.2, is shown in figure 39.4.

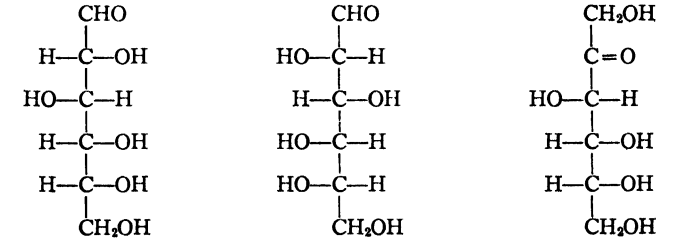


FIGURE 39.4. Projection formulas of three hexoses.

Fischer subsequently named other sugars on the basis of their being relatives of D-glucose or of L-glucose. If a sugar can be derived from D-glucose by simple reactions, he called it a member of the D-series of compounds. Thus, fructose, the fruit sugar which occurs in nature, can be made from D-glucose; its structure, as we have written it in figure 39.4, shows that most of the molecule is similar to the D-glucose molecule. Therefore, it was named D-fructose. This is confusing, because D-fructose rotates polarized light to the left and we like to call such compounds members of a left-handed family. However, we still adhere to the principle of relating the carbohydrates to D and L families regardless of the direction in which they affect light.

The system initiated by Fischer for allocating a sugar to a D or L family (based on glucose isomers) turned out to be troublesome and was modified (M. A. Rosanoff, 1906) by the selection of D-glyceraldehyde and L-glyceraldehyde as the *reference standards* of the two families. The glyceraldehyde structure was mentioned briefly in the introduction to this chapter and should be reviewed. Its projection formula is written in (*b*) of figure 39.5, where it is

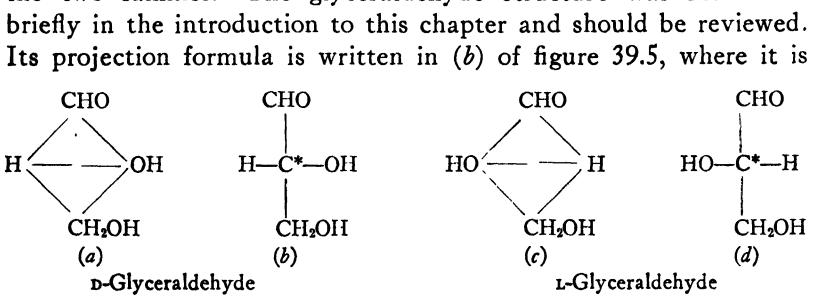


FIGURE 39.5. Projection formula of glyceraldehyde (C* is the asymmetric carbon atom).

arbitrarily stated that when the asymmetric carbon atom is placed with its back edge on the page as shown in (*a*), with the –OH group to the right of the observer, the molecule is to be called D-glyceraldehyde (it is also a *dextro* molecule). Similarly, L-glyceraldehyde, which is a *levo* molecule, arbitrarily has the structure shown in (*c*) of figure 39.5, with the projection formula (*d*).

The current practice in naming sugars is to use the prefix D or L to indicate whether its *configurational family* is that of D-glyceraldehyde or L-glyceraldehyde. This is done by projecting the formula of the sugar in the conventional Fischer manner (as in figures 39.1 to 39.5) and examining the *asymmetric* carbon atom farthest removed from the –CHO group (in other words, the asymmetric carbon atom with

the highest number according to the scheme in figure 39.2 (*d*), where it is the C atom next to the $-CH_2OH$ group). If that carbon atom has the same configuration as the C* atom in figure 39.5 (*b*), with –OH on the right, the molecule belongs to the D family. If –OH is on the left, as in figure 39.5 (*d*), it belongs to the L family; an example is L-talose in figure 39.3.

The prefixes D and L are pronounced "dee" and "ell," not "dextro" and "levo." If desired, the fact that the compound is right-handed or left-handed with respect to plane-polarized light can be shown by the supplementary use of *dextro* and *levo*. This may be illustrated by the name D (*levo*)-fructose for the compound in figure 39.4. Similarly, the arabinose in figure 39.1 is a D sugar because of its family relations, but it is levorotatory and may be written D(*levo*)-arabinose.

The D and L names of the hexoses in figure 39.3 show their chemical relationship to D- and L-glyceraldehyde, but do not indicate the direction of their effect on plane-polarized light. Fortunately, the three aldehyde sugars prevalent in nature, D-glucose, D-galactose, and D-mannose, are *dextro* molecules as well as members of the D family of sugars. This may assist the memory.

Before leaving this topic, we should recall a similar problem among the proteins (section 38.6) where an α-amino acid is allocated to a D or L family according to the configuration at the α-carbon atom, regardless of the direction of the optical activity. The reference standard for the amino acids is serine (table 38.1), the projection formula of which is worked out in figure 39.6. Nearly all of

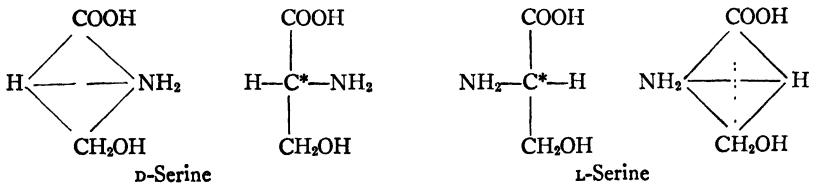


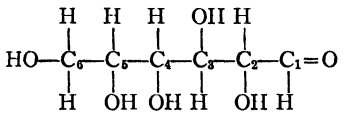
FIGURE 39.6. Projection formula of serine (C* is the asymmetric α-carbon atom).

the α-amino acids in natural proteins have the L configuration, possibly indicating a uniform method of synthesis in nature.

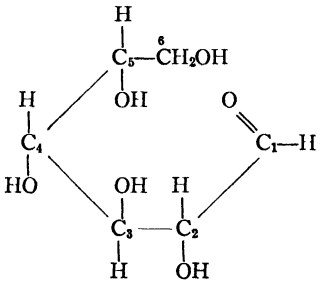
39. 6 Ring Isomerism in Sugar Chemistry. The projection formula described in section 39.3 and figure 39.2 is an artificial way of pictur-

ing an open chain of carbon atoms. We found in section 12.3 that a carbon chain zigzags, and that the ends may meet if the chain is long enough.

We shall now permit the chain in figure 39.2 (*b*) to coil on itself, as it should to give C–C bonds of customary angles. In figure 39.7, model I shows the same chain as depicted in figure 39.2 (*b*), and model II is the ring version. (A look ahead at figure 39.9 will help the student with the physical picture.)



I. Straight-chain formula of the hexose, D-glucose. (The C atoms are numbered for reference in the discussion.)



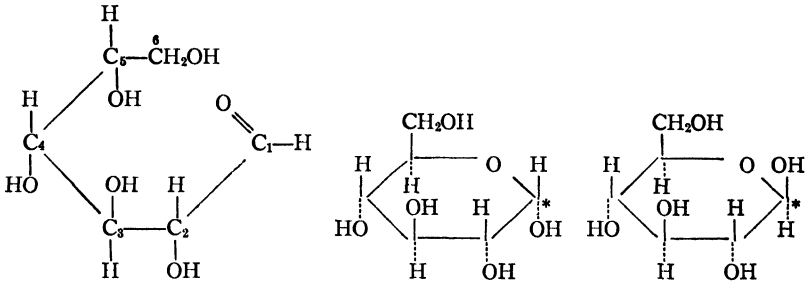
II. Space model of the hexose, D-glucose.

FIGURE 39.7. Transition from projection formula to coiled structure of D-glucose.

In model II the partly closed chain is to be visualized as resting on a table. Certain –H and –OH groups then point upward, while others point downward and are in actual contact with the table. When we read the flattened (straight-chain) formulas of sugars on a printed page as in model I, we should picture them as uncoiled versions of the partially closed ring shown in model II. The atoms on the *left* of the chain are on *top* of the ring.

The cyclic structures of the sugars pictured in the rest of this chapter are referred to as *perspective* formulas (Haworth and Peat, 1929).

It is not surprising that the sugars exist in cyclic forms, in view of the great reactivity of the C=O group and the probability of its proximity to the –OH on a supposedly distant carbon atom. The result of the chain closure is shown by the transition from model II to models III and IV in figure 39.8.

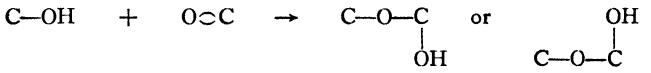


II. D-Glucose, open-chain form III. α-D-Glucopyranose IV. β-D-Glucopyranose

FIGURE 39.8. Ring closure in glucose (* marks the "potential C=O group," as explained in section 40.2).

The six-membered ring in these *alpha* and *beta* sugars is known as the *pyranose* ring. It is a modification of the pyrone cycle described in section 36.4. The sugars in models III and IV are often called simply *alpha*-glucose and *beta*-glucose.

Although the mechanism by which the closure takes place is uncertain, it is convenient for our purpose to picture it as a simple addition across the double bond as described in section 30.5*c*. The picture of the double bond itself should be referred to once more in figure 15.1 and it should then be observed that the reaction between the first and fifth carbon atoms in glucose can take place as follows,



to give two possible products. The structural relationships in these products are shown in figure 39.9*a* and 39.10*a*, where the bonds carrying –OH groups are labeled to make easier the comparison of these illustrations with those in figure 39.8. Most experts in carbohydrate chemistry are convinced that these six-membered rings are puckered, like the cyclohexane structure in figure 12.15 and that they have a *trans* configuration.

By means of the Fisher-Hirschfelder models illustrated in figure 18.6, it has been shown that the most plausible structure is one in which the oxygen atom in the ring is *trans* to the C_3 atom, with respect to the plane of the rest of the ring. This conclusion is based mostly on the steric hindrance effects (section 32.10) that would

prevail in other possible *trans* structures which can be built with atom models. In the D- series, illustrated by figures 39.9*a* and 39.10*a* the ring oxygen atom is above, and the C_3 atom is below, the plane containing atoms C_1-C_2-C_4-C_5. In the L- series, the oxygen atom in

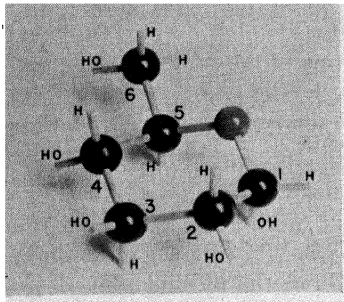


FIGURE 39.9*a*. Model of α-D-glucopyranose.

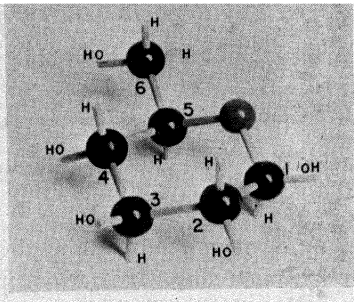


FIGURE 39.10*a*. Model of β-D-glucopyranose.

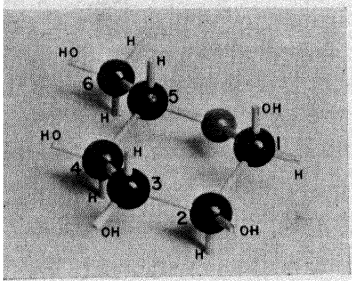


FIGURE 39.9*b*. Model of α-L-glucopyranose.

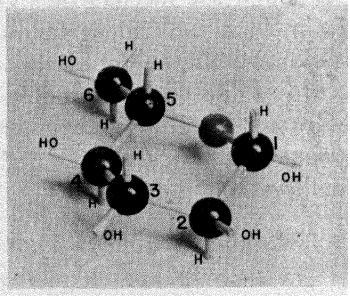


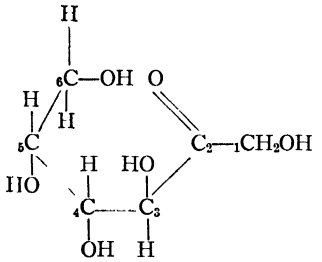
FIGURE 39.10*b*. Model of β-L-glucopyranose.

the ring is below the plane and the C_3 atom above, as shown in figures 39.9*b* and 39.10*b*. On the bond between C_4 and C_5, considerable rotation takes place in order to swing C_6 out of the ring and permit reaction between –OH on C_5 and the carbonyl oxygen on C_1.

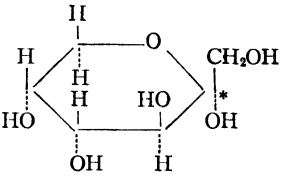
There is ample evidence that in α-D-glucopyranose the –OH groups on the C_1 and C_2 atoms are on the *same side* of the ring, whereas in β-D-glucopyranose they are on *opposite sides* (see models III and IV in figure 39.8). The *important difference between the two isomers* is in the position of –OH on the C_1 atom; in the α sugar,

the –OH bond on C_1 is at right angles to the –OH bond on C_4, whereas in the β sugar, the bonds on C_1 and C_4 are parallel. These two sugars are common building blocks in nature and the different linkages taking place at the C_1 atom are an important factor in the different configurations and properties of substances like starch and cellulose (see sections 41.4 and 41.8, and the photographs of models in section 46.3).

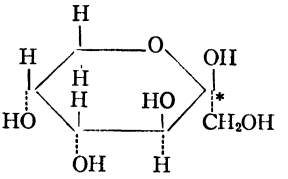
All of the aldohexoses exist in an α-pyranose and a β-pyranose form, and there is an L series as well as a D series. In the analogous ring structures of α-D-fructopyranose and β-D-fructopyranose, shown in models VI and VII of figure 39.11, it will be seen that the difference consists in the positions of the –OH groups on the second and



V. D-Fructose, open-chain form



VI. α-D-Fructopyranose



VII. β-D-Fructopyranose

FIGURE 39.11. Ring closure in fructose (* marks the "potential C=O group," as explained in section 40.2).

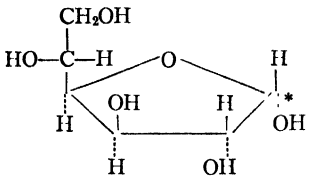
third carbon atoms. In the β form, they are both on the same side of the ring. Ordinary commercial fructose, or levulose, is the β variety. The α form has not yet been obtained pure. (The numbering of the carbon atoms in models II and V should be studied.)

These cyclic forms of the sugars can be regarded as examples of the *cis*, *trans* (geometric) isomers described in section 22.3. For example, α-D-glucopyranose has a *cis* and β-D-glucopyranose has a *trans* pair of –OH groups on the C_1 and C_2 atoms. However, the

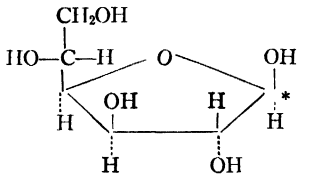
important thing is that the ring closure gives rise to a new asymmetric carbon atom. In glucose, it is the C_1 atom and in fructose, it is the C_2 atom. The α- and β- isomers are optically active, and are said to be anomeric forms, or *anomers*.

The two anomers of D-glucose are not mirror images; they are, therefore, *diastereoisomers* as discussed in this chapter in section 39.4. By means of molecular models, however, it can be shown that mirror-image pairs in this sugar family do exist. Examples are α-D-glucopyranose and α-L-glucopyranose. The models are illustrated in figures 39.9 and 39.10.

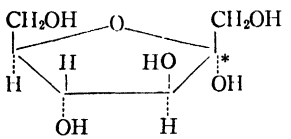
39. 7. Sugars with Five-Membered Rings. The simple sugars also exist in a very active modification, which was called *gamma* sugar before its structure was well understood. This structural modification is the five-membered ring resembling furan (section 36.2) and, consequently, known as the *furanose* form. This ring can yield α and β anomers just as the six-membered rings. The α and β anomers of D-glucofuranose and of D-fructofuranose are shown in figure 39.12. These forms of the sugars are generally not stable enough to exist independently, but their derivatives are known. An example is sucrose (section 41.2).



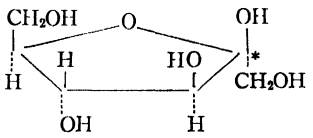
VIII. α-D-Glucofuranose



IX. β-D-Glucofuranose



X. α-D-Fructofuranose



XI. β-D-Fructofuranose

FIGURE 39.12. Furanose forms of the sugars (* marks the "potential C=O group," as explained in section 40.2).

39. 8. Summary of the Possible Isomers of Glucose. When the six-carbon aldehyde sugars are written in a straight chain, we find there are eight different fundamental isomeric forms (figure 39.3).

Each of these can exist in a D- or an L- modification, so that there are sixteen possible isomers in the glucose family.

D-Glucose can exist in an α and a β cyclic pyranose form. So can L-glucose. In fact, all sixteen open-chain isomers can exist in α and β forms. There are then 32 + 16, or forty-eight possible isomers in the glucose family.

As we have just seen, each of the sixteen open-chain isomers can possibly exist in two furanose forms, that is, there are thirty-two more possible isomers, making eighty in all.

Recently, it has been found that the sugars can also probably exist in a so-called *septanose* ring form. This is a seven-membered ring, in which the –CHO group at one end of the molecule reacts with the $-CH_2OH$ at the other end. (See model II of figure 39.8.) This means an even greater number of possible isomers.

All these isomers have the same composition, $C_6H_{12}O_6$!

39. 9. Chemical Relatives of Glucose. Although the mass of information already given on the sugars is sufficient to prove their structure, it is instructive to note how the general nature of a sugar like glucose can be proved by chemical means.

In the series of compounds shown in figure 39.13, glucose is compared with a number of other substances with which it is closely related. The common occurrence of the prefix gluc- (or sometimes glyc-) in so many compounds of this type is due to derivation from the Greek word *glykys*, meaning sweet.

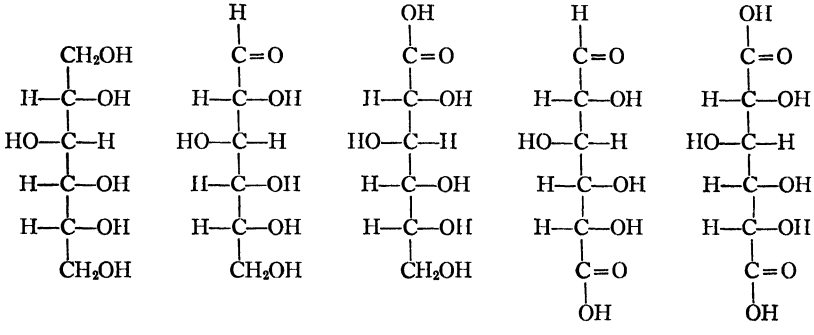


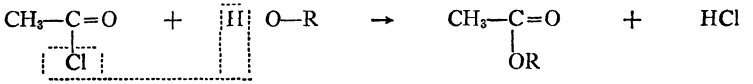
FIGURE 39.13. Chemical relatives of glucose.

When sorbitol is oxidized it yields glucose; conversely, if glucose is reduced we obtain sorbitol. We know that sorbitol is an alcohol in which there is one –OH group on each carbon atom, and this gives us a good idea of the general structure of glucose.

When glucose is oxidized it takes only one oxygen atom to convert it to gluconic acid; this shows the presence of an aldehyde group in glucose, for we know that when $-\underset{\displaystyle H}{\underset{|}{C}}=O$ is oxidized to $-\underset{\displaystyle OH}{\underset{|}{C}}=O$ only one oxygen atom is necessary. Further oxidation of gluconic acid yields saccharic acid, which has a $-\underset{\displaystyle OH}{\underset{|}{C}}=O$ group at both ends of the chain; this requires two oxygen atoms, because it is the oxidation of a primary alcohol group, $-CH_2OH$ (section 27.4*c*). By special methods, the –CHO group of glucose can be protected (muzzled) and the oxidation of glucose then yields glucuronic acid.

These reactions, by which glucose is converted to compounds of known structure, show that there are –CHO and $-CH_2OH$ groups in glucose, at the ends of the chain.

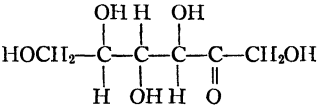
The fact that glucose contains five –OH groups is shown by its behavior toward acetylating agents. In section 38.1*c* we showed how acetyl chloride, $CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}=O$, reacts with –OH groups and is useful for detecting —OH groups in compounds:



When glucose is treated with acetyl chloride, five acetyl groups are introduced into the molecule to form a pentaacetate, proving that glucose has five –OH groups. The method by which the *positions* of these five –OH groups in the molecule have been determined is too complex for us to consider.

D-Sorbitol is widespread in plants, being found in the *fresh* juice of mountain ash berries, in certain seaweeds, and in fruits, such as pear, cherry, etc. It is made on a large scale by hydrogenation of D-glucose to serve as a source of L-sorbose, which, in turn is, used to synthesize vitamin C (section 44.4).

L-Sorbose is a *keto* sugar, found originally in the *fermented* juice of the mountain ash berry; its presence is due to a bacterial oxidation of D-sorbitol. The D and L family relations are interesting. D-Fructose (figure 39.4) can be regarded as the product of oxidation of D-sorbitol (figure 39.13) at the C_2 atom in the chain, reading from the top. L-Sorbose is made by bacterial oxidation of D-sorbitol at the C_5 atom in the chain, and has the structure



L-Sorbose

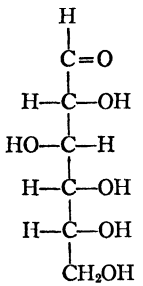
If this formula is rotated 90° clockwise in the plane of the paper, its relation to D-sorbitol in figure 39.13 will be apparent. However, it is conventional to use the smallest possible number for the C=O group, and, to regard it as a *2-ketose*, we rotate the formula 90° counterclockwise. In this aspect, L-sorbose is shown to be related to L-glucose (figure 39.4), since now the C_5 atom has –OH on the left.

SUGGESTED READING

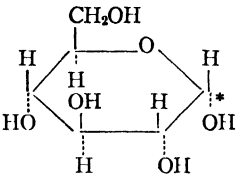
See references to chapter 41.

40. CHEMISTRY OF SUGARS

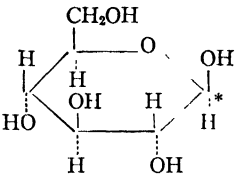
40. 1. Composition of a Glucose Solution. There is so much evidence to show that the simple sugars exist in a cyclic rather than a straight-chain form that the question arises as to how we explain their "aldehyde" or "ketone" properties. The answer is that the cyclic modifications must exist *in solution* in equilibrium with the open-chain type. Thus, in a glucose solution we probably have the following substances present, and perhaps also some of the furanose



D-Glucose
(Aldehyde form)



α-D-Glucopyranose



β-D-Glucopyranose

form described in the last chapter, and maybe other cyclic types which have not yet been identified. However, we know definitely that most of the glucose in solution is cyclic, about two-thirds of it in the β form, one-third in the α form, and only very small amounts in the open-chain, aldehyde form.

A similar reasoning applies to solutions of fructose, the ketone sugar.

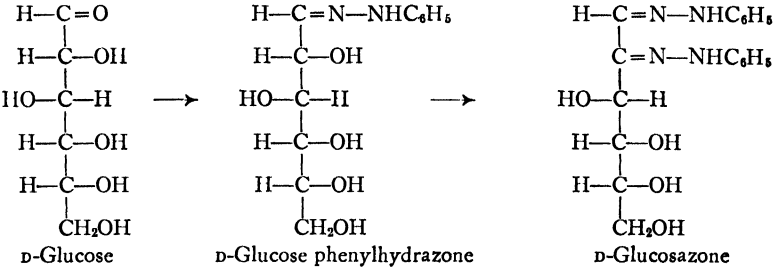
40. 2. Potential Carbonyl Groups. Since the sugars are so often written in the cyclic form, the beginner is often puzzled in trying to pick out the C=O group. Glucose, for example, has the properties of an aldehyde, but there is no $-\overset{|}{\underset{H}{C}}=O$ group apparent in the cyclic structure. In this book, for convenience, we have put an asterisk (*) on that C–OH group in the cyclic structure which forms the C=O group when the ring opens to the straight chain (review figure 39.8). This particular C–OH is the "potential C=O group" that gives the molecule the typical sugar properties to be described in this chapter.

40. 3. Chemistry of the Sugars. The reactions of glucose which we shall consider in this section are characteristic of all aldoses, and, in general, of all the reducing sugars. These are the properties usually associated with sugar chemistry. It should be observed that the sugar properties are essentially aldehyde properties, altered more or less by the presence of –OH groups in the molecule.

1. Glucose shows most of the reactions used as qualitative tests for aldehydes. It reduces a solution of silver nitrate in ammonium hydroxide ($AgNO_3/NH_4OH$), depositing a film of metallic silver. It also reduces the copper in Fehling's solution (section 30.5*b*) to cuprous oxide, Cu_2O. This test with Fehling's solution differentiates sugars like glucose, which have a free or potential C=O group in the molecule, from those like sucrose (section 41.2) that do not. Glucose is called a *reducing* sugar, whereas sucrose is a *nonreducing* sugar.

2. A glucose solution forms a brown resin when boiled with dilute alkalies, as is characteristic of aldehydes.

3. In section 30.5*e* we showed how aldehydes and ketones enter into a double decomposition with hydrazine, $H_2N–NH_2$, forming *hydrazones*. This should be reviewed. Emil Fischer used this type of reaction in his brilliant work on the configuration of the various sugars. He found that phenylhydrazine, $H_2N–NHC_6H_5$ (section 33.9), gives better results than hydrazine. The reactions with the sugars are quite complex, but the final products are as follows:



D-Glucose D-Glucose phenylhydrazone D-Glucosazone

The osazones are more important than the phenylhydrazones formed at first, because they are less soluble and more easily crystallized. The melting point and solubility of their osazones are among the important constants used in the identification of sugars.

The reader should examine the structure of D-fructose in figure 39.4 and observe that its osazone must be identical with that of D-glucose. In fact, this is one of the reactions which proved that outside of the first and second carbon atoms, D-glucose and D-fructose are identical.

Fructose, even though it is a keto sugar, gives most of the reactions of glucose. This is due to the influence of the neighboring –OH groups in the molecule on the C=O group.

40. 4. Specific Rotation. One of the most important constants employed in the identification of the sugars is the specific rotation. In section 22.5, we discussed optically active substances, which rotate the plane of polarized light, and we mentioned the polarimeter, an instrument by which the angle of rotation can be measured.

The sugars are optically active, and each sugar rotates plane-polarized light through a certain number of degrees and in a certain direction, that is, right (+) or left (−). The specific rotation data for sugars are usually obtained at 20° C., with the D line of the spectrum (yellow sodium light). The specific rotation of glucose (dextrose) is +52.7°, and of fructose (levulose) is −92.4°.

Specific rotation is calculated from the equations

$$[\alpha]_D^{20^\circ} = \frac{\alpha}{ld} \times 100$$

(for pure liquids)

$$[\alpha]_D^{20^\circ} = \frac{\alpha}{lgd} \times 100$$

(for solutions)

where α is the measured rotation in degrees, l is the length of the sample in decimeters, d is the density of the pure liquid or of the

solution, and g is the concentration of solute in g./100 g. solution. The result is "specific" in that the rotation is calculated for unit quantity of solute, unit volume, and unit length of sample.

40. 5. Mutarotation. When α-glucose is dissolved in water, the solution has a specific rotation of +112.2°, but the value is not constant. It gradually decreases to a lower limit of +52.7°, at which it does remain constant. The phenomenon is known as mutarotation (from the Latin *mutare*, to change).

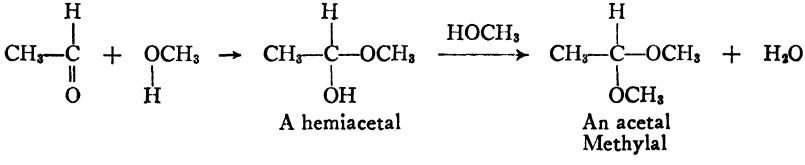
When β-glucose is dissolved in water its initial rotatory power is +18.7°, but this value gradually *increases* until it reaches an upper limit of +52.7°. The same specific rotation, therefore, is reached, no matter which of the two glucose isomers we start with, because of the phenomenon of mutarotation. One form changes into the other until equilibrium is reached.

An ordinary glucose solution has a specific rotation of +52.7°. It is an equilibrium mixture of the α- and β- cyclic forms, in which the β- form predominates. If we add an additional quantity of either of these isomers the specific rotation of +52.7° is disturbed, but is soon regained after mutarotation has taken place and has restored the balance between the two cyclic forms.

40. 6. How α- and β- Sugars are Named. As indicated in the preceding pages, the α- and β- sugars are the two anomers formed when closure of the straight-chain modification results in a new asymmetric carbon atom. The anomers differ in the arrangement of the groups around the new asymmetric center.

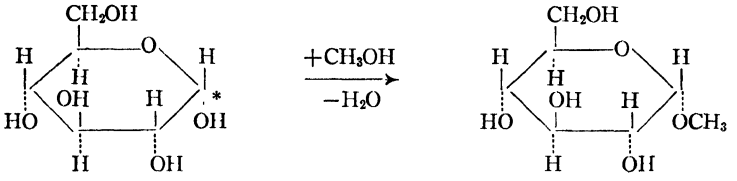
The nomenclature of the α- and β- anomers follows rules suggested by Hudson. In the D series, the more dextrorotatory of a pair of anomers is named α and the other is then β. Examples are α-D-glucopyranose (rotation, +112.2°) and β-D-glucopyranose (rotation, +18.7°). In the L series the more levorotatory anomer is given the name α and the other β.

40. 7. Glucosides. When an aldehyde and an alcohol react, the initial unstable product is a hemiacetal, which, in the presence of acids, reacts with more of the alcohol to yield a stable acetal:



It will be observed that hemiacetals and acetals have an ether type of linkage in the molecule.

The formation of a hemiacetal consists in "addition across the double bond," explained in section 30.5*c* and further illustrated in the ring closure of sugars in figure 39.8. The cyclic forms of the sugars shown in diagrams III, IV, VI, and VII, in figures 39.8 to 39.11 are, therefore, referred to as hemiacetals by sugar chemists. The cyclic form of α-glucose shown in figure 39.8 behaves just like a hemiacetal in that it can be made to react with an alcohol to yield an acetal, but the product is generally called a glucoside. With methyl alcohol the product is α-methyl glucoside. From β-glucose, we can obtain by this procedure the β-methyl glucoside.



α-Glucose
α-D-Glucopyranose
(A hemiacetal)

α-Methyl glucoside
Methyl α-D-glucopyranoside
(An acetal)

The α- and β- glucosides have markedly different properties:

	α-Methyl glucoside	*β-Methyl glucoside*
Specific rotation	159°	−34.2°
Melting point	165° C.	104° C.
Hydrolyzed by	Maltase	Emulsin

The interesting fact is that the two compounds cannot be broken down by the same enzyme. Maltase acts only on the α-compound, whereas emulsin affects only the β- compound. Immediately after hydrolysis, α-glucose or β-glucose shows its characteristic initial specific rotation, which later, by mutarotation, goes to the equilibrium value of +52.7°.

Enzymes are substances secreted by living cells and are capable of acting as catalysts in chemical reactions. Maltase, for example, is found in blood serum, saliva, and various seedlings. Zymase is found in yeast, and emulsin in plant tissues.

Glucosides are important constituents of most vegetable matter. In most plants, substances needed as reserve food or for emergencies are stored up by combining them with glucose in the form

of glucosides. Some natural glucosides and their component parts obtained by hydrolysis or fermentation are the following:

Amygdalin (in bitter almonds) yields glucose + benzaldehyde + HCN.

Salicin (in willow bark) yields glucose + saligenin. When administered to man, the saligenin is changed internally to salicylic acid.

Arbutin (in bearberry leaves) yields glucose + hydroquinone. The hydroquinone is an antiseptic.

Glucosides are used by plants to combat diseases and for other purposes; they were used by man long before the reason for their powers was known. It will be shown in the next chapter that the more complex sugars, like cane sugar and milk sugar, are also formed in the manner of the glucosides. Most natural glucosides are derivatives of β-D-glucopyranose.

40. 8. Glycosides. All compounds of the aldoses and ketoses similar in structure to the glucosides which we have described in the preceding section are known as *glyco*sides. Galactosides, mannosides, and fructosides, for example, are known and for convenience these compounds have been given the class name of glycosides.

SUGGESTED READING

See references to chapter 41.

41. COMPLEX CARBOHYDRATES

41. 1. Complex Sugars. The sugars that we have discussed up to this point are called the *simple* sugars because they cannot be broken down by hydrolysis into any types of sugars that are less complex. Instead, these simple sugars are apparently used in nature for the building up of more complex sugars, and of those highly complex carbohydrates known as starch and cellulose.

The most important complex sugars are those formed by the union of two simple six-carbon sugars, thus:

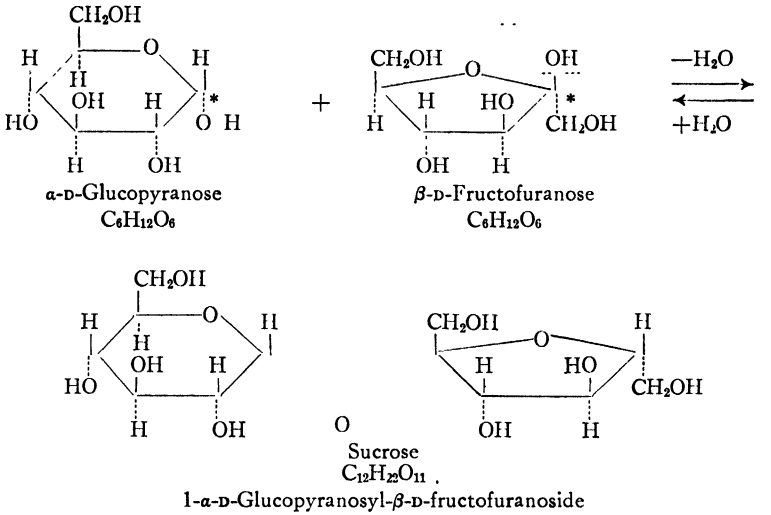
$$\underset{\substack{\text{Two molecules of same, or}\\ \text{different, sugars}}}{C_6H_{12}O_6 + C_6H_{12}O_6} \rightleftarrows H_2O + \underset{\text{A complex sugar}}{C_{12}H_{22}O_{11}}$$

It will be observed that a molecule of water is eliminated when the complex sugar is formed. This is important, *even though nature may not build the complex sugars in exactly this way.* The process can be reversed in the laboratory; water can be added to the complex sugar in such a way as to decompose it into the two simple sugars.

41. 2. Sucrose. By far the most important of all the complex sugars is sucrose. It occupies among the sugars the same position as alcohol among the "alcohols," and ether among the "ethers." It is, therefore, usually called simply "sugar." Other names for it are cane sugar, beet sugar, and saccharose. These names indicate where sucrose comes from, and also that it is sweet.

The following formula shows that sucrose is regarded as the α anomer of D-glucose in the six-membered ring form (figure 39.8,

model III), combined with the β anomer of D-fructose in the five-membered ring form (figure 39.12, model XI).



1-α-D-Glucopyranosyl-β-D-fructofuranoside

(The arrows in this equation do not represent an equilibrium. The upper arrow represents the hypothetical method of formation of the sucrose molecule. The lower arrow shows how the molecule of sucrose can be hydrolyzed in dilute acid to the two component sugars.)

Sucrose is interesting because it is stable toward several chemical reagents with which other sugars react easily. For example, it does not have reducing properties toward Fehling's solution, and it does not react with phenylhydrazine (section 40.3). Also, it does not show mutarotation (section 40.5), but has a constant specific rotation of +66.4°.

These characteristics make it quite certain that, when glucose and fructose unite to form sucrose, the union takes place through the —OH groups marked with an (*). As we explained in section 40.2, these -OH groups come from the $-\overset{|}{C}=O$ groups in the straight-chain forms of the sugars, and are "potential carbonyl groups."

In the sucrose molecule, the "potential carbonyl groups" are no longer present. Sucrose, therefore, does not have aldehyde or ketone properties, does not reduce Fehling's solution, and is called a *nonreducing* sugar. In section 40.7, we also showed that when the (*)-OH groups in sugars react with other substances, *glycosides*

are formed. In the case of sucrose, we can look on the molecule as a glucose-fructoside, or as a fructose-glucoside.

Sucrose was synthesized for the first time only recently (1944). Fructose was made to combine with a glucose phosphate, by the aid of an enzyme, producing sucrose with the elimination of a molecule of phosphoric acid. The synthesis was of great importance in the search for the mechanism by which these complex sugars are made in nature (sections 44.5 and 44.7). A purely chemical synthesis was accomplished in 1953.

41. 3. Inversion. When sucrose is boiled with dilute acids, it is hydrolyzed to its constituent sugars, glucose and fructose. Sucrose has a positive rotation of $+66.4°$. The mixture of glucose and fructose has a negative rotation of $-39°$. Since sucrose is dextrorotatory and the mixture of sugars obtained from it by hydrolysis is levorotatory, the hydrolysis is called inversion. The mixture of glucose and fructose is called *invert sugar*. It is a good food.

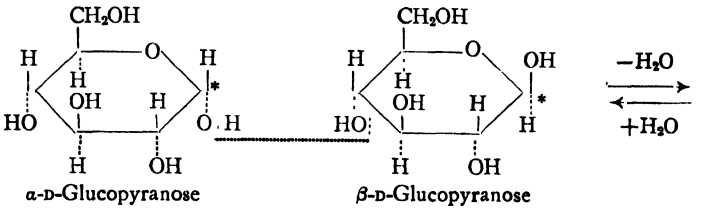
A certain enzyme from yeast breaks down sucrose into glucose and fructose just as easily as boiling with acids. This enzyme is called invertase.

41. 4. Maltose, $C_{12}H_{22}O_{11} \cdot H_2O$, is a complex sugar found in malt, which is the sprouted seeds of cereals. Barley malt is the most common malt. Maltose is also the final product of the action of certain enzymes on starch.

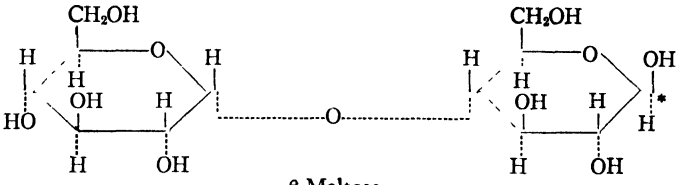
Like sucrose, maltose can be regarded "hypothetically" as built up of two hexose molecules by elimination of a molecule of water. In the case of maltose, however, both hexose molecules are the same, namely, D-glucose. Inspection of its structure shows that it is a glucose-α-glucoside. It is known to be an α-glucoside because maltose is broken down to its constituent sugars by the enzyme maltase, which splits only the α-glycoside linkage (section 40.7).

The chemistry of maltose is much different from that of sucrose. It is a *reducing* sugar. It behaves like the simple sugars in that it reduces Fehling's solution and it reacts with phenylhydrazine. Any sugar which behaves this way must have a "potential C=O group" (section 40.2) in its molecule and in the formula for maltose the position of this group is shown as usual by the asterisk (*). As already stated, sucrose is a nonreducing sugar because there is no potential C=O group in its molecule. In the sucrose structure,

both potential C=O groups are used up to form the –O– bridge. In the maltose structure, however, only one of them is used and the other remains with its typical sugar properties.



α-D-Glucopyranose β-D-Glucopyranose



β-Maltose

4-(α-D-Glucopyranosyl)-β-D-glucopyranose

In the equation, it is indicated that that half of the molecule which retains its potential C=O group is β-glucose, and that it is linked through the 4 carbon atom. This molecule is known as β-maltose (specific rotation is +111.7°). An isomeric sugar known as α-maltose should be possible, in which the second half of the molecule is α-D-glucose. Its name is 4-(α-D-glucopyranosyl)-α-D-glucopyranose, but this isomer has not yet been identified. These two forms of maltose can be more readily understood by referring back to the two forms of D-glucose in section 40.1. The specific rotation for the equilibrium mixture is +130.4°, following mutarotation from β-maltose.

Starch (section 41.7 and section 46.3) is essentially a chain of α-maltose units. This means that the fundamental building unit in starch is α-D-glucopyranose.

41. 5. Lactose. The principal sugar in the milk of all suckling mammals is known as lactose, or milk sugar. It is obtained as a by-product of the manufacture of cheese. Rennet, an enzyme, precipitates the casein and fat (the cheesy materials) from the milk, and leaves a clear liquid which is called whey. Crystalline lactose, $C_{12}H_{22}O_{11} \cdot H_2O$, is obtained from the whey by evaporation, after

neutralizing with a mild alkali. Sour milk is produced by an organism capable of fermenting the lactose in milk to lactic acid.

Lactose is a complex sugar built up from two simple sugars D-glucose and D-galactose. The fact that it can be split by the enzyme emulsin and not by maltase (section 40.7) shows that it has the β-glycoside type of structure. It has been proved to be a glucose-β-galactoside.

Like maltose, lactose has typical sugar properties. The glucose half of the molecule contains the potential C=O group which gives a sugar these properties. Lactose can accordingly be isolated in two forms, namely α-lactose and β-lactose, which show mutarotation when freshly dissolved in water. Just as with maltose, the linkage with the glucose part of the molecule of lactose takes place at the 4 carbon atom. Lactose is, therefore, 4-(β-D-galactopyranosyl)-D-glucopyranose; this name does not consider the fact that the glucopyranose can be either α or β.

41. 6. Raffinose. This is a complex sugar built up from *three* simple sugars and has the composition $C_{18}H_{32}O_{16} \cdot 5H_2O$. When hydrolyzed, it breaks down to glucose, fructose, and galactose. It is practically tasteless. Raffinose is found in beet-sugar molasses, and in seeds, such as barley and cottonseed. It is a nonreducing sugar and consequently has no potential —C=O group in its structure.
|

41. 7. Starch. In this chapter we have shown how complex sugars may be regarded as derived from the simple sugars by *elimination of water*:

$$C_6H_{12}O_6 + C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$$

When we hydrolyze a complex sugar the molecule of *water is taken up* again and the complex sugar is broken down to its constituent simple sugars:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

It is clear from this relationship that we can regard the complex sugars as *anhydrides* of simple sugars.

The starches are like the complex sugars in that they are anhydrides of simple sugars; on complete hydrolysis they take up water to form simple sugars. Since the starches yield C_6 sugars (hexoses) when hydrolyzed, we call them *hexosans*; this means they are anhydrides of hexoses.

The starches are the reserve food material of most plants. The various starches are classified, according to their source, as potato starch, wheat starch, corn starch, etc. When a starch is boiled with dilute acids, or acted on by certain enzymes, it is gradually broken down according to the following scheme:

Starch → Series of dextrins → Maltose → D-Glucose

Although starch is accordingly an anhydride of glucose (a *glucosan*) it is probably better considered as built up of maltose units. This will be discussed further in section 46.3, where it will be pointed out that starches from various sources contain variable amounts of an *amylose* fraction and an *amylopectin* fraction, which have different properties.

The dextrins obtained by breaking down the starch molecule are similar to starch in appearance, but are more readily soluble and are used as adhesives. The enzyme *diastase*, present in leaves and seedlings of plants, hydrolyzes starch to dextrins and finally to maltose. Another enzyme, *maltase*, completes the process by hydrolyzing maltose to glucose, in which form the plant uses carbohydrates as food.

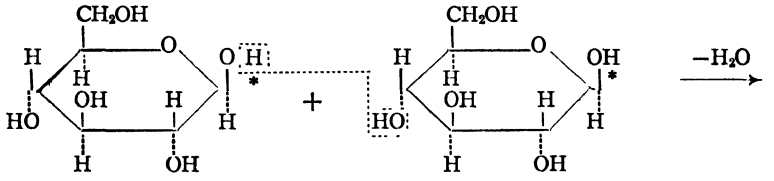
41. 7α. Glycogen. Animals lay by a reserve food material called "animal starch" or glycogen. This substance is manufactured by mammals when there is an excess of sugar in the system, and is stored in the liver as reserve. When hydrolyzed, glycogen yields the same products as obtained from starch, namely, maltose and glucose (section 46.3).

41. 8. Cellulose, $(C_6H_{10}O_5)_n$, is a hexosan and is more particularly a glucosan, because it can be hydrolyzed to glucose. It is, therefore, closely related to starch, which is also a glucosan and yields glucose when hydrolyzed.

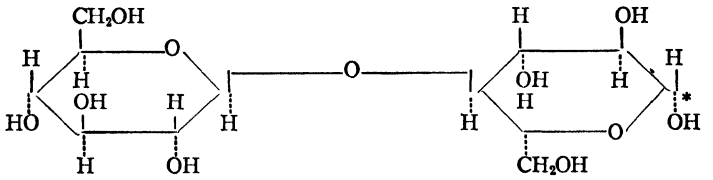
Cellulose is the chief constituent of the cell walls of plants, that is, it is the framework of the vegetable kingdom. It is always found associated with other substances. It is insoluble and very inert; it can be easily obtained from all kinds of plant tissue by first removing other substances by appropriate extraction methods. Cotton is nearly pure cellulose.

Much research has been done on the structure of cellulose. When D-glucose units combine to form cellulose, the union formed is β-glucose β-glucoside. This is a complex sugar known as cellobiose,

and is an isomer of maltose, with which it should be carefully compared. Maltose is D-glucose α-D-glucopyranoside, whereas cellobiose is D-glucose β-D-glucopyranoside. These two sugars bear the same relation to each other as methyl α-D-glucopyranoside and methyl β-D-glucopyranoside, described in section 40.7. Of these two closely related sugars, one is the building unit of starch and the other is the building unit of cellulose (section 46.3).



β-D-Glucopyranose (2 molecules)



β-Cellobiose

4-(β-D-Glucopyranosyl)-β-D-glucopyranose

In the hypothetical equation for the formation of cellobiose, which is given here, it is indicated that there is a potential C=O group in the product. Cellobiose is a reducing sugar and exhibits mutarotation. We have formulated the preparation of a β-cellobiose, linking β-D-glucopyranose at the 4 carbon atom through the –O– bridge with the 1 carbon atom of the other molecule. Cellulose consists of a long chain of these glucose units in the pyranose form, linked at the 1 and 4 positions. The reactivity of the –OH groups in the glucose rings of cellulose will be described in section 46.10*b*.

41. 9. Other Complex Carbohydrates. The complexes described in the preceding pages are anhydrides of glucose. In this section, we shall mention briefly certain substances in nature which are built up of other units of simple sugars. *Inulin* is a substance which resembles starch, but is not now classified as a starch. However, just as starch is a glucosan, inulin is a fructosan which yields D-fructose when

hydrolyzed. It occurs in Jerusalem artichokes and dahlia tubers; in fact, D-fructose is obtained commercially from the second source.

Xylan and *araban* are examples of naturally occurring pentosans which yield pentoses when hydrolyzed, as mentioned earlier in section 39.2. Xylan is found widely distributed in such substances as straw, wood, and peanut shells and araban is present in complexes in peanuts. Gum arabic contains araban and the calcium salt of arabic acid (the gums, in general, are complex carbohydrates which are partially oxidized to acids).

41. 10. Nomenclature and Classification of Carbohydrates. The name "carbohydrate" is an old one, but it is not considered so good a name now as it was in the early days of organic chemistry. When the early chemists isolated certain sugars from nature, they found that the sugars appeared to be hydrates of carbon (carbohydrates), as in the case of cane sugar, which may be written $C_{12}H_{22}O_{11}$, or $C_{12}(H_2O)_{11}$. This apparent water of hydration may be eliminated easily, as is familiar in the charring of burnt sugar and the charring caused by dehydration of sugar with concentrated sulphuric acid. In both cases, pure carbon remains.

Some sugars are known, however, in which the ratio of hydrogen to oxygen is not the simple 2:1 ratio of H_2O. An example is rhamnose, $C_6H_{12}O_5$, the structure of which is CH_3–CHOH–CHOH–CHOH–CHOH–CHO.

Moreover, many compounds are known which cannot possibly be classed as carbohydrates, yet have the same molecular composition as a carbohydrate. Two examples are formaldehyde, CH_2O, and acetic acid, $C_2H_4O_2$.

We still cling to the class name carbohydrate for sugars, starches, and cellulose, but now that we know their composition so much better, we realize that the name does not mean what it at first implied.

The classification of carbohydrates is easily understood. We have discussed the simple sugars and have found that they are aldehyde-alcohols or ketone-alcohols. In this chapter, we examined the complex sugars and showed that they may not contain aldehyde and ketone groups, but on hydrolysis they yield simple sugars.

Similarly, the highly complex starches and cellulose contain alcohol groups, but never aldehyde and ketone groups; they are classed

as carbohydrates, however, because they, too, yield simple sugars when hydrolyzed.

The classification of carbohydrates, in a very brief outline, runs as follows:

	Examples
I. Monosaccharides, or simple sugars	
Trioses, $C_3H_6O_3$	Glycerose
Pentoses, $C_5H_{10}O_5$	Arabinose
Hexoses, $C_6H_{12}O_6$	Glucose and Fructose
(Simple sugars from trioses up to decoses, $C_{10}H_{20}O_{10}$, are known.)	
II. Polysaccharides, or complex sugars	
Disaccharides, $C_{12}H_{22}O_{11}$	Sucrose
Trisaccharides, $C_{18}H_{32}O_{16}$	Raffinose
(These are dihexoses and trihexoses. Complex sugars derived from pentoses are also known.)	
III. Colloidal polysaccharides	
Pentosans, $(C_5H_8O_4)_n$	Araban
Hexosans, $(C_6H_{10}O_5)_n$	Starch and Cellulose
(These are not true sugars. Their molecular weights are of the order of 50,000 to more than 1,000,000 and, in modern terminology, they are referred to as colloids.)	

In the introduction to this chapter, we stated that the complex carbohydrates found in nature are built up of the simpler sugars. This is true, as far as the framework of the complex molecule is concerned. We are certain that cellulose, for example, consists of glucose units, but we do not know how nature assembles the glucose molecules, before building the complex molecule. The natural synthesis of complex carbohydrates is still a mystery to the chemist (section 44.7).

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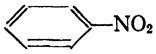
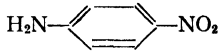
42. DYES

42. 1. Color and Structure. Dyes are substances which have color and can be firmly fixed to textiles by the dyeing process.

The principal problems of dyeing are illustrated by the following two compounds:



Nitrobenzene (a colored substance)



p-Nitroaniline (a dye)

Nitrobenzene is yellow, but it does not dye fabrics; the color is easily washed away. *p*-Nitroaniline, however, is not only yellow but also sticks to fabrics and is, therefore, a dye.

Accordingly, there are two facts about a dye molecule that are of interest: the reason for its color and the reason for its ability to stick to a textile fiber. Let us consider first the reason for color.

The reader will recall that ordinary white light consists of "all the colors of the rainbow," and that these colors are committed to memory in the order V B G Y O R, that is, violet, blue, green, yellow, orange, and red. When a beam of light is passed through a prism and allowed to fall on a white surface, these colors are arranged side by side in what is called a spectrum, as shown in figure 42.1.

Our eyes do not see all the colors in the spectrum, but only those in the "visible spectrum." When the visible spectrum is intact it appears to us as white light. Although the very rapid vibrations (ultraviolet) and the relatively slow vibrations (infrared) make no impression on our eyes, they do make an impression on a photographic plate, and that is the way spectra are usually mapped.

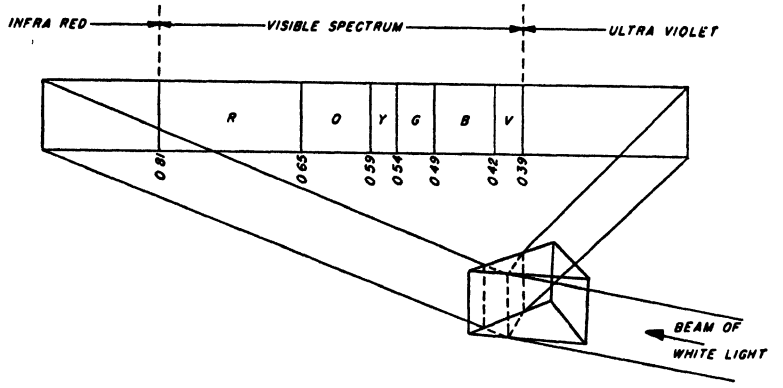


FIGURE 42.1. The spectrum.
(Wave lengths are given in microns. A micron is 0.001 millimeter)

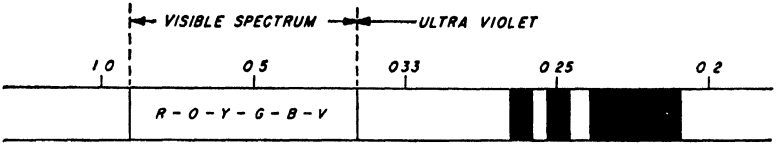


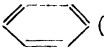
FIGURE 42.2*a*. Absorption spectrum of benzene,  (colorless).

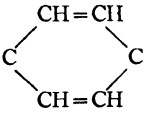
FIGURE 42.2*b*. Absorption spectrum of quinone,  (yellow).

FIGURE 42.2*c*. Absorption spectrum of quinol, HO— —OH (colorless).

Now suppose that the beam of light in figure 42.1 is made to pass through a sample of benzene before it passes through the prism and is spread out into its spectrum. The result is shown in figure 42.2*a*. A spectrum of this nature, obtained after a beam of light passes through a solution or a liquid, is called an *absorption spectrum*. That portion of the spectrum which is absorbed is called an *absorption band* (section 13.13*a*).

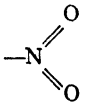
There may be several bands, but for a layer of definite thickness and definite concentration, these bands always occur in the same positions and are characteristic of the substance being examined. It will be seen from figure 42.2*a* that when a beam of light passes through benzene the visible spectrum is not disturbed. That is why benzene has no color. Light transmitted through benzene, or reflected from it, has no part of its visible spectrum absorbed, and benzene is therefore said to be colorless.

When a light beam passes through a quinone solution (figure 42.2*b*), part of the visible spectrum is removed. The light which emerges has had its violet and blue colors absorbed and what we see then is a mixture of colors which is yellow. Light reflected from quinone crystals or transmitted through quinone in solution is yellow because the quinone molecule disturbs the visible spectrum. Coal is black because it absorbs all the visible spectrum when light falls on it.

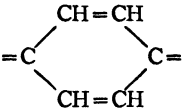
In contrast with quinone there is the closely related compound, quinol, the absorption spectrum of which is given in figure 42.2*c*. Quinol is colorless because the absorption bands occur in the ultraviolet spectrum and our eyes are not adjusted to changes in that part of the spectrum.

If we examine the structures of benzene, quinol, and quinone, it will be apparent that quinone is much different from the other two compounds; it does not have the typical structure of the benzene ring. A great amount of data is available to show that compounds with the quinone (or quinoid) structure are generally colored. In other words, the arrangement of the atoms in the quinoid structure tends to shift the absorption bands into the visible spectrum, to produce color. We have much evidence of a similar nature proving that, in general, the color of an organic compound is a function of its structure.

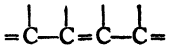
42. 2. Chromophore Groups. Typical structures which frequently give color to the common dyes are the following unsaturated groups:



Nitro



Quinoid structure
(section 30.6)



Conjugate system
(section 18.1)

Such groups are called chromophores, meaning color-bearer in Greek. Typical dyes in which the chromophores are quite evident will be found described in the following pages.

42. 3. Auxochrome Groups. At the beginning of this chapter we stated that nitrobenzene, C_6H_5–NO_2, is simply a colored substance, whereas the amino derivative, H_2N–C_6H_4–NO_2, is a dye. The color, in both cases, is due to the chromophore, –NO_2. The dye qualities of the second compound must, therefore, be due to the –NH_2 group, which is an anchoring group that fixes the molecule to the fabric. Groupings that can be used for attaching dye molecules to textiles are either acidic or basic in character:

—NH_2	—OH	—C(=O)OH	—S(=O)(=O)OH
(also —NHR or —NR_2) Amino	Hydroxy	Carboxy	Sulphonic acid
In basic dyes	In acid dyes		

These anchoring groups are sometimes called auxochrome groups (Greek, meaning aid to color) because of their fixative effect, but this name is, at present, more often used in connection with another characteristic which will be described in section 42.15.

Wool and silk are *animal* fibers, whereas cotton is a *vegetable* fiber. Wool and silk are essentially proteins in composition (section 38.4) and they therefore contain both acid groups and basic groups. They are accordingly easily dyed, since they are capable of reacting with both acid dyes and basic dyes. Cotton is nearly pure cellulose (section 41.9) and is rather inert to chemical reagents. It is, therefore, more difficult to dye cotton than to dye wool or silk.

Rayon is made from cotton or other cellulose materials, such as wood, but the cellulose is so modified in the process that rayon is more reactive and easier to dye than cotton. Nylon resembles a protein in composition (section 46.12) and, thus, its behavior to dyes resembles that of wool and silk.

42. 4. Mordants and Lakes. In order to dye cotton it is often necessary to use mordants. These are substances that easily penetrate cotton fibers and, for some reason, possibly because of physical adsorption, are capable of sticking firmly to the fibers. After the fabric has been mordanted (impregnated with the mordant), a dye is added which forms an insoluble precipitate with the mordant which is firmly attached to the cotton.

The precipitate obtained from the reaction between the mordant and the dye is called a *lake*. The dye is said to be "laked out." When a basic dye is applied, an acid mordant, such as tannic acid, is used. For an acid dye, basic mordants, like aluminum salts or iron salts, are employed. The ability of some dyes to form lakes with certain salts is probably due to a structural configuration which permits chelate compounds to form like those described in section 32.12.

Classification of Dyes according to Their Method of Application

Dyes are sometimes classified very broadly as acid dyes or basic dyes, depending on whether the auxochrome group is acid or basic. This division of dyes is not common in commerce. The usual classification is based on the methods of application to the fabric.

42. 5. Substantive Dyes. These are also known as direct dyes, since they are capable of dyeing fabrics directly. This is usually a simple matter in the case of silk and wool, but for cotton, there are comparatively few direct dyes. A common example of direct dyes for cotton is Congo red (section 42.10).

42. 6. Adjective Dyes. These are also called indirect dyes, because they do not form a stable union with fabrics but need the aid of mordants to obtain firm combinations. An example of an indirect dye is alizarin (section 42.9). Adjective dyes, incapable of dyeing cotton directly, are often capable of dyeing silk and wool without a mordant.

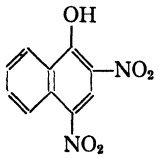
42. 7. Vat Dyes. The vat dyes are formed by chemical reaction while in contact with the fiber. The dyes of the other two classes that have just been defined are all ready-made by the manufacturer, and dissolved as needed. The vat dyes, however, are not bought completely made. Most vat dyes are put into the dye bath in a leuco, or colorless state (section 42.11) and the cloth is thus impregnated with a practically colorless substance. When the cloth is

removed from the vat, oxidation by the air converts this leuco substance to the colored dye, right on the fibers. An example of a vat dye is indigo blue (section 42.12). As a rule, vat dyeing yields very stable colors.

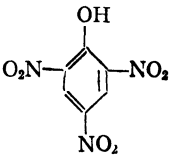
Classification of Dyes according to Structure

In comprehensive books on dyes, they are usually classified according to their structures. More than two dozen such classes are known, of which only a few will be described here with specific examples. The structural classification is often based on the chromophores.

42. 8. Nitro Dyes. The $-NO_2$ group in a molecule usually tends to impart a yellow color. Most nitro dyes are phenol derivatives, the phenol group acting as the anchoring group. Martius' yellow



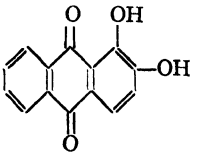
Martius' yellow



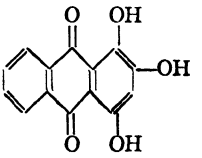
Picric acid

was at one time used as one of the food colors. These are dyes which the government certifies for use in foods, to give them a more appetizing appearance. Picric acid was formerly used extensively as a yellow dye for silk and wool. It is better known as an explosive.

42. 9. Anthraquinone Dyes. The most common members of this class of dyes are alizarin and purpurin. The chromophore is the



Alizarin
1,2-Dihydroxyanthraquinone



Purpurin
1,2,4-Trihydroxyanthraquinone

quinoid structure. These dyes occur in nature in the madder root as complex compounds in combination with glucose (see the glucosides in section 40.7). When mordanted in the proper way, alizarin produces the well-known Turkey red color on cotton. The madder root was used for several thousand years as a source of alizarin, but

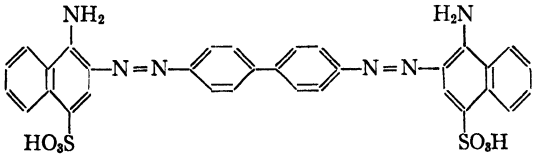
alizarin is now made synthetically. The structure of anthracene should be reviewed in section 36.5.

42. 10. Azo Dyes. It is interesting to compare the following two compounds from the standpoint of color:

Azomethane (colorless) Azobenzene (yellow)

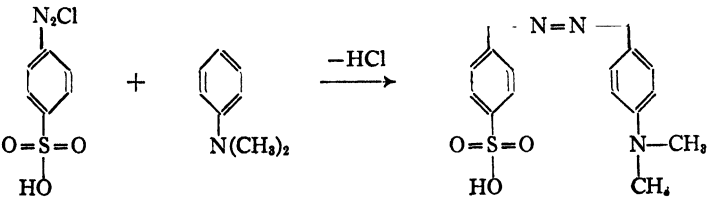
Azomethane has an absorption band in the ultraviolet and, therefore, has no color, whereas azobenzene absorbs in the visible spectrum and is a deep yellow. The color in azobenzene is attributed to the long conjugate system, C=C–C=C–N=N–C=C–C=C, formed with –N=N– (the azo group) and the two ring structures.

The azo dyes are among the most important of the synthetic dyes. The auxochrome (anchoring group) is usually the basic —NH_2 group or the acidic sulphonic acid group, or both. The simple dyes derived from azobenzene are yellow to orange, but more complex derivatives vary from orange to red and even to black. One well known azo dye is Congo red, and another is methyl orange.



Congo red (see naphthalene, section 36.5, and diphenyl, section 25.4)

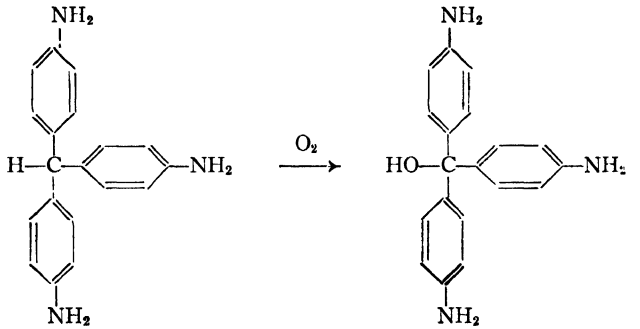
The synthesis of azo dyes was briefly mentioned in section 33.7 in the discussion of diazonium salts. If this is reviewed, the preparation of methyl orange can be easily understood as a reaction in which *diazotized* sulphanilic acid (section 33.8) is *coupled* with dimethylaniline (section 33.2):



Diazotized sulphanilic acid Dimethylaniline Methyl orange (See figure 42.7)

The coupling takes place in the *para* position to the dimethylamino group.

42. 11. Triphenylmethane Dyes. Many dyes are derived from triphenylmethane, $(C_6H_5)_3CH$, and are closely related to triphenylcarbinol, the structure of which is shown in section 26.2. They are rather complex substances, the nature of which may be illustrated by the dye known as pararosaniline.



Leuco base of pararosaniline — Color base of pararosaniline

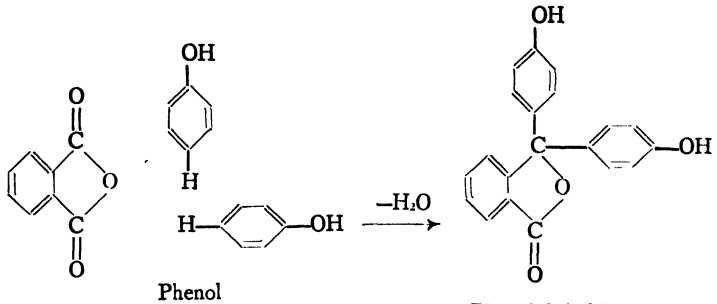
The synthesis of many of the dyes in this class results initially in a colorless compound which is called a *leuco* base, from the Greek leucos, meaning white. Mild oxidation converts the leuco base to the *color* base. In some cases, the color base is made directly without an intermediate leuco stage, an example of this procedure being the preparation of pararosaniline itself. The color base is without color, but dissolves readily in acids to form highly colored salts in which the weakly basic —OH group is replaced by acid radicals:

$$(H_2N—C_6H_4)_3C—OH + HCl \rightarrow HOH + [(H_2N—C_6H_4)_3C]^+ Cl^-$$

This will be discussed further at the close of the chapter in connection with the reason for color of these compounds, the chromophore (color-bearing) group not being evident in the structure as written here.

The triphenylmethane dyes fall into two categories. There are the basic dyes of which pararosaniline with its basic $-NH_2$ group is typical. There are also the acid dyes, such as the *phthaleins*, in which acid groups, e.g., phenolic –OH anchor the dye molecules to fabrics. The phthaleins are made by the action of phenols on phthalic anhydride (section 36.5). This accounts for the class name of

phthaleins. The most common member of this class of compounds is phenolphthalein.



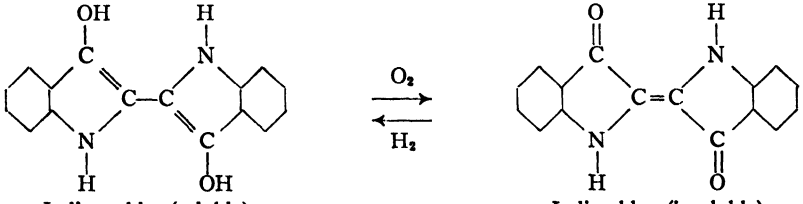
Phthalic anhydride — Phenol (2 molecules) — Phenolphthalein

Phenolphthalein is a colorless solid which dissolves readily in alkaline solutions with development of a deep-red color. This is to be compared with pararosaniline which is a base and dissolves in acids. Phenolphthalein is used extensively in patent medicines as a laxative. It is also widely used in analytical chemistry as an indicator, the theory of which will be given in section 42.16.

Fluorescein is a phthalein dye made from resorcinol (section 28.4) and phthalic anhydride. A bromine derivative of fluorescein known as *eosin* is used in red inks and is employed extensively as a dye. Mercurochrome (section 43.8) is a derivative of fluorescein.

42. 12. Indigoid Dyes. Indigo and a number of its derivatives constitute a family of dyes called indigoids. Most of the indigo used now is made synthetically and is much purer than the natural product obtained from the blue coloring matter in the leaves of the indigo plant.

Indigo is one of the vat dyes. It is insoluble in water and in strong alkalies and, therefore, cannot be directly applied to fabrics. It must be converted to the leuco compound, which is soluble. In the



Indigo white (soluble) — Indigo blue (insoluble)

dyeing process, the fabric is dipped into an alkaline solution of indigo white. When it is removed from the vat and exposed to air, the colorless compound on the fibers is oxidized to indigo blue.

The indigoids, in general, are fast to light and wear. The purple of Tyre, or Tyrian purple, was highly prized and reserved for the use of the aristocracy in ancient times. It is an indigoid dye, found in certain small marine animals.

42. 13. Color Indexes. From the brief account of dyes in this chapter, it is obvious that nomenclature of dyes can be quite confusing. Descriptive names (or even nicknames) are used more commonly than systematic names that would throw light on their chemical structure. The dye chemist usually has at his elbow reference works which catalog the dyes and assign numbers to them. One such catalog is the *Color Index* (the C. I. numbers); another is Schultz's *Farbstofftabellen* (the S. numbers).

42. 14. Chromophores. In the opening section of this chapter, we showed that the color of a substance is associated with the absorption of light, and in section 13.14, we found that this absorption occurs when certain particles in a molecule are oscillating at the same frequency as the electromagnetic vibration passing through it. To look for the reason for color we must look for particles in constant oscillation; these particles are certain *valence* electrons.

The explanation for the color-producing activity of chromophore groups is closely associated with the resonance theory and with unsaturation (that is, double-bond structures, such as N=N and C=C). In connection with the resonance theory, we showed in sections 17.3, 18.10, and 21.2 how certain molecules can plausibly be assigned structures in *polarized* states as well as in *normal* states. The transformation to a polarized state is essentially one in which there is a shift or oscillation of electrons from one part of the structure to some other part, accompanied by rupture or formation of double bonds as illustrated in section 18.10. Electrons taking part in such changes are relatively loosely bound, which means that a relatively small amount of energy is associated with their oscillations. In table 13.2, which shows the relation between wavelength and energy, it is clear that lower energies correspond to longer wavelengths. If the bonding energies associated with the structure of a molecule are such that electron oscillations can take place in it at

frequencies corresponding to wavelengths of visible light, the conditions are favorable for color phenomena. Specifically, the absorption frequency is equivalent to the energy separation from the ground level of the molecule (section 13.13*a*) to the excitation level. It is also essential that the movement of electrons from one part of the molecule to another results in a change in dipole moment and in a *polarized* structure, that is, a structure which can be represented as resulting from a transfer of electric charge. This will be more apparent if we review the resonance structures of benzene (figure 19.3) which can be pictured as having pairs of π electrons chasing each other around a closed ring. Such structures, which are not polarized, are not conducive to color production.

The function of a chromophore in a colored molecule is to offer a path by which electronic oscillations can take place to give polarized structures. The conjugate system (see especially *glyoxal* in section 30.6, and see section 18.10) is useful for this function, and is a highly important chromophore structure. The student should also review the carotenes (section 37.7) which are very long conjugate systems; they are all intensely colored.

42. 15. Auxochromes. Some groups are highly effective in increasing the color when inserted into structures which already have color and are, therefore, called auxochrome groups. They were defined in another sense in section 42.3. The ability of auxochrome groups to increase the color is due to their ability to act as electron donors; electron donors were discussed in section 17.3, where the descriptive term "electron source" was employed. The electrons supplied by the auxochrome groups require, of course, a chromophore path through which to travel. The chromophore, on this basis, is an electron acceptor, or "electron sink."

For a first illustration, consider the fact that nitrobenzene, C_6H_5–NO_2, is yellow, but *p*-nitroaniline, H_2N–C_6H_4–NO_2, is much more intensely colored. In section 21.5 we discussed the resonance structures of nitrobenzene and showed that the $-NO_2$ group tends to draw an electron pair from the ring, leaving the ring positively charged as shown in figure 42.3. The stability of this resonance structure (which is a quinoid, color-bearing type) is considerably increased when an $-NH_2$ group is attached to the

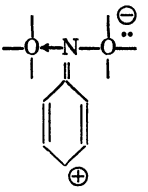


FIGURE 42.3. A resonance structure of nitrobenzene (see structure IX in figure 21.2)

ring, because the N atom acquires the positive charge more easily by losing an electron pair. This is illustrated in figure 42.4.

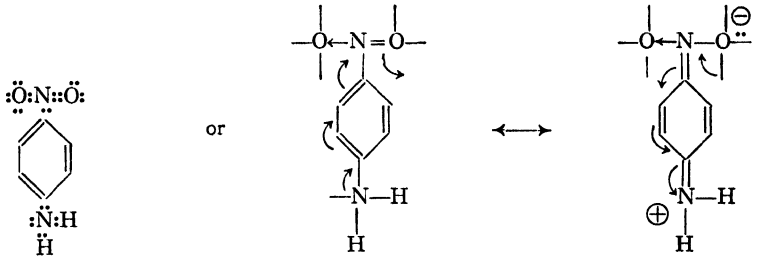
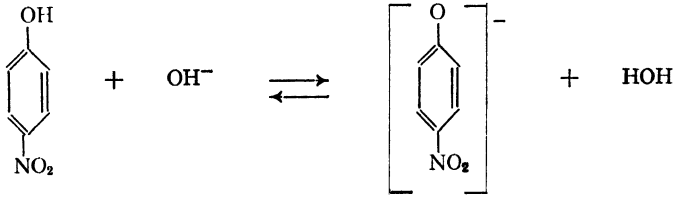


FIGURE 42.4. In *p*-nitroaniline the auxochrome (—NH_2) donates an electron pair to the chromophore (a conjugate system).

In section 42.3 several types of groups, acidic and basic, were referred to as auxochromes that serve to attach dye molecules to fibres. The –OH group is useful not only in that respect, but also as a color intensifier according to the mechanism just described for the $-NH_2$ group. The –COOH group and $-SO_3H$ group, however, are not auxochromes in the sense discussed in this section; they are not electron donors.

42. 16. Acid-Base Indicators. The dye *p*-nitrophenol is an acid, just like phenol. It is colorless in acid solution, but intensely yellow when the solution is made alkaline. The reason for this is that the original unionized molecule is colorless, but its corresponding negative ion is colored. In alkaline solution, excess base removes H^+



Colorless molecule in acid — Yellow ion in alkalies

p-Nitrophenol

ion from the molecule as shown here and the solution becomes yellow because of the freed negative ion. The salts of *p*-nitrophenol, like $[O_2N-C_6H_4-O]^-\ Na^+$, are colored since they contain the negative ion.

The presence of color in the ion of *p*-nitrophenol as compared with lack of color in the acid itself is explained by the resonance theory. The explanation is similar to that employed in discussing the acidity of phenol in section 28.2 (which the reader should review), where it was shown that phenol, C_6H_5OH, has resonance possibilities, but that resonance energy of the phenate ion, $C_6H_5O^-$, is even greater because of absence of the proton (H^+) from the molecule. Similarly, resonance of the negative ion of *p*-nitrophenol is more effective than that of the unionized molecule and tends to stabilize those polarized structures which are important in light absorption. Using the method of writing formulas as shown in figure 21.2, a few resonance possibilities indicated in figure 42.5 can be formulated for this negative ion. In the resonance resulting

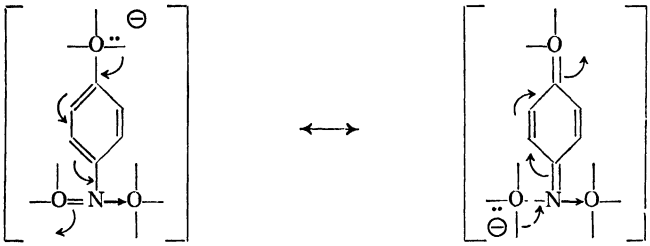


FIGURE 42.5. Some resonance structures of the negative ion of *p*-nitrophenol.

from ionization of *p*-nitrophenol there are quinoid structures which are sufficiently active toward the visible spectrum to produce color.

As illustrated by the preceding simple example, an indicator may be defined as an acid (or base) the ionization of which is accompanied by a change in the absorption of light in the visible spectrum. The ionization of different indicators takes place at different pH values, that is, at different concentrations of the H^+ and OH^- ions in solution. Indicators can, therefore, be used in analytical chemistry to determine the degree of acidity or alkalinity of solutions.

A more complex example of an indicator which is a weak acid is that of phenolphthalein. It is colorless in acid or neutral solution but, at a certain concentration of OH^- ions in a weak alkali, the

two H^+ ions shown in its structure (section 42.11) are removed. The resulting negative ion of phenolphthalein is doubly charged. When freed from the two H^+ ions, highly symmetrical structures of the quinoid type become possible which are in resonance and which shift the absorption of light into the visible spectrum. This ion is red, whereas the original molecule is colorless. The nature of the two quinoid rings in the red negative ion of phenolphthalein in alkaline solution can be pictured by referring to the one quinoid ring which is shown in the structure of mercurochrome (section 43.8). Mercurochrome is red; it is a salt of a dye derived from fluorescein, one of the phthalein group of dyes.

Although pararosaniline is not useful as an indicator, its use as a dye is similarly explained as the result of ionization. The color base of pararosaniline (section 42.11) differs from the two phenol derivatives which we have just described in that it is a weak base. It becomes highly colored when dissolved in acid solution, the color in this case being due to ionization in which the OH^- ion is lost and the colored positive ion is liberated. The structures in figure 42.6

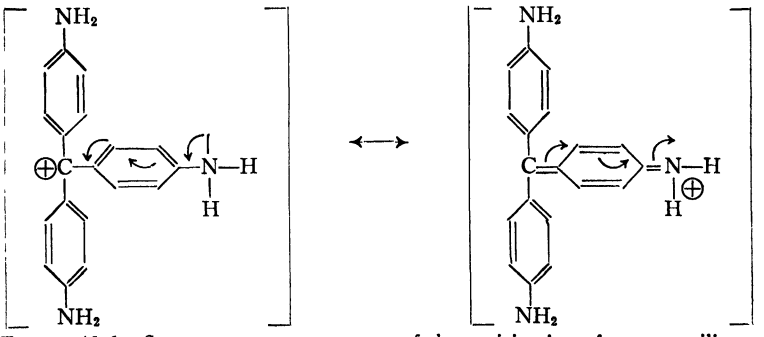


FIGURE 42.6. Some resonance structures of the positive ion of pararosaniline.

are written with the electron pairs represented by the scheme shown in figure 21.2. When the molecule is freed from the blocking effect of the OH^- (refer to the structure in section 42.11), resonance can take place as shown, the resonance structures being highly absorbent in the visible spectrum.

Methyl orange (section 42.10) is an indicator which is both a weak base and a strong acid; its structure is probably not that shown earlier in the chapter, but it is more likely an inner salt (dipolar

ion) of the type described in section 33.8, which the reader should review. On this basis, the unionized molecule of methyl orange, pictured in section 42.10, can be rewritten as resonance structures which are present in acid solution and give it a red color (figure

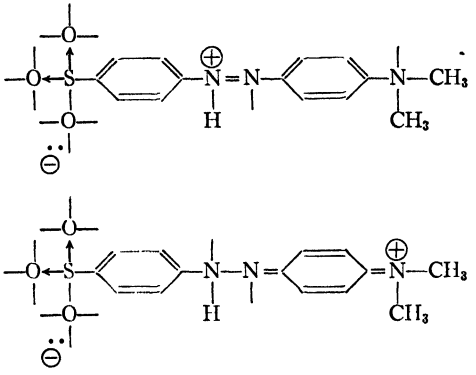
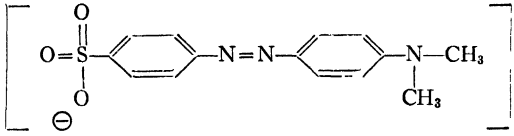


FIGURE 42.7. Resonance structures of methyl orange. Electron pairs are represented as shown in figure 21.2.

42.7). The reader should not be confused by the + and − charges in the molecule; it is an electrically neutral molecule, not an ion.

When the methyl orange molecule does ionize (lose H^+ ion by reaction with a base, such as OH^-) the color turns yellow, the color in alkaline solution being due to:



This negative ion has the simple azo structure as the molecule in section 42.10, and we have written the structure in the normal manner, without indicating the shared or unshared electron pairs. Methyl orange is generally sold as the sodium salt, $[O_3S{-}C_6H_4{-}N{=}N{-}C_6H_4{-}N(CH_3)_2]^-\ Na^+$.

The need for the single positive charge on certain of the N atoms in figure 42.7 can be shown by summing up the number of valence electrons actually on the atoms as compared with the *five* on the neutral atom of nitrogen. For example, in the upper structure of figure 42.7 the N atom shown with a + charge is linked to other atoms by *four* covalence bonds, to each of which one electron is

contributed by nitrogen; the equivalent of the fifth electron is on an oxygen atom at the end of the molecule. The other N atoms in the molecule have their normal quota of *five* (*three* in covalence bonds by which they are linked to other atoms, and *two* as shown by an unshared bond).

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43. DRUGS AND RELATED COMPOUNDS

43. 1. Introduction. It is not a simple matter to define drugs. A drug is commonly supposed to be a substance of medicinal value, but this is indefinite. For example, the general public would hardly call sodium bicarbonate a drug, yet it has a decided medicinal value. Perhaps the most acceptable definition is the statement that a drug is a substance with an abnormal effect on certain body functions. Thus, strychnine stimulates the action of the heart, and aspirin stills its action; both have abnormal effects and are, therefore, drugs.

Vitamins and hormones are among the most recent types of compounds which may be said to have a druglike action.

The pharmacologist would like very much to be able to do the same thing with drugs that the dyer has been able to do with dyes. In the preceding chapter, we showed how the colors of dyes are due to certain structural groups in the molecule. With his knowledge of the relation between color and structure, the dye-maker can quite often work out his prospective dyes on paper and obtain the expected results in the laboratory.

Similarly, the pharmacologist would like to find some relation between the chemical constitution of a substance and the action of the substance on the human body. In other words, the pharmacologist is making an effort to classify various chemical groups as "pharmacophores," which would be analogous to the chromophores in dyes. That this is a difficult problem is evident from the widely different types of compounds which have the same type of action on the human body.

Classification of Drugs according to Physiological Action

General Anesthetics are substances which cause deep sleep and general insensibility to pain. They are all very volatile compounds, administered by inhalation. The most used anesthetic is ether, C_2H_5–O–C_2H_5. Others are chloroform, $CHCl_3$; nitrous oxide, N_2O; ethylene, $CH_2{=}CH_2$; *cyclo*propane, C_3H_6; and avertin, CBr_3–CH_2OH.

Local Anesthetics are substances that bring about temporary insensibility to pain in isolated regions of the body. Cocaine and related substances (section 43.6) paralyze local nerve centers.

Soporifics and Hypnotics are sleep producers and sedatives, useful when pain does not interfere with their effect. Many classes of compounds are used for this purpose. Some of these are paraldehyde (section 30.5*d*), chloral hydrate (section 30.6), acetophenone (table 30.2), and barbituric acid derivatives (section 43.4).

Narcotics diminish pain and produce sleep. Some of these, such as morphine (section 43.6), have unpleasant, habit-forming properties.

Analgesics and Antipyretics are painkillers which do not necessarily cause sleep. An analgesic has only a soothing effect, whereas an antipyretic also reduces body temperature in fevers. Analgesics such as oil of wintergreen (section 32.8), are often used in ointments. Commonly used antipyretics are acetanilid (section 43.2), quinine (section 43.10), and aspirin (section 32.8).

Stimulants and Depressants affect the action of the heart, usually by their effect on the arteries. Stimulants, which contract the blood vessels, increase the force of the heart beat. This is the "pressor effect." Examples of such drugs are adrenaline and ephedrine (section 43.3).

Depressants lower the blood pressure by dilating the blood vessels. Nitroglycerine, $CH_2(ONO_2)$—$CH(ONO_2)$—$CH_2(ONO_2)$ (which is really glyceryl trinitrate), and ethyl nitrite, C_2H_5–ONO, have such an effect.

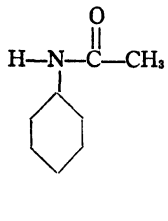
Diuretics and Purgatives promote elimination of waste products from the body. The common diuretics, notably caffeine, are members of the purine group of compounds (section 43.5). Many types of compounds are useful as purgatives; phenolphthalein (section 42.11) is probably used as much as any.

Antiseptics and Disinfectants are usually included in the category of drugs, even though they are useful, not for their direct action on the animal body, but for their ability to destroy lower forms of animal and vegetable life. Among the organic compounds used for this purpose are formaldehyde (section 30.6), salvarsan (section 43.8), phenols (chapter 28), mercurochrome (section 43.8), and sulfanilamide (section 43.9).

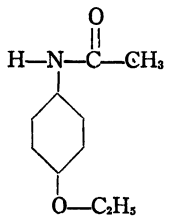
The examples we have just cited of the kinds of drugs in common use indicate the difficulty of developing a general law by which we can relate the physiological action of substances to their chemical constitution. That the activity of drugs is closely related to their structure, however, even though no general law is available at present to cover all cases, can easily be demonstrated. In the rest of this chapter, we shall consider representative classes of compounds that have been thoroughly studied and have certain types of behavior in the animal body.

43. 2. Aniline Derivatives. The normal effects of ammonia, NH_3, are quite familiar. In alcohol solution it is used to stimulate heart action and increase blood pressure (this is the spirits of ammonia used by persons prone to fainting). In large doses, ammonia causes paralysis and death.

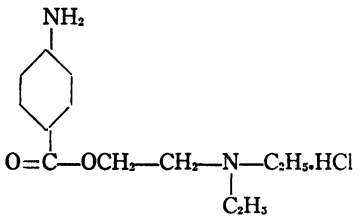
The toxicity of NH_3 is diminished in the aliphatic amines, such as methylamine, CH_3–NH_2, but is increased in the aromatic amines such as aniline, –NH_2. Derivatives of aniline are also quite toxic, but in small doses are useful as drugs.



Acetanilid
Used as antipyretics, for fevers and headaches.



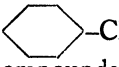
Phenacetin

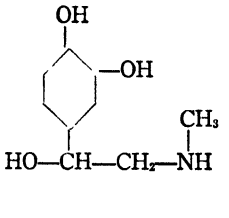


Novocain
Local anesthetic, by injection.

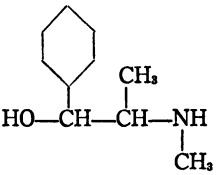
The structure of Novocain is of great interest from the standpoint of relation between drug action and chemical constitution. It contains the essential arrangement of groups which was found to

give cocaine (section 43.6) its characteristic properties. In other words, when the "pharmacophore" group in cocaine was discovered, several better compounds were developed containing that essential group, one of the best known of which is Novocain (new cocaine).

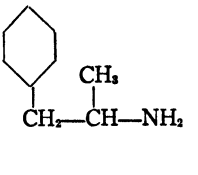
43. 3. Phenylethylamine Derivatives. One of the most extensive studies of the drug activity of compounds of similar structure has been done on derivatives of β-phenylethylamine,  $-CH_2-CH_2-NH_2$. Important members of this series of compounds are the following:



Adrenaline



Ephedrine



Benzedrine

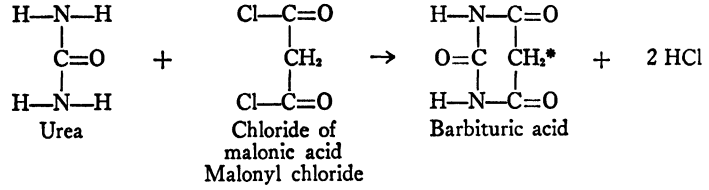
These substances all have a styptic effect. They contract the blood vessels and raise the blood pressure (the "pressor" effect). They are also referred to as *sympathomimetic* amines in that they produce effects which mimic those obtained when the sympathetic nervous system is excited by other agencies.

Adrenaline is a hormone (section 44.2) secreted by the adrenal glands and serves to regulate blood pressure. It is also known as suprarenine and epinephrine. It was the first hormone obtained in crystal form and subsequently synthesized. One of the disadvantages of adrenaline is that it is not effective on blood pressure except by subcutaneous injection. Ephedrine produces the same type of results as adrenaline equally well when taken by mouth as by injection. It was first obtained in certain Chinese plants. The salts of ephedrine are used extensively for hay fever and asthma, and for circulatory stimulation. Benzedrine sulphate is administered by mouth. It is a circulatory stimulant and is used to arouse patients from certain depressive conditions.

When compounds related to adrenaline were studied it was found that the "pressor" or circulatory stimulant effect is obtained only when the compound has the general structure ring –C–C–N–. If

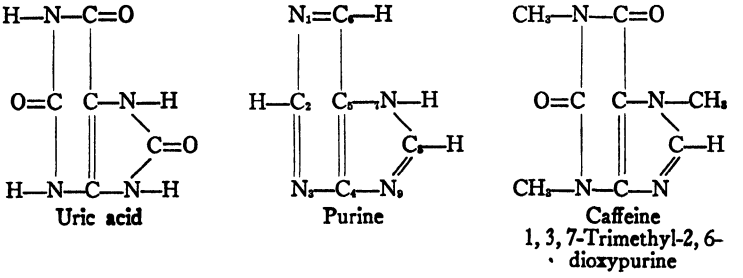
the side chain is lengthened to more than three carbon atoms the pressor effect is diminished while toxicity is increased. When there are three carbon atoms in the side chain, as in ephedrine the compound is effective when taken by mouth. These are just a few conclusions from a vast amount of data which have been collected on compounds with a pressor effect.

43. 4. Barbituric Acid Derivatives. Malonic acid (section 31.13) and urea (section 33.12) can be condensed as follows:



The two hydrogen atoms in barbituric acid marked by an asterisk (*) can be replaced by radicals to give a series of compounds widely used as soporifics, or sleep-producers. If these H atoms are replaced by ethyl ($-C_2H_5$) groups, the soporific obtained is *veronal.* Related compounds are *luminal, dial, amytal, allonal,* etc., all of which are sleep-producers, and have individual characteristics due to the specific radicals used to replace the H atoms in the ring.

43. 5. Purine Derivatives. Uric acid is present in the urine of mammals to a small extent, but occurs in the excreta of birds and reptiles to a very large extent. Uric acid has been known since 1776, but it took 100 years of patient investigation to determine its structure. It is somewhat similar to barbituric acid, which has just been described, in that it contains urea and malonic acid residues, but it contains two urea skeletons to one of malonic acid. This is shown in the formula given in the following.



After the constitution of uric acid had been uncovered, it was found that several other important compounds called the *purines* are related to uric acid. These may all be considered as derived from a mother substance which has been isolated and is named purine.

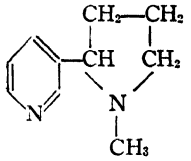
The purines are widely distributed in nature, associated with proteins and carbohydrates in more complex compounds. Derivatives of purine are named in accordance with the number system indicated in its formula as we have written it. The drug *caffeine,* as we all know, is obtainable from coffee and tea; its relationship to purine is indicated in its systematic name.

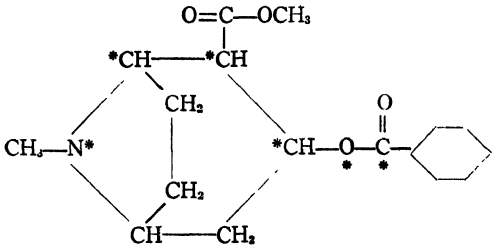
A large number of compounds of importance in nature contain ring systems with two nitrogen atoms in *meta* position to each other. The six-membered ring compound, $C_4H_4N_2$, is called *pyrimidine* and is roughly similar in properties to pyridine (section 36.4). An isomer of pyrimidine with nitrogen atoms *para* to each other is called *pyrazine.* The pyrimidine ring will be seen in the purine compounds, and, together with pyrazine, in some of the B vitamins (section 44.4).

43. 6. Alkaloids. Formerly, all basic compounds that were found in plants and contained nitrogen atoms were called alkaloids. In more recent times, when the structures of many of these compounds were determined, it was found best to classify them into more or less distinct groups. For example, caffeine and related purine compounds are called *vegetable bases* and certain amines described in section 33.8 are called *ptomaines.*

This leaves the term *alkaloid* reserved for certain ring compounds containing nitrogen which occur almost exclusively in the form of salts in plants. The N atom is in the form of a tertiary amine (section 33.2) except in comparatively few cases. Alkaloids are nearly always optically active and they are all poisonous.

The alkaloids can be classified according to their source as the opium alkaloids (the opium poppy), cinchonine alkaloids (the cinchona tree), etc., but chemically it is convenient to group them according to the ring systems they contain. This gives four classes of alkaloids, namely, pyridine, quinoline, isoquinoline, and phenanthrene alkaloids. These ring structures should be reviewed in sections 36.4 and 36.6.


Nicotine


Cocaine

Nicotine is present in tobacco leaves in the form of its salts. The nicotine molecule contains two heterocycles, the *pyridine* ring and the reduced pyrrole ring (section 36.2). The symptoms of acute nicotine poisoning are familiar to those mammals who have smoked two cigars when physically capable of but one.

Cocaine is both a reduced pyrrole ring and a reduced *pyridine* ring. Cocaine is present in the coca leaf. It is widely used as a narcotic by drug addicts and as an anesthetic by surgeons. Much research has been done on the relation between structure and physiological action of cocaine and related compounds, in an effort to obtain a substance more easily sterilized at 100°C., less toxic, and as good an anesthetic. It has been found that the structure essential to the activity of cocaine is R–N–C . .–C–O–C–Ar, where R is an open-chain radical and Ar is a ring radical. The atoms in this structural arrangement are indicated by asterisks (*) in the formula of cocaine. A cocaine substitute which has this structure and has practically replaced cocaine in surgery is Novocain. It is described in section 43.2.

Cinchonine and *quinine* occur together in the bark of the cinchona tree, grown in tropical countries. The two alkaloids are closely related, belonging to the *quinoline* group of alkaloids. Quinine is an antipyretic and is especially useful as a specific for malaria (see section 43.10).

Many alkaloids of the *isoquinoline* group are obtained from opium. Better known, perhaps, among the alkaloids obtained from opium are the *phenanthrene* alkaloids. Compounds in this group are built up on the *phenanthrene* nucleus (section 36.5), which contains no

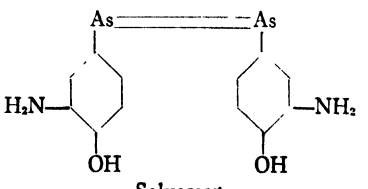
nitrogen, the N atom in these alkaloids being contained in a subsidiary ring. The most important member is *morphine,* the first alkaloid isolated from plants (1806). It is exceedingly poisonous, and is used principally to relieve pain. *Codeine* is closely related to morphine, and occurs along with it in opium, but it does not have the habit-forming properties of morphine. *Heroin,* also, is closely related to morphine in structure but it does not occur in nature.

43. 7. Chemotherapy. Certain diseases are caused not by improper functioning of the organs of the body, but by various parasites, mostly protozoa or bacteria. Since these parasites are often difficult to destroy, especially when in the blood stream, attempts have been made to combat them with specific chemical agents. Treatment of this type is called chemotherapy, a good illustration of which is the action of quinine on the malaria organism (a blood parasite).

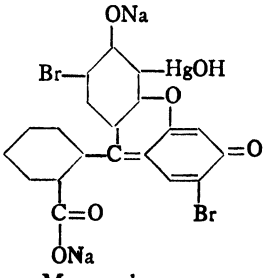
The first applications of chemotherapeutic methods were in general more successful against the protozoan infections that cause syphilis and malaria than against bacterial infections such as undulant fever (Brucellosis).

The "therapeutic index" of drugs, such as the arsenicals, to be described in section 43.8, is the ratio of the amount necessary to kill the patient to that required for a curative dose. Practitioners seldom use a drug with an index lower than ten. An index of ten means that ten times the dosage used would kill the patient as well as the parasite.

43. 8. Mercurials and Arsenicals. Historically, the most spectacular use of chemical antiseptics (chemotherapy) was that of *salvarsan* for combating syphilis. In this case, the chemical agent is injected directly into the blood stream. The name salvarsan is from the Latin *salvare sanitas,* to preserve health.



Salvarsan

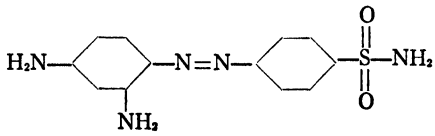


Mercurochrome

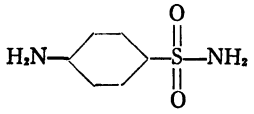
The use of salvarsan has been practically superseded in medical practice by the use of *neosalvarsan.* This is derived from salvarsan by replacing one $-NH_2$ group with the group $-NH-CH_2-SO_3Na$.

The red dye *mercurochrome* was used in Europe in the war of 1914–1918 for the treatment of gonorrhea. It has become quite popular as an iodine substitute for local antiseptic use. Mercurochrome is a derivative of fluorescein (section 42.11).

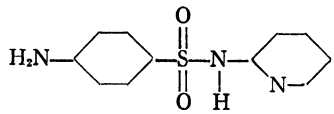
43. 9. Sulfa Compounds. A group of drugs remarkably effective against bacterial infections was recently discovered among the dyes. Their discovery is an illustration of the frequent reward of the painstaking search for "pharmacophores," which were defined at the start of this chapter. It was found that the red dye, *prontosil,*



has bactericidal powers. It was soon determined that the active, or pharmacophore, group is the right-hand half of the molecule when it is divided between the N atoms in the $-N=N-$ group. Research on compounds containing this pharmacophore then showed the value of *sulfanilamide,* an excellent cure for streptococcic infections. Of the many important derivatives of this compound in which ring structures are inserted into the $-SO_2NH_2$ group we shall list only *sulfapyridine,* a specific for certain types of pneumonia.



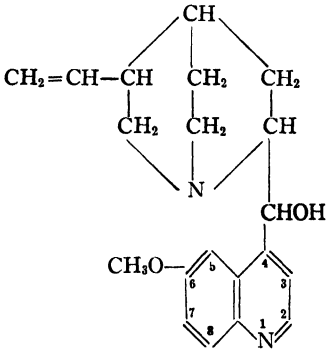
Sulfanilamide



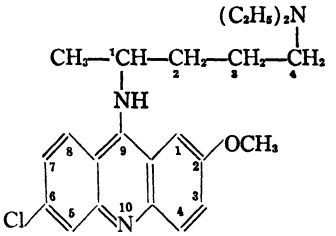
Sulfapyridine

43. 10. Antimalarials. One of the most serious obstacles to progress in tropical countries is malaria, a disease due to protozoa. It has been treated principally with quinine, which occurs in nature (section 43.6). Quinine had its structure worked out in 1908 and was laboriously synthesized in 1945, but there is no satisfactory manufacturing process for it. Because of the great demand for antimalarials by the armies in World War II, a mighty effort was made to find an easily made compound to substitute for quinine. Atabrine

(quinacrine hydrochloride), discovered in the early 1930's, was used in large quantity. During World War II, about 14,000 compounds were studied, nearly half of them synthesized for this special survey.



Quinine



Atabrine
(sold as dihydrochloride)

Most of the promising compounds found in the survey have the quinoline nucleus of quinine, with side chains of the type in atabrine. The side chains are most effective when substituted in the 4 or 8 positions of the quinoline nucleus.

The names of some of these compounds are listed in table 43.1. From these names and the number system shown in the formulas of quinine and atabrine, the student should try to work out their structures. Plasmochine has been known since about 1925. Paludrine is structurally derived from a condensation product of guanidine (section 33.12).

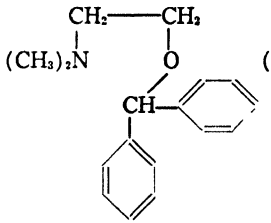
TABLE 43.1. ANTIMALARIALS

Common Name	*Systematic Name*
Atabrine	6-Chloro-2-methoxy-9-(1-methyl-4-diethylaminobutylamino)-acridine
Plasmochine (Pamaquine)	6-Methoxy-8-(1-methyl-4-diethylaminobutylamino)-quinoline
Chloroquine (as diphosphate)	7-Chloro-4-(1-methyl-4-diethylaminobutylamino)-quinoline
Pentaquine (as diphosphate)	6-Methoxy-8-(5-isopropylaminopentylamino)-quinoline
Paludrine (as acetate)	$Cl\text{-}C_6H_4\text{-}NH\text{-}C(=NH)\text{-}NH\text{-}C(=NH)\text{-}NH\text{-}CH(CH_3)_2$ 1-(*p*-chlorophenyl)-5-isopropyl-biguanidine

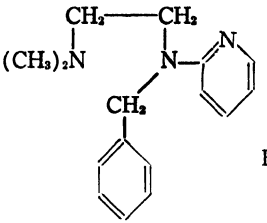
43. 11. Antiallergics. In table 38.1 will be found the formula of histidine, one of the essential amino acids. Certain organisms

in the intestinal tract are capable of decarboxylating it (as stated in section 31.13, this is removal of CO_2 from the carboxy group). The product is called *histamine*. Many allergy diseases are now thought to be due to release of histamine and related compounds in the body.

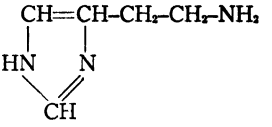
Several amino compounds (called antihistamines) are available that have proved to be a boon to sufferers from hay fever and related ills. Two popular remedies are benadryl hydrochloride and pyribenzamine hydrochloride. Their relation to histamine is discussed further in section 44.6.



Benadryl



Pyribenzamine

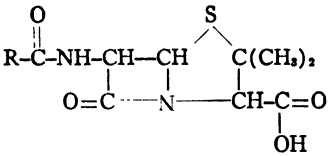


Histamine

43. 12. Antibiotics. In this chapter we have described certain compounds, such as sulfa drugs and quinine, which suppress the growth of microorganisms and alleviate diseases caused by them. These drugs are referred to as chemotherapeutic agents (section 43.7). Ever since the time of Pasteur (1877), it has been recognized that certain harmless microorganisms have the ability to destroy pathogenic varieties; for example, it was known that some soil bacteria produce substances which kill other bacteria around them. These substances were not thoroughly studied until just recently. It is now known that some of them have remarkably good therapeutic properties when administered to humans infected with disease-producing microorganisms. Chemotherapeutic substances isolated from culture media containing bacteria, molds, and related microorganisms are known as *antibiotics*. Antibiotics have also been obtained from the higher plants, such as the tomato.

In 1939, the antibiotic called *gramicidin* was discovered; it is a product of metabolism of *Bacillus brevis*, found in the soil. This compound protects against pneumococcal and streptococcal infections, but is so toxic to humans that it is used principally as a skin antiseptic. *Penicillin*, made famous during World War II, was first isolated in 1929, and is obtained from the mold, *Penicillium notatum*.

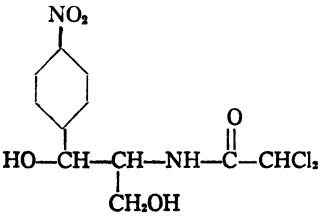
It is water soluble and practically nontoxic, and has been used effectively in the treatment of gonorrhea, syphilis, pneumococcic pneumonia, and a number of other infectious diseases. There are several penicillins, which vary in the R group, and in their effects on microorganisms. Two of the penicillins are as follows.



Penicillin G (benzyl penicillin) R is $C_6H_5-CH_2-$
Penicillin F (2-pentenyl penicillin) R is $CH_3-CH_2-CH=CH-CH_2-$

Streptomycin is an antibiotic produced by a funguslike microorganism, called *Streptomyces griseus,* present in the soil, and was isolated in 1944. The great value of this antibiotic is that it is one of the relatively few therapeutic agents effective against bacteria classified as *Gram-negative.* In that respect, it supplements penicillin, which is most effective against *Gram-positive* bacteria.

The first antibiotic for which a commercially feasible synthesis was realized is *chloromycetin,* the common chemical name of which is *chloramphenicol.* It was isolated from a *Streptomyces* organism. A most unusual feature in its structure is the halogen atom, a rare occurrence in natural organic compounds. The ephedrine structure in section 43.3 should be compared.



Chloromycetin

43. 13. Chemical-Warfare Agents. The restrictions imposed by battle conditions make it possible to use relatively few toxics in warfare. Compounds used medicinally can be introduced into the body in various ways, such as into the alimentary canal by mouth, into the blood stream or muscle by injection, into the lungs by inhalation, etc. Many toxic compounds are useless as chemical warfare agents,

because they are effective only when introduced into parts of the body not normally accessible with known munitions."

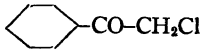
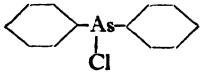
Representative chemical-warfare agents are listed in table 43.2 which shows some of the properties important in warfare. Compounds like phosgene, with low boiling points, are called nonpersistent agents and are used for rapid effects. With such agents it is necessary to set up an effective concentration quickly on an area; they generally act through the respiratory tract against an enemy with inadequate gas mask protection. Substances such as mustard gas and lewisite are called persistent agents, because they will contaminate an area for a considerable time. They not only are toxic by inhalation but will also attack through the skin and will form blisters (vesication).

The effectiveness of a chemical-warfare agent is generally stated in terms of the concentration in the vapor state which is lethal (or incapacitating) to 50 per cent of the victims. As an example, the lethal concentration of hydrocyanic acid to mice for 10-minute exposure is 0.5 mg./l. or 500 mg./cu.m. The LCt_{50} is then 5,000, which means that 50 per cent of the animals will die when concentration (C) is 500 mg./cu.m., and time (t) is 10 minutes. From this one can calculate the concentration to kill at other exposures, such as 5,000 mg./cu.m. for a 1-minute exposure. The constancy of the Ct product is only approximate, especially for hydrocyanic acid.

The possibility of setting up effective concentrations on a battle field can be estimated from columns (A) and (V) in table 43.2. The (V) column shows the concentration which prevails in the *saturated* vapor as calculated from the vapor pressure and molecular weight. Dividing (V) by (A) shows how many physiologically active units are contained in the saturated vapor. It will be seen that toxic concentrations are easily set up with hydrocyanic acid and with phosgene, but this factor is offset by the fact that the compounds evaporate very quickly, that is, have high volatility.

43. 14. The Body as a Chemical Laboratory. Advances in organic chemistry which take place in the laboratory are always followed with interest by the biochemist in his study of the chemistry that takes place in the body. The introduction of a new drug, or of a new chemical widely used by industry, is accompanied by a survey of its physiological effects. It is well known that nature makes use

TABLE 43.2. REPRESENTATIVE CHEMICAL WARFARE AGENTS*

	Symbol	Formula	M.P. °C.	B.P. °C.	Principal Physiologic Effect	(A) Concentration for Indicated Physiologic Activity mg./cu. m.	(V) Volatility 5°C. mg./cu. m.	(V) Volatility 40°C. mg./cu. m.
Hydrocyanic acid	AC	HCN	−13.2	25.9	Nerve paralysis	500 LC_{50} (mice) t = 10 min.	506 × 10^3	—
Phosgene	CG	$COCl_2$	−104	8.3	Lung edema	375 LC_{50} (mice) t = 10 min.	3,820 × 10^3	—
Chloropicrin	PS	Cl_3CNO_2	−64	111.9	Lacrimation	146.7 Intolerable t = 2 min.	79.7 × 10^3	455 × 10^3
Mustard gas	H	$(ClCH_2CH_2)_2S$	14.5	224(d)	Vesication	450 Blister t = 10 min.	159	2,860
Lewisite	L1	$ClCH{=}CHAsCl_2$	−2.4	190	Vesication	1040 Blister t = 10 min.	1,438	17,540
Chloroacetophenone	CN		54	*d*	Lacrimation	17.5 Intolerable t = 2 min.	8.91	348
Diphenylchloroarsine	DA		41	333	Sternutation	10.9 Intolerable t = 2 min.	—	—

*Reproduced in condensed form from "Gas Warfare Agents-Survey" in Volume 7 of *Encyclopedia of Chemical Technology*, R. E. Kirk and D. F. Othmer, Editors. Copyright 1951, Interscience Publishers, Inc., New York, N. Y.

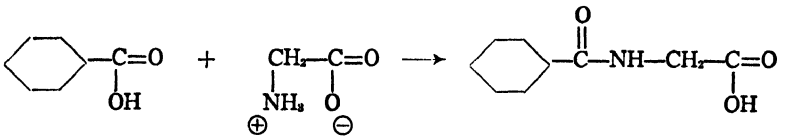
of defense mechanisms; such defense methods as protective coloring of insects and animals are readily observable, but chemical defense to substances absorbed through the lungs, or skin, or alimentary tract is usually far from obvious. However, just as foods must be metabolized into forms which can be used by the animal, poisons and drugs must be modified to structures that the organs are equipped to assimilate or eliminate.

The body makes use of processes of oxidation, reduction, and synthesis. Certain alcohols, for example, are destroyed in the body by complete oxidation to carbon dioxide and water, through intermediate aldehyde and acid stages. An example of reduction is the transformation of chloral (section 30.6) to the corresponding alcohol; this metabolite (product of metabolism) is not eliminated as such, but is combined by a synthesis with a compound supplied by the body:

$$\underset{\text{Chloral}}{CCl_3CHO} \longrightarrow \underset{\text{Trichloroethyl alcohol}}{CCl_3CH_2OH} \xrightarrow[\text{acid}]{\text{Glucuronic}} \text{Urochloralic acid}$$

Glucuronic acid (section 39.9) is one of the defense compounds used by the body for conjugation with a toxic substance or its metabolite and subsequent elimination in the urine. The term *conjugation* is extensively used in biochemical literature, but should not be confused wth conjugation phenomena described elsewhere in this book (section 18.1). In this example, glucuronic acid forms a glycoside type of compound (section 40.8), but it also forms esters through the carboxy group, and ethers through the hydroxy groups.

A simpler compound, used by the animal body for detoxication, is glycine (section 33.8). In fact, the first such mechanism discovered



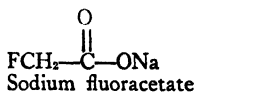
Benzoic acid Glycine Hippuric acid

(1842) was the conjugation of glycine with benzoic acid to give hippuric acid, eliminated in the urine. When studying the effects of drugs on experimental animals, pharmacologists must establish that the defense mechanism of the animal is similar to that of man. For

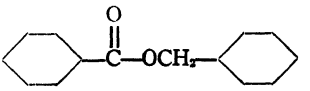
example, glycine is one of the twenty or more amino acids required by the body for normal growth. In young rats, the glycine supply is more limited than in man, so that use of the compound by a rat to destroy a toxic compound may interfere with his growth, whereas this situation may not prevail for other animals and man. Similarly, nearly all animals detoxify drugs of the aniline type (section 43.2) by introducing an acetyl group into the $-NH_2$ group attached to the benzene ring, but the dog cannot. In the case of sulfanilamide (section 43.9), the product of acetylation is more toxic than the drug itself and tends to cause kidney damage.

In section 34.2, it was stated that BAL reacts with lewisite to give an innocuous product. This treatment resulted from the discovery that lewisite reacts with sulfhydryl (–SH) groups in the side chains of certain body proteins. In the competition to react with lewisite the winner is BAL, to the benefit of the body.

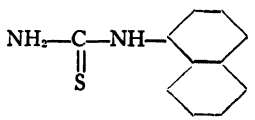
43. 15. Pesticides. It has been said that the cockroach is the most aristocratic occupant of this earth; he has been here *essentially unchanged* for millions of years. The roach exemplifies the highly important battle between insect life and human life for survival. World-wide disposition of the armies in World War II made this even more apparent, and brought forth a multitude of compounds specifically designed for destruction of insects. These are "economic poisons," or pesticides, a term that includes not only insecticides, but also rodenticides and fungicides. The insecticides are further subdivided to lousicides, miticides, etc. For the armies, there were also developed rather effective insect repellents. The field is vast; in this brief sketch, we shall mention only a few of the outstanding compounds and give their structures.



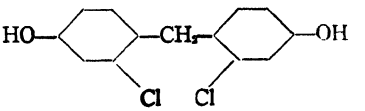
Sodium fluoracetate
(Rodenticide)



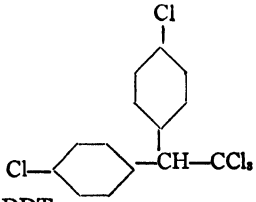
Benzyl benzoate
(Miticide)



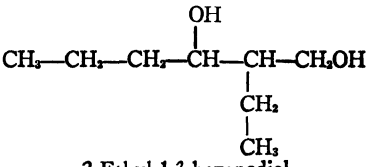
ANTU
alpha-Naphthylthiourea
(Rodenticide)



bis(2-Chloro-4-hydroxyphenyl)-methane
(Fungicide)

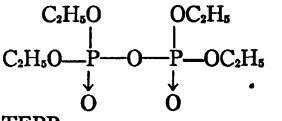


DDT
2,2-*bis*(*p*-Chlorophenyl)-1,1,1-trichloroethane
(Insecticide)



2-Ethyl-1,3-hexanediol
(Insect repellent)

A *lethane*
2-Butoxy-2'-thiocyano-diethyl ether
(Insecticide)



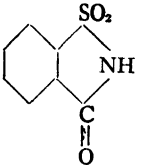
TEPP
Tetraethyl pyrophosphate
(Insecticide)

Special mention should be made of ANTU, a rat poison which is relatively harmless to other animals and humans. Its toxicity to rats was a lucky finding. The analogous compound, phenylthiourea, had been used to study a certain aspect of heredity, namely, the manner in which taste buds are transmitted through generations of animals and humans. When the tests were run with rats, they quickly died. It was subsequently found that ANTU was far better than the phenyl compound as a rat poison.

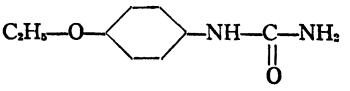
It should not be inferred that efficient poisons were not available before World War II. Pyrethrins (for insects) and red squill (for rats) are examples of well-known economic poisons obtained from nature; the supply, however, is rather limited. The student should also refer to compound 666 (section 19.2), compound 1068 (section 36.8), and to the quaternary salts (sections 31.11 and 33.8). Martius' yellow (section 42.8) was the first dye found (accidentally) to have moth-proofing qualities. This discovery has been used on a large scale in the manufacture of dyes with this property.

43. 16. Sweet Compounds. We shall end this chapter with a note on sweetness. In section 34.6, it was shown how *p*-toluenesulphonic acid can be converted to a valuable disinfectant. *o*-Toluenesulphonic acid can be oxidized to *o*-benzosulphonic acid, which is easily ammoniated to the imide known as saccharin. This is about 500 times as sweet as sucrose and is used in large quantities as a sweetening

agent. The discovery of its sweetness is one of the favorite stories in the history of accidental discoveries (about 1880, by Remsen). Another important sweet compound is dulcin, which is about 200 times



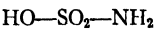
Saccharin



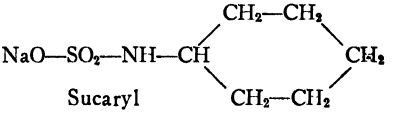
Dulcin

as sweet as sucrose. Structurally, it is a derivative of phenylurea.

Saccharin and sucaryl are the only compounds approved for use in the sweetening of foods. Sucaryl is about 30 times as sweet as sucrose. It has the advantage of being stable in cookery, even at baking temperatures. It is a fairly recent accidental discovery. Sucaryl is the sodium salt of the cyclohexyl derivative of sulphamic acid.



Sulphamic acid



Sucaryl

This is an appropriate place at which to comment once more on the taste buds referred to in the discussion of ANTU. A stimulant for taste buds is monosodium glutamate, often called MSG. This is the sodium salt of glutamic acid, the structure of which is shown in table 38.1. MSG enhances the flavors of nearly all foods, and can be added like salt and pepper before or after the food is cooked.

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44. HORMONES AND VITAMINS

44. 1. Nature of Hormones. Those glands in the animal body with which man has been most familiar in the past carry their secretions to some body surface by means of channels or ducts and discharge their secretions at the surface. For examples, we may cite the salivary glands in the mouth, the sweat glands on the skin, and the milk glands of the female.

There are some glands in the body, however, which have no ducts to carry their secretions from one place to another. The secretions of these "ductless" glands are called "internal" secretions. Substances called hormones are secreted by these glands under some body conditions, are drawn directly into the blood stream through the veins of the gland, and arouse certain functional activities of the body. The name hormone comes from the Greek *hormaein,* meaning "to arouse."

44. 2. Animal Hormones. As we mentioned at the beginning of the chapter on drugs, the hormones (and vitamins) have a drug-like action.

Adrenaline is secreted by the adrenal gland. Its chemical composition and properties were described in section 43.3. It controls blood pressure, and also acts to set free the stores of glycogen (section 41.7*a*) in the liver when fatigue of the body requires that the glycogen is converted quickly to carbohydrates for use as body fuel. The great physiological activity of the hormones is shown by the fact that adrenaline exhibits a definite activity when in a dilution of 1 part in 250,000,000.

Acetylcholine (section 33.8) and adrenaline are the hormones of the autonomic nervous system. This portion of the nervous system controls the involuntary movements of muscles in the body: that is movements not requiring a mental effort, such as contraction of the pupil of the eye, motility of the intestinal tract, beat of the heart, etc. This automatic control of muscles is accomplished through a sympathetic system of nerves and a parasympathetic system, which are essentially antagonistic (when their nerve fibers reach the *same* muscle). Thus, a stimulus through the sympathetic nerves will open the eye pupil, but a parasympathetic-nerve stimulus will close it; the sympathetic stimulus will accelerate heart beat, whereas the parasympathetic will slow it down.

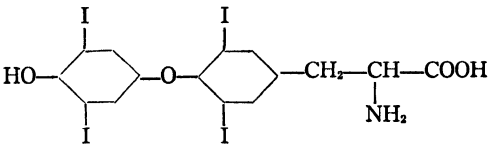
A nerve consists of a series of segments called neurons, each of which has a cylindrical core (the axon) and fine, branchlike appendages (the dendrites). The surface contact between the axon of a neuron and the dendrites of the next neuron is called a synapse. Transmission of a stimulus past these synapses through a system of neurons is made possible by acetylcholine and is apparently an electrochemical process. At the nerve-muscle junctions of the sympathetic system, the hormone liberated is *adrenaline* or a closely related substance; similarly, in the parasympathetic system, the hormone liberated is *acetylcholine*. Ultimate control of these competing systems is up to the enzymes present, which destroy the hormones as soon as they have served their purposes (aminoxidase for adrenaline, and choline esterase for acetylcholine).

When the hormones are injected into the animal body in small amounts, they cause effects which *mimic* the stimulations of their corresponding nervous systems, by overpowering the enzyme concentration normally present in the body. Many drugs are known which similarly have a sympathomimetic effect (section 43.3) and others are known that are parasympathomimetic; an example of the second is the insecticide TEPP (section 43.15), which is quite toxic to warm-blooded animals, its potent inactivation of choline esterase causing death due to paralysis when acetylcholine is left uncontrolled.

Insulin is one of the most famous of the hormones. This hormone is discharged from the pancreas into the blood stream in proportion to the sugar content of the blood. Its general purpose is to remove

excess blood sugar, and cause it to be stored up in the liver and muscles after it has been converted into glycogen. In diabetes, high blood-sugar concentrations are found, due to insufficient insulin secretion.

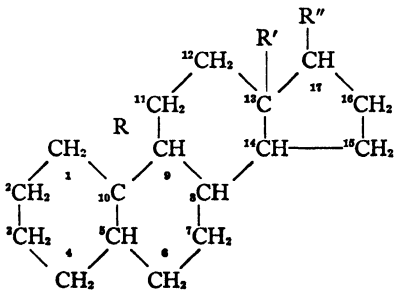
Thyroxine, the hormone from the thyroid gland controls the rate of metabolism of the body, that is, the rate at which the heart beats and the rate at which oxygen is used up in combustion of fats and carbohydrates. The active principle in the secretion from the thyroid gland is a protein-like substance from which the following compound has been isolated:



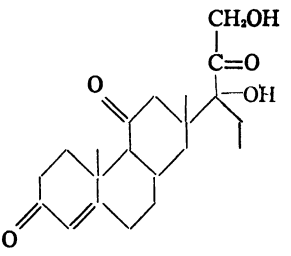
Thyroxine

A solution of 1 part thyroxine in 10,000,000 parts water affects the metabolism of tadpoles by speeding up the rate at which the tail is shortened in the metamorphosis to frogs. The structure of thyroxine should be compared with the structure of compounds of the "pressor" type in section 43.3. It should also be observed that it is an *alpha*-amino acid (see section 38.1).

Cortisone is a hormone from the cortex (outer layer) of the adrenal gland, and is remarkable for the effectiveness with which it counteracts the crippling effects of rheumatoid arthritis. The hormone is 17-hydroxy-11-dehydrocorticosterone. Cortisone belongs to a large family of compounds known as steroids, the outline structure of which is shown together with the number system used in their nomen-



Ring system in steroids



Cortisone

clature. If R is present, it is a CH_3 group or its oxidation product; R′ is a CH_3 group; and R″ is any of a wide variety of structural groups. In cortisone, R and R′ are CH_3.

The steroids include sterols, sex hormones, vitamins, and many other physiologically active compounds. Sex hormones and vitamins (see vitamin D) will be discussed later. It is of interest to interpolate here a brief mention of the sterols. The sterols are waxy substances found in plants and animals, often associated with true fats (section 31.8*b*). They contain –OH groups and their name comes from the Greek word for solid (section 22.1) and *-ol* for alcohol. The chief animal sterol is *cholesterol,* an essential constituent, in very small amounts, of the blood. It is present in the brain, in the bone marrow, in the skin, and in the bile (a fluid secreted by the liver). A biliary calculus, the medical term for gallstone, is often nearly pure cholesterol.

Associated with *cholesterol* in animals, but in very small amounts, is another sterol known as ergosterol; its plant source is ergot. The structures of these two sterols can be worked out from the following information:

Cholesterol, $C_{27}H_{45}OH$
–OH at position 3
C=C at 5,6
R and R′ are $-CH_3$
R″ is $-CH(CH_3)-CH_2-CH_2-CH_2-CH(CH_3)-CH_3$

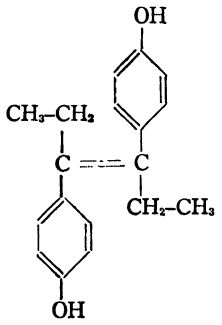
Ergosterol, $C_{28}H_{43}OH$
–OH at position 3
C=C at 5,6 and at 7,8
R and R′ are $-CH_3$
R″ is $-CH(CH_3)-CH=CH-CH(CH_3)-CH(CH_3)-CH_3$

Sex Hormones are the internal secretions which control the development in male and female animals of secondary sex characteristics, such as growth of the comb of roosters, periodic phenomena called estrus in the female, the beard on the face of man, etc. Several hormones of this nature have been isolated and identified, and have been found to be structurally related to the sterols. They have either a short side chain or none at all. For example, a hormone of the testes, obtained from male urine, has the usual –OH at position 3, but only a C=O at position 17. This hormone is a ketone, as well as an alcohol, and is called *androsterone.*

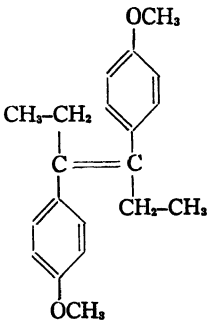
The male hormones as a class are known as androgens (from the the Greek *andros,* meaning man). The female hormones are estrogens (from the Latin *oestrus,* meaning the female sex cycle).

The most potent of the estrogenic hormones is *estradiol,* obtained from the urine of mares and from pregnancy urine. This compound has an –OH group instead of the side chain at position 17. It also lacks a $-CH_3$ group at carbon atom 10; and the first ring in the molecule is aromatic, which makes the –OH at position 3 phenolic. It is thought that these sex hormones originate from oxidation and partial decomposition of sterols and bile acids.

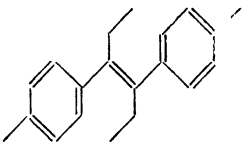
Practically as potent as estradiol is *diethylstilbestrol,* which is a derivative of stilbene (diphenylethene). The dimethyl ether of diethylstilbestrol is authorized for use in changing male chickens into



Diethylstilbestrol



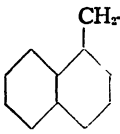
Dimethyl ether of diethylstilbestrol



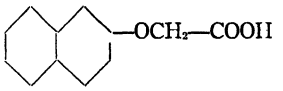
capons. The outline structure shown here indicates the relation to the estrogens; it is believed that the distance apart of the –OH groups is an important factor.

44. 3. Plant Hormones. A variety of substances has been extracted from bark, seeds, etc., which, when applied to growing plants, bring about responses that resemble activity of hormones in animals and man. Many relatively simple organic compounds have been found to be far superior to these crude extracts in their hormonelike behavior.

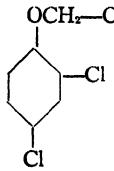
Perhaps the simplest of these plant hormones is ethene, $CH_2{=}CH_2$, which is used extensively to accelerate ripening of citrus fruits and bananas in warehouses, after being picked green. When treated with 1-naphthaleneacetic acid, potatoes can be stored almost indefinitely without shrinkage and the budding tendency is delayed. The same compound is used in orchard sprays to prevent apples from dropping before they are harvested. T he 2-naphthoxyacetic



1-Naphthaleneacetic acid



2-Naphthoxyacetic acid



2,4-Dichlorophenoxyacetic acid "2,4-D"

acid, and several related compounds, are highly effective in promoting growth of seedless fruit, such as seedless tomatoes. For purposes of inhibiting bud formation and causing formation of seedless fruit, 2,4-D is far more effective than other compounds that have been tested.

A very important result of the study of plant growth regulators is the discovery that they can be used as *herbicides*. At the extremely low concentration of 10 parts per millions, or less, the hormones have a beneficial effect on a plant, but if the concentration is raised to between 100 and 1,000 parts per million, the abnormal growth results in death. This action as a plant killer is quite different from that of herbicides used earlier, which had a caustic action on plants that showed up in such symptoms as "burning" of the leaves, etc. These new herbicides have a selective action which often permits eradicating pestiferous plant life without injury to crop plants. 2,4-D has been outstandingly successful as a weed killer. However, herbicides are known which will kill cereal crops in preference to weeds.

44. 4. Vitamins. The vitamins are extremely active substances physiologically, and seem to be necessary for the welfare of all living things. There is no essential difference between vitamins and hormones. They both serve to regulate body functions. The only difference between them is that hormones are manufactured by certain glands of the body, whereas vitamins are produced in other various ways. So far as man is concerned, the principal source of vitamins is foodstuffs. The fact that substances essential to health are present in certain foods has been known for several hundred years. That these substances are chemical in nature could not, of course, become apparent until recent years. It is now believed that vitamins are structural parts of coenzyme systems (see cozymase in section 44.5).

By 1860, Pasteur had established the fact that most diseases are due to bacteria and related organisms. By 1887, it was also certain

that some diseases, like beriberi, are not due to wicked bacteria, but to absence of certain foods in the diet. By 1912, it was shown that foodstuffs contain at least two kinds of "essential substances"; one of these, which is necessary for growth of young animals, was called fat-soluble A and the other, which is necessary for prevention of beriberi was called water-soluble B.

These names indicated the solubility of these potent substances and also the method of extracting them from certain foods in more concentrated form. They were generally called *vitamines,* because it was *proved* that they are essential to life (vital), and because it was *thought* that they are amine compounds, analogous to amino acids (chapter 38).

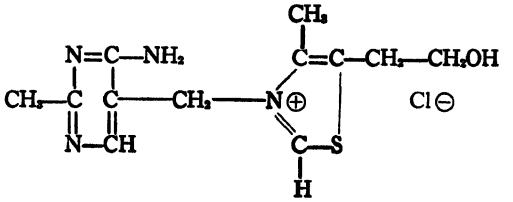
By 1920, it was recognized that a third in this series of substances, water-soluble C, is present in certain foods and prevents scurvy. It was also clear by this time that these vitamines are not amines, and it was suggested to drop the "e" from the end of their name, using the alphabet to record the order of their discovery, thus: vitamin A, vitamin B, vitamin C, etc. Today scientists prefer to call vitamins by their chemical names.

The potency of these substances is extremely great. Vitamin D, for example, shows a detectable physiological effect on a rat when diluted 2,240,000,000 times. The daily human requirement is said to be only 0.000,025 gram.

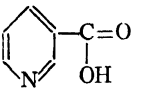
The chemical nature of the vitamins was determined so rapidly that ideas concerning vitamins often changed overnight. In 1930, an expert in the field of vitamin chemistry declared that "vitamin A and vitamin C isolation seems, at present, quite remote," but in the following two years these same vitamins were thoroughly investigated and their chemical nature was well established.

Vitamin A is a close relative of the red and yellow pigments present in carrots, tomatoes, egg yolks, etc. It is found in large quantity in certain liver fats, and was originally called fat-soluble A. It is a growth factor, it cures "night blindness," and it helps to prevent bacterial infections of mucous membranes which cause colds, tongue ulcers, etc. We have given the structure of vitamin A in section 37.8, where we showed that it is practically one-half the molecule of the yellow pigment β-carotene.

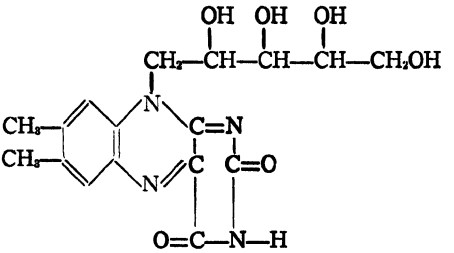
B Vitamins are found principally in the cereal grains, liver, meats, eggs, yeasts, etc. They have in general a beneficial effect on the digestive and nervous systems. What is often referred to as vitamin B is not a uniform substance; depending on its source, it consists of variable amounts of a number of compounds with slightly different effects, called B_1, B_2 and so on.



Thiamine hydrochloride



Nicotinic acid

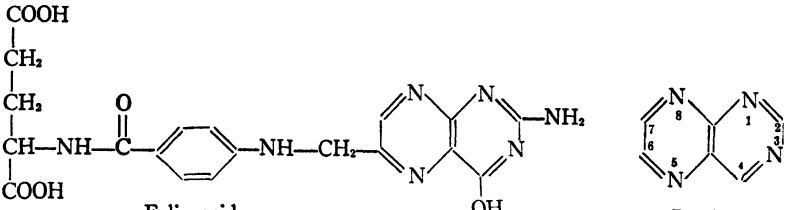


Riboflavin

Thiamine hydrochloride, generally known as thiamin (or vitamin B_1) was originally isolated from rice bran. Now, it is made synthetically. *Riboflavin* is so named because its side chain is essentially the ribose sugar structure; it is a yellow coloring agent in lean meat, milk, and yeast; therefore its alternative name is *lactoflavin* (Latin *flavus* means yellow). Riboflavin is vitamin B_2. Both the B_1 and B_2 vitamins contain the pyrimidine ring, which is part of the purine structure described in section 43.5. *Nicotinic acid,* also known as *niacin,* is a derivative of pyridine (section 36.4). It is effective in treating pellagra.

An important B vitamin identified (1946) by synthesis of the active substance is *folic acid.* The folic acid molecule contains one glutamic acid residue (see table 38.1) and its central structure is *p*-aminobenzoic acid, a molecule of biochemical importance (section 44.6). This vitamin is being used successfully in the treatment of

pernicious anemia. The nitrogen ring system in folic acid is apparently widespread in animals and insects. The fundamental struc-



Folic acid
Pteroylglutamic acid

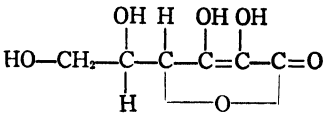
Pteridine

ture is *pteridine*. Folic acid has the long side chain at position 6, with $-NH_2$ at 2 and –OH at 4. The pigments in butterfly wings are called *pterins*; they have no lengthy side chains. For example, *xanthopterin* (a yellow pigment) has $-NH_2$ at position 2, –OH at 4, and another –OH at 6.

Vitamin B_{12}, the most effective of all the vitamins, was isolated in 1948 as a red crystalline compound from liver extract. It is used in the treatment of pernicious anemia, and can be employed in doses as small as 0.000 005 g., as compared with about 0.05 g. of folic acid. The molecule of B_{12} contains cobalt; it is the only vitamin known to have a metal atom in its structure.

Vitamin C is the antiscorbutic (antiscurvy) vitamin. It is found in citrus fruits, especially in lemons and oranges; in tomatoes and most fresh vegetables; in green and red peppers; and it is also present in small amounts in the animal body in the adrenal gland.

. Vitamin C is related to the hexose sugars. It is a lactone (section 32.6) derived from a six-carbon sugar acid (see sorbose, in section 39.9). Vitamin C has been named ascorbic acid, from its antiscorbutic properties, and the following structure has been assigned to it:



Ascorbic acid, or vitamin C

Ascorbic acid is optically active, and occurs in the form of *dextro* and *levo* molecules. Vitamin C is the *levo*-ascorbic acid; this molecule is more than forty times as active physiologically as the *dextro*

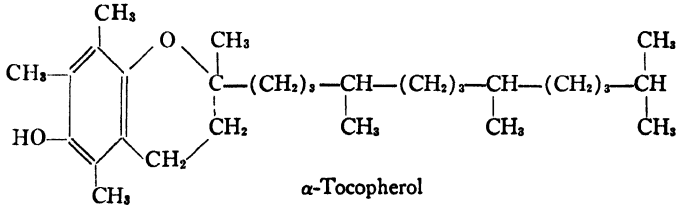
compound. In fact, the *dextro* molecule is practically useless for the prevention of scurvy.

Vitamin D is a fat-soluble vitamin family, and is found in such substances as milk, butter, and eggs. A favorite source is fish-liver oil. Vitamin D is a growth-promoting vitamin, and is essential for proper assimilation of calcium and phosphorus. For this reason, it is necessary for the prevention of rickets and imperfect teeth, and is called the antirachitic (antirickets) vitamin.

The vitamin D family is related to the sterols, especially ergosterol and cholesterol, the structures of which were presented earlier in this chapter. Vitamin D_2 can be obtained from ergosterol by ultraviolet irradiation. The change consists in breaking the ring system between C_9 and C_{10}; there is left a $=CH_2$ group linked to C_{10} when an H atom from the R group ($-CH_3$) migrates to C_9. Vitamin D_3 occurs in fish-liver oils and can be obtained by ultraviolet irradiation from 7-dehydrocholesterol; the molecular change due to high-energy radiation is similar to that in the formation of vitamin D_2.

Exposure of certain foods to ultraviolet converts the traces of ergosterol in the foods to vitamin D_2. A similar change probably takes place in the skin of animals exposed to sunlight, for the sterols are present in the skin. This explains the medicinal value of sunlight as a cure for rickets.

Vitamin E is the fertility vitamin and its chemical name is *α-tocopherol* (from the Greek *tokos,* meaning childbirth, and *pherein,* meaning to bear). It is present in large quantity in wheat germs and can be made synthetically. It is essential for normal functioning of the placenta in females and for normal formation of germ cells in males. Note its structural similarity to vitamin K (section 37.9):



α-Tocopherol

Vitamin K, the blood-clotting vitamin, has already been described. It may be noted that vitamin K Substitute, which does not have the side chain shown in the structure in section 37.9, is said to be more

effective than vitamin K itself. The chemical name of the substitute is 2-methyl-1,4-naphthoquinone.

44. 5. Enzymes. The decompositions and syntheses that take place in living things are catalyzed by complex protein substances known as enzymes. Although enzymes are formed by living tissue, they may retain activity outside the tissue. As an illustration, the cell-free juice pressed from yeast contains twenty or more enzymes. Each acts at the proper time to break down sugar successively into smaller fragments, finally yielding alcohol and carbon dioxide.

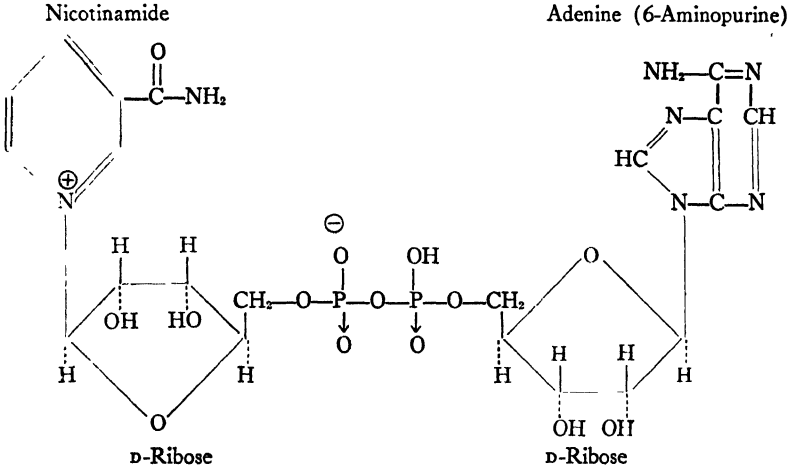
Many enzymes, such as pepsin and trypsin, consist only of protein material. As shown in section 38.4, the chemistry of a protein depends on the nature of the side chains on a molecule of colloid dimensions. Some enzymes are conjugated proteins; they consist of proteins from which relatively small compounds can be detached. The protein body is called the *apo*enzyme, whereas the attached (that is, *prosthetic*) group is called the *co*enzyme:

Apoenzyme. A protein of high molecular weight. The configuration of this colloid is said to be responsible for the *specificity* of reactions with only certain molecules (the familiar lock-and-key theory of enzyme action). The apoenzyme diffuses slowly.

Coenzyme. Not a protein. A compound of relatively low molecular weight. Necessary for *activity* of the enzyme system. Diffuses rapidly and can be separated by dialysis from the apoenzyme.

Enzymes that have been named systematically have names ending in *-ase,* the rest of the name indicating the substrate on which it acts. For example, maltase catalyzes the hydrolysis of maltose to glucose (section 41.7) and cellulase hydrolyzes cellulose to cellobiose (section 41.8). *Zymase* is the original name of the mixture of enzyme systems that decomposes sugar. One of the coenzymes in this complex is *cozymase,* the formula of which is given here. Cozymase is the catalyst responsible for oxidations and reductions during the various stages in the decomposition of sugar by enzyme action. It is a diester of pyrophosphoric acid, $H_4P_2O_7$. As an oxidizing agent, it readily accepts two hydrogen atoms (one at the pyridine ring and one at the pyrophosphate radical), and as a reducing agent, it also readily releases them to a hydrogen acceptor.

The addition of 2 H· to this molecule may be understood if the electron situation is examined at the N atom and at the O atom

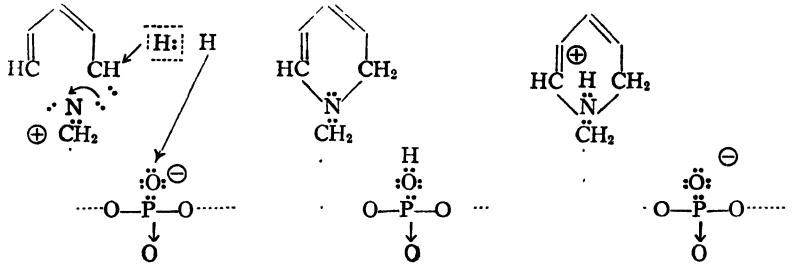


Cozymase. The structural parts of the molecule are labeled. Nicotinamide is one of the B vitamins (compare nicotinic acid in section 44.4).

as shown in (I) to (III). The student will recall (section 30.3) that half the shared electrons around an atom are considered the property of that atom, in addition to all the unshared electrons. In cozymase, the N atom possesses four electrons whereas it requires five to be neutral; it, therefore, has a ⊕ charge of one. The O atom has seven electrons instead of the normal quota of six and accordingly has a ⊖ charge of one. Addition of two hydrogen atoms by the mechanism indicated in (I) would result in a "normal" situation (II) with respect to the electron envelopes around these atoms. The cozymase molecule is obviously dipolar. It is likely that this dipole nature persists after addition of H_2, in that the proton (H), which is shown attached to O in diagram (II), is more likely to be on the N atom in the pyridine ring. This situation is shown in (III), which is similar to the dipole structure of glycine in section 33.8. In other words, simple addition of H_2 across the double bond N=C in the pyridine ring, to produce an inner salt, does not change the charge distribution in the cozymase molecule.

The cozymase molecule contains a B vitamin residue. It is possible that all the vitamins are parts of coenzymes. If this is true,

it explains the necessity for vitamins in life processes. Thiamin (vitamin B_1 in section 44.4) is present as a pyrophosphate in the coen-



(I) (II) (III)

zyme known as *cocarboxylase*. This coenzyme is involved in the elimination of CO_2 from a certain carboxy acid by the enzyme *carboxylase* in one of the stages of sugar decomposition. Another group of coenzymes is formed from the pyrophosphates of the vitamin riboflavin (section 44.4).

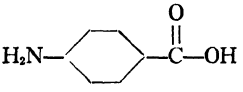
The structural formula of cozymase which is given in this section helps to illustrate other compounds of biochemical importance. The combination of a purine (or a pyrimidine) with a pentose is called a *nucleoside*; the fragment on the right-hand side of the cozymase molecule, which consists of adenine combined with ribose, is *adenosine*. The intact adenosine molecule, of course, whould have $-CH_2OH$ on the fifth carbon atom of the ribose segment.

The phosphoric acid esters of nucleosides are called *nucleotides*. The H_3PO_4 ester of adenosine is adenylic acid. It has been found that in certain natural substances the esterification takes place either through the –OH of the third carbon atom of the ribose fragment or through the –OH of the fifth carbon atom, as in cozymase. Dinucleotides are formed with $(HO)_2OPOPO(OH)_2$ as in the cozymase structure; adenosine diphosphate is known as ADP. Similarly, adenosine triphosphate, from $(HO)_2OP–O–PO(OH)–O–PO(OH)_2$, is called ATP.

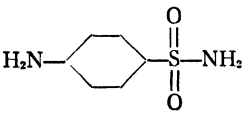
The *nucleic acids*, normally present in all cells and tissues combined with proteins, yield on hydrolysis: phosphoric acid (H_3PO_4), nitrogen bases derived from purine, nitrogen bases derived from pyrimidine, and a pentose sugar (or a close relative of such a sugar). The general structure of a nucleic acid should be apparent from the discussion in the preceding paragraphs.

44. 6. Biochemical Antagonism. One of the important developments in science in the period since 1940 is the realization that compounds of similar chemical structure often interfere with each other in body processes. This phenomenon has been studied rather extensively in connection with metabolites, that is, substances which occur as a result of a metabolic process in a living organism. An example of metabolites is histamine, the unpleasant effects of which are offset by several structurally related compounds as described in section 43.11. The interfering compounds are called *antimetabolites,* or biochemical antagonists.

A milestone in the history of this phenomenon was the discovery that the effectiveness of sulfanilamide in destroying bacteria is competitively reversed by *p*-aminobenzoic acid. This led to the finding



p-Aminobenzoic acid



Sulfanilamide

that *p*-aminobenzoic acid is essential to the growth of the bacterial cell (in the nature of a vitamin), and that it is important generally as a biochemical (see folic acid in section 44.4). Because of its similar size and shape, sulfanilamide can take up the same position in the cell or on an enzyme structure which is normally occupied by *p*-aminobenzoic acid; but the ultimate effects are different and the organism dies.

Many analogous antagonistic systems have been found in the enzyme reactions of animals and man. Among mice, for example, beneficial effects of nicotinic acid in the diet can be offset by feeding 3-acetylpyridine. This compound is structurally the same as nicotinic acid (see its formula in section 44.4) except that the $-\overset{\overset{O}{\|}}{C}-OH$ group is replaced by $-\overset{\overset{O}{\|}}{C}-CH_3$. The inhibitory action is reversible (competitive), that is, if nicotinic acid is used in larger quantity it overcomes the antagonist. In other words, it is a reversible, mass-action effect. An animal capable of making its own vitamin (or essential metabolite) is usually not affected by the inhibitory compound. In

some instances, however, the action of the antimetabolite is irreversible (noncompetitive). This is generally the case if the antimetabolite contains a reactive group or atom, such as a halogen; the chemical reaction that takes place may be such that the original substance cannot be reassembled and subsequently pushed away by the normal metabolite.

SUGGESTED READING

See references to chapter 43.

45. ISOTOPIC CHEMISTRY

45. 1. The Hydrogen Atom. Organic chemistry has been properly called the chemistry of carbon, but the observing reader will have noticed that it is almost as truly the chemistry of hydrogen. The hydrogen atom is found associated with carbon in most of the carbon compounds.

When the H atom (turn to figure 6.1) is employed in the building of molecules, it appears in several modifications. Most important of these is the covalent bond, the normal valence bond, as in the molecule H:H. We have also seen how the hydrogen atom is used as a bridge to link strongly electronegative elements like O, N, and F (see, for example, section 27.7), due to its ability to hold two electron pairs in what superficially looks like doubly bonded hydrogen.

The hydrogen atom can give rise to the H^+ ion as described in sections 31.6 and 31.7, and this ion can be used to form a hydronium ion (section 27.3). The hydrogen atom also gives rise to the negative H^- ion, in the salt, lithium hydride, the formula of which is $Li^+:H^-$. The size of the H *atom,* relative to other atoms, is shown in figure 6.2. The H^+ *ion* is a proton and is negligibly small. The H^- *ion,* however, has an effective diameter even larger than those of the F^- and Cl^- ions shown in black in figure 6.2. In fact, the H atom may be considered not only as the first alkali metal in group 1 of the periodic table (inside back cover of this book), but also as the first halogen of group 7. This is shown by its tendency to add *one* electron to complete a valence shell (containing two electrons) in

H:H, and in $:H^-$. The halogens, also, add *one* electron to acquire stability by filling a valence shell (containing eight electrons).

The preceding paragraph sums up the chemistry of the H atom. As to the H:H molecule, it can exist in *ortho* and *para* forms, depending on the directions in which the two electrons spin. In *ortho* hydrogen, the electrons spin in opposing directions, which is normal behavior for an electron-pair bond as described in section 7.5, but in *para* hydrogen, the spins are in the same direction. The *para* modification is produced when hydrogen is in contact with a charcoal surface at very low temperatures.

In 1932, a type of hydrogen was discovered with atomic weight 2, as compared with atomic weight 1 of ordinary hydrogen atoms. We are now also familiar with a hydrogen which has an atomic weight of 3. Similarly, in addition to carbon with atomic weight 12, there are also carbon atoms with weights of 10, 11, 13, and 14. The rest of this chapter will be devoted to the role played in organic chemistry by these recently identified substances. However, we must first consider the meaning of the terms *atomic number* and *isotope*.

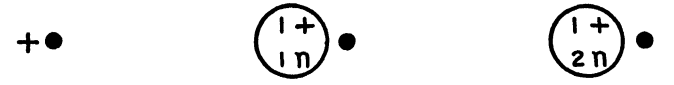
45. 2. Atomic Number. The reader should refer, once again, to the schematic pictures of the atoms in figure 6.1. He will see that each element contains one more planetary electron than the preceding element. This means that each element contains one more proton in the nucleus than the preceding element. Hydrogen has one such proton, helium has two, lithium three, beryllium four, and so on.

The number of protons, or planetary electrons, is the atomic number, or element number. This number gives the sequence of the elements in the periodic system.

On the back cover of this book will be found a chart of the elements which includes their atomic numbers as well as their atomic weights. According to the periodic law as originally stated, the chemical properties of the elements are a periodic function of their atomic weights. This law does not always hold, as becomes evident by examining the positions in the table occupied by argon and potassium with respect to their weights. Potassium is lighter than argon and according to its weight it should precede argon in the table, but that would put it in the wrong column of the table with respect to its chemical properties.

A more exact statement of the periodic law is that the properties of the elements are a periodic function of their atomic numbers. There are no exceptions to this rule; it will be observed that argon and potassium are placed in their proper positions in a table arranged according to atomic numbers.

45. 3. The Hydrogen Isotopes. If we refer again to the pictures of the elements in figure 6.1, we notice a gap between hydrogen and helium, with respect to atoms which may have atomic weights of 2 and 3. For some time, it was suspected that atoms may exist which contain the combinations of 1 proton + 1 neutron and 1 proton + 2 neutrons in the nucleus and occupy intermediate positions between hydrogen (atomic weight = 1) and helium (atomic weight = 4). These atoms can be represented diagrammatically as follows, using the same scheme as in figure 6.1; the hydrogen structure is included for reference:



Hydrogen (H)	Deuterium (D)	Tritium (T)
Atomic wt. 1	Atomic wt. 2	Atomic wt. 3
Atomic No. 1	Atomic No. 1	Atomic No. 1

Since protons (+) and neutrons (n) have nearly the same weight, atoms D and T have weights of 2 and 3, respectively. However, they have only one planetary electron (atomic number 1) and they, therefore, belong *in the same place* in the periodic system of elements as hydrogen, which is atom number 1. The three kinds of hydrogen are called *isotopes*, from the Greek words *iso*, meaning the same, and *topos*, meaning place. In each family of isotopes, the atomic weights vary, but the number of planetary electrons, which controls the chemical properties, is the same.

The symbols used most generally for representing isotopes of an element can be illustrated by ${}_1H^1$, ${}_1H^2$, and ${}_1H^3$ for hydrogen, deuterium, and tritium, respectively. The lower numeral indicates the atomic number and the upper numeral is the atomic weight. On this basis, the symbol for a neutron is ${}_0n^1$ and for a proton is ${}_1p^1$. Often the lower numeral is omitted, where obvious, as in H^3 for tritium.

The proportion of deuterium in ordinary hydrogen is 0.02 per cent. Tritium is a radioactive isotope (section 45.6); its concentration in ordinary hydrogen has been estimated at about one part in

10^{18} parts of hydrogen. The term *heavy hydrogen* applies to deuterium.

When isotopes were first recognized, they were defined as atoms with different atomic weights but *identical* chemical properties. This is nearly true for most families of isotopes but is far less true for the hydrogen isotopes, which differ markedly in properties because of the great difference in weight. Since deuterium is twice as heavy as hydrogen there is a considerable variation in physical properties and chemical reactivity, not only of the elements but also of their compounds.

With respect to physical properties, for example, hydrogen (H_2) boils at 20.38° K., whereas deuterium (D_2) boils at 23.50° K. Similarly, water (H_2O) has a freezing point of 0.00° C. and boiling point of 100.00° C., whereas heavy water (D_2O) freezes at 3.82° C. and boils at 101.42° C.

The difference in chemical reactivity is not of *kind* but of *degree*. For example, both water and heavy water react with aluminum carbide,

$$12\,H_2O + Al_4C_3 \rightarrow 4\,Al(OH)_3 + 3\,CH_4 \text{ (methane)}$$
$$12\,D_2O + Al_4C_3 \rightarrow 4\,Al(OD)_3 + 3CD_4 \text{ (deutero-methane)}$$

but ordinary water reacts twenty-three times as fast as heavy water. (There is one molecule of heavy water in about five thousand molecules of ordinary water.)

It has been found that in water solution, the removal of D^+ ions from acids like deuteroacetic acid, CH_3—COOD, is more difficult than separation of H^+ ions from hydrogen acids like acetic acid, CH_3–COOH. This is proved by the smaller ionization constant of the deutero acid. In other words, the D atom is less mobile than the H atom.

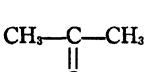
45. 4. Exchange Reactions. When acetylene is passed into heavy water containing an alkaline catalyst it is found that the H atoms are replaced by D atoms:

$$H—C{\equiv}C—H + D_2O \rightarrow D—C{\equiv}C—D + H_2O$$

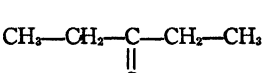
This is called an exchange reaction. Only those compounds in which the H atoms tend to split off as ions go through this type of exchange. The fact that acetylene is capable of ionization was stated in section 15.3*b*, where it was observed that acetylene is capable of forming

salts. The exchange mechanism is to be explained by the fact that the water solution contains both H^+ ions and D^+ ions, both of which can attach to the carbon atom. Since the molecule C_2D_2 forms in preference to the C_2H_2 molecule it is evident that the C–D bond is chemically more stable than the C–H bond. The H atoms in compounds like methane (CH_4) and benzene (C_6H_6) are not ionizable and are not replaceable by heavy hydrogen atoms in such exchange reactions.

In section 32.11, it was shown that compounds in which C–H is adjacent to $\begin{array}{c}|\\ C{=}O\\ |\end{array}$ have acidic properties, due to ionizability of the hydrogen. It is, therefore, not surprising that acetone dissolved in heavy water containing an alkaline catalyst will have all six of its hydrogen atoms replaced by dueterium atoms to give CD_3–CO–CD_3. It is a relatively slow process which can be readily followed; the catalytic effect of the base should be reviewed in section 32.11.



Acetone



Diethyl ketone

The related compound, diethyl ketone, under the same conditions, will exchange only four of its ten hydrogen atoms, since only four are on carbon atoms *adjacent* to C=O. The product is CH_3–CD_2–CO–CD_2–CH_3.

Since hydrogen and heavy hydrogen are so different, as explained in the preceding section, it is a comparatively simple matter to devise analytical methods for determining to what extent the D atoms have replaced H atoms in certain compounds.

45. 5. Isotope Indicators. An atom like heavy hydrogen is often referred to as a "tagged" atom in that we can replace ordinary hydrogen with it, and since it is quite different from ordinary hydrogen, we can follow it in the course of a reaction. It is also called a "tracer" or "indicator" atom.

If sugars are dissolved in heavy water with appropriate catalysts, the H atoms in C–OH but not in C–H can be exchanged for D atoms. In section 39.6, some of the possible structures of the glucose molecule in solution were pictured and it was explained that the straight-chain form can change into a cyclic form as the result of

migration of the H atom from a certain –OH group from one position to another. It has been observed that the velocity of mutarotation of *alpha*-glucose (section 40.5) is considerably lower in heavy water than in ordinary water. This, of course, is due to the slower rate of travel of the heavy hydrogen atom that has replaced the lighter hydrogen atom in the molecule of the sugar. These results with the sugars help to confirm current ideas on the equilibria in their water solutions as described in section 39.6.

The problem in photosynthesis is to determine how CO_2 and H_2O are employed in biochemical reactions to build up complex carbon compounds with the aid of the energy supplied by light. Advances in the elucidation of this important problem of mankind have lagged somewhat behind developments in other fields, but progress is rapidly being made as a result of the availability of new techniques. According to one of the older theories of photosynthesis, plants synthesize carbohydrates by means of an intermediate synthesis of formaldehyde:

$$CO_2 + H_2O \longrightarrow H{-}CHO + O_2$$

This is a reduction process, in which it was thought that the liberated O_2 comes from the CO_2. This theory has been tested by means of "tracer" oxygen atoms with an atomic weight of 18. Although systematically we should differentiate between the light and heavy oxygen atoms by the symbols ${}_8O^{16}$ and ${}_8O^{18}$, in this discussion we shall simply indicate them by O and **O**, respectively.

Experiments have been conducted in which plants were fed CO_2 and H_2O containing light or heavy oxygen atoms, with results as indicated below:

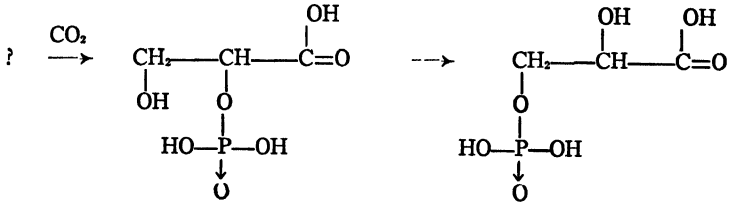
$$CO_2 + H_2\mathbf{O} \rightarrow \text{some plant product} + \mathbf{O}_2$$
$$\mathbf{CO}_2 + H_2O \rightarrow \text{some plant product} + O_2$$

(Note: these are not balanced equations)

It was thus proved that, in photosynthesis characterized by liberation of oxygen, the oxygen which is liberated originates from the water and not from the carbon dioxide as previously assumed. The oxygen from the carbon dioxide is built up into the plant structure.

The reduction of the carbon in CO_2 to groups such as $-CH_2OH$ probably is accomplished by oxidation-reduction systems. It was shown in section 44.5 that phosphorus compounds play an important

part in enzyme reactions of this nature, and it is likely that they are essential to photosynthesis. By employing CO_2 made with radioactive carbon atoms, the first compound that is found to appear (within 5 seconds) in the fixation of CO_2 by the green plant is phosphoglyceric acid. Data are being rapidly accumulated on the



2-Phosphoglyceric acid 3-Phosphoglyceric acid

probable subsequent steps in the enzymatic synthesis of larger compounds and the sugars, and reasonable postulations have been made on the nature of the phosphate compound that initially causes fixation of the carbon dioxide.

45. 6. Radioactive Isotopes. In section 45.3, we described three isotopes that correspond to element number 1. Of these, two are *stable,* namely, hydrogen and deuterium. The third isotope, tritium,

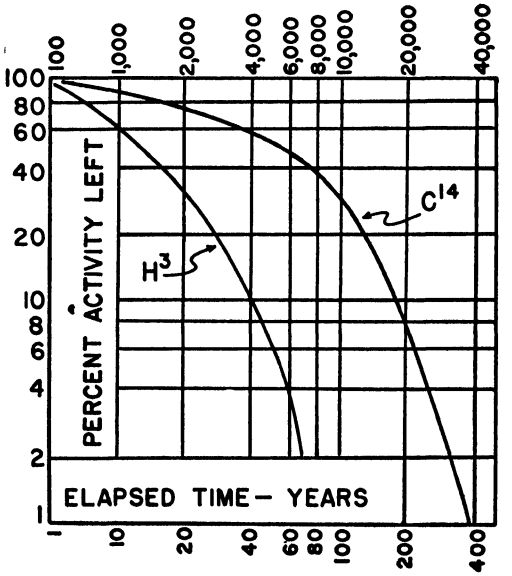


FIGURE 45.1. Decay curves for tritium (H^3) and for C^{14}. The scale is logarithmic. *Half-life* is time at which 50% of activity is left. This is 12.4 years for H^3 and 5,400 years for C^{14}. Activity is insignificant after about 5 × half-life.

is unstable and is called the *radioactive* isotope; when the nucleus of this atom breaks down, it eliminates a charged particle which is an electron (e), also referred to as a *beta particle* or *beta ray* (β^-). If a certain amount of tritium is available at a given time, half of this amount will have decomposed in 12.4 years; this is called the *half-life* of the isotope.

The reaction for the decomposition of tritium is

$$_1H^3 \longrightarrow {}_2He^3 + {}_{-1}e^0$$

and can be written down readily when we know the nature of the particle thrown out. The symbol $_{-1}e^0$ for an electron distinguishes it from a positron, which is $_{+1}e^0$. In symbol $_1H^3$ the lower numeral, the element number, indicates the number of protons in the nucleus. The upper numeral is the weight of the atom (protons and neutrons in the nucleus). Elimination of an electron causes no change in weight, but the decomposition of a neutron which results in elimination of the electron sets free a proton ($_0n^1 \rightarrow {}_1p^1 + {}_{-1}e^0$). This results in an element $_2/^3$ with a nuclear charge of two protons and an atomic weight of 3, and from figure 6.1 this must be an isotope of helium; its nucleus has two protons and one neutron, and its symbol is $_2He^3$.

The trace amounts of tritium present in ordinary hydrogen probably originate from nuclear processes occurring in the atmosphere. For use in chemical experiments tritium can be made in weighable amounts from lithium. The shorthand expression for this reaction is Li^6 $(n,\alpha)H^3$, which means that when lithium of atomic weight 6 is subjected to bombardment by neutrons (n) it eliminates helium ions (α) and is transformed into tritium. The more conventional equation is

$$_3Li^6 + {}_0n^1 \longrightarrow {}_2He^4 + {}_1H^3 ,$$

It should be observed that the upper numerals (weights) balance on the two sides of this reaction, and that this is also true of the lower numerals (positive charges). The *alpha particle* (α) is the helium ion He^{++} rather than the helium atom, but this is not evident in the *nuclear* reaction written here, which is not concerned with loss of *planetary* electrons resulting in ionization.

Radioactive atoms can be used like ordinary atoms because their chemical reactivities are practically identical. Like the deuterium

atoms and the heavy oxygen atoms discussed earlier in the chapter, the radio atoms are useful as "tracer" atoms in the study of reaction mechanisms.

Since it is possible to detect an atom through its radioactivity about a million times more easily than by chemical analysis, the ability to make and use artificially radioactive elements is one of the most important advances in recent years. To illustrate, it is possible to feed a compound containing radioactive atoms to animals, insects, or plants and to determine into what organs the compound penetrates and exactly to what extent. Its travel can be followed by the charged particles which it emits.

45. 7. The Isotopes of Carbon. There are five members of the carbon family of isotopes, as already mentioned in section 45.1. Ordinary carbon contains 98.9 per cent of the stable isotope C^{12} and 1.1 per cent of the stable isotope C^{13}. The second is known as *heavy carbon.* The presence of heavy carbon in ordinary carbon accounts for its atomic weight of 12.01 as listed in the chart on the back cover of this book.

There are three radioactive isotopes of carbon, namely, C^{10} with a half-life of 8.8 seconds; C^{11} with a half-life of 20.5 minutes; and C^{14}, the half-life of which is 5,400 years. It is obvious that only this last isotope can have extensive use as a radioactive tracer atom, although C^{11} has been employed by investigators near the source of a supply of the material. The decomposition of C^{14} atoms takes place with elimination of beta rays. The use of C^{14} as a tracer atom is more convenient than that of C^{13}; the first requires a comparatively simple detection instrument, such as the Geiger–Müller counter, whereas the second requires the more complicated mass spectrometer.

The advent of chain-reacting piles in World War II, with their abundant neutron supply, makes the manufacture of C^{14} rather simple. One procedure is the nuclear reaction ${}_7N^{14}(n, p){}_6C^{14}$. Ammonium nitrate ($NH_4NO_3$) solution in a suitable container is placed in the pile and the neutron bombardment causes a nuclear transformation in which protons are ejected and nitrogen atoms are changed into carbon. The product can be worked up by the usual syntheses to yield organic compounds with the labeled carbon atom.

There are many problems in reaction mechanism which can be solved with C^{14} tracer atoms. For example, we showed how CO_2

containing heavy oxygen was used in the study of the fate of oxygen in photosynthesis by plants. Similarly, the use of $C^{14}O_2$ will indicate the ultimate disposition of the carbon atom. Very wide use is being made of C^{14} in studying metabolism in the animal body, according to principles described in section 43.14. If a labeled substance is fed to an animal the identification of the excreted compounds containing the tracer atom furnishes a clue as to the chemical reactions involved during its progress through the body.

It is probable that C^{14} is produced by nuclear reactions in the upper atmosphere and subsequently finds its way into plant and animal life. It is apparently present in all living things. Since the half-life is about 5,400 years it would be difficult to detect the radioactivity from samples more than about 40,000 years old, but the age of geologic deposits involving carbonaceous materials can be estimated from the radioactive carbon content if they are not older than that.

SUGGESTED READING

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46. GIANT MOLECULES

46. 1. Introduction. The compounds of carbon can vary in size between wide limits from small molecules like methane (CH_4) to the very large diamond molecule. The student should review figure 19.1 where we showed how the carbon atoms in a diamond crystal are linked in a three-dimensional network, the diamond crystal being one giant molecule. We have also discussed the structure of graphite (figure 19.2) which consists of parallel, giant sheet molecules; the distance between these parallel sheets is such that they are nearly out of range of intermolecular attraction forces and the layers can readily slide past each other when placed under stress.

46. 2. Long-Chain Hydrocarbons. In chapter 10 we described the architecture of carbon compounds which take the open-chain form, and in section 10.4 we showed how seventy carbon atoms can be tied together into a long chain by the Wurtz synthesis. A paraffin hydrocarbon with seventy carbon atoms in the chain has the composition $C_{70}H_{142}$; it has a molecular weight of nearly 1,000 and is a very large molecule indeed. It is a small molecule, however, in comparison with most of those to be described in this chapter.

46. 3. Starch and Cellulose. In addition to diamond and graphite, we have mentioned a number of other giant molecules in this book, examples of which are starch and cellulose. These substances have molecular weights of the order of 50,000 to more than 1,000,000 and are built up of a large number of glucose units. The difference between starch and cellulose is that starch is composed of glucose units

in the *alpha* linkage (section 41.7) whereas in cellulose the *beta* linkage connects the glucose units (section 41.8). This may not appear to be an important difference when we examine their flat structures as shown on a printed page, but if we employ space models of the molecules the difference will be seen to be very great.

In cellulose the C_1 atom of a β-glucose ring is joined to the C_4 atom of the next ring through an oxygen bridge. Alternate β-glucose rings are reversed, thus, and , and it should be observed in figure 46.1 that this yields a pattern in which the β-glucose units zigzag along an essentially straight line. The numbering of the atoms in the ring should be compared with that in figure 39.10*a*, where it was indicated that the C–OH bonds on C_1 and C_4 are *parallel;* this is an important factor in the ability to build a *linear* cellulose model. The formula of cellulose given in section 41.8 should also be reviewed. The structure shown in the upper model of figure 46.4 was built from atom models described in figure 18.6.

The structure of starch is not so certain as that of cellulose due to greater difficulty in the interpretation of X-ray diffraction data and other constants. It is known, however, that a starch contains two types of structures; one is a supposedly linear molecule, known as *amylose,* which has a molecular weight range of 10,000 to 100,000 and does not form a paste with water. The other structure in starch is called *amylopectin;* it is present in greater amount than amylose, has a molecular weight of more than 300,000, is highly branched, and forms a paste with water.

The linear starch structure is also known as the *A-fraction,* and the branched structure as the *B-fraction.* The A-fraction is soluble in hot water, but precipitates from solution at ordinary temperatures. This molecule, in aqueous solution to which certain reagents are added, is believed to coil into the helical form shown in the lower model of figure 46.4. In starch, just as in cellulose, the C_1 atom of a glucose ring is joined to the C_4 atom of the next ring through an oxygen bridge. However, the α-glucose ring is the structural unit, and it was shown in figure 39.9*a* that the generally accepted configuration for α-glucose is *trans* and that the C_1–OH bond is *perpendicular* to the C_4–OH bond. When *trans* α-glucose units are joined end

to end by elimination of HOH, this perpendicularity of the two C–OH bonds forces the chain into a constant curvature as shown in

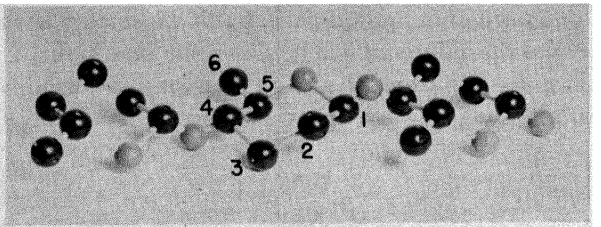


FIGURE 46.1. Model of cellulose, showing three β-D-glucos units. The glucose rings are *trans* as in figure 39.10*a*. Ther are —OH groups on carbon atoms 2, 3, and 6.

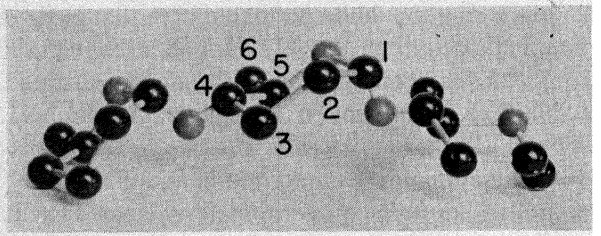


FIGURE 46.2. Model of the A-fraction of starch, showing thre α-D-glucose units. The glucose rings are *trans* as in figu 39.9*a*. This does not give a linear structure.

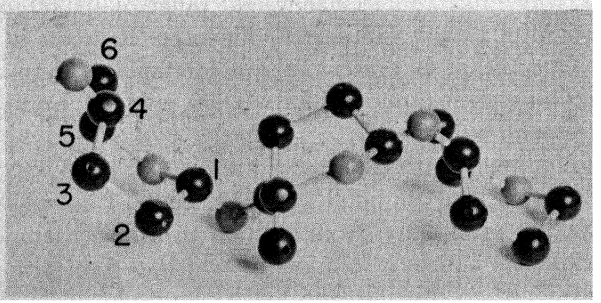


FIGURE 46.3. A suggested model of the A-fraction of starch which gives a zigzag but linear chain. The glucose rings have a *cis* configuration. With this *cis* configuration a helical structure can also be built, if the alternate rings are not reversed.

figure 46.2. The result is a helix illustrated by the lower model of figure 46.4, which contains six glucose units per coil. It has been

claimed that the A-fraction of starch has the helical structure in the native state, but others believe that the molecule is an extended linear chain with random kinks.

Some investigators state that the linear fragment of starch is made up of *cis* glucose molecules in which the C_1 and C_4 atoms are *cis* and elevated above the plane of the other atoms in the ring. This configuration makes the C_1–OH and C_4–OH bonds *parallel,* as in cellulose, and it is then possible to construct a linear zigzag, but highly puckered, chain as shown in figure 46.3, if alternate rings are reversed as in cellulose. Moreover, if the alternate rings are not reversed, the *cis* glucose rings yield a helix which is said to have dimensions which are in better agreement with X-ray data than the helix obtained from *trans* glucose rings.

Since the X-ray spacings for glucose units in starch and cellulose are nearly the same, it has also been suggested that the glucose units in starch may be essentially flat rather than puckered into either a *cis* or *trans* shape. The assumption of a *cis* form disagrees with the conclusion cited in section 39.6 that all aldohexoses have the *trans* configuration illustrated by figures 39.9 and 39.10.

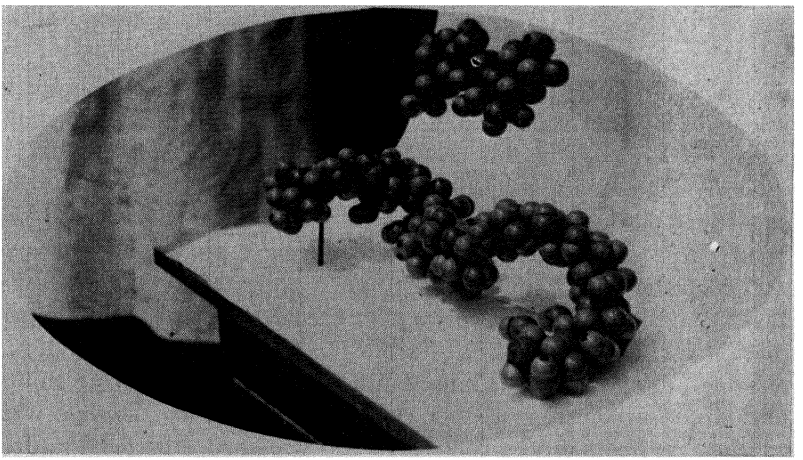


FIGURE 46.4. The upper model is the probable cellulose structure. The lower model is a suggested structure for the A-fraction of starch. [From G. V. Caesar and M. L. Cushing, *J. Physical Chemistry,* **45**, 776 (1941).]

The extensive branching of the molecules in the B-fraction of starch results in a three-dimensional spatial configuration (see sec-

tion 46.10*b*). In this structure a chain of α-glucose units sends out branches, which, in turn, branch out, just like a tree. The branch chains probably originate through oxygen links at the C_6 atom. The primary difference between *glycogen,* the animal starch (section 41.7), and the B-fraction of starch is believed to be one of chain length. In glycogen each branch contains about ten glucose units, whereas in the B-fraction of starch they appear to be about twenty-five to thirty glucose units in length. The properties of starch paste are currently ascribed to this interlacing network of branch chains.

46. 4. Proteins. It was shown in section 38.3 that α-amino acids condense to form long-chain compounds called polypeptides. Proteins are polypeptide chains of such great length that they reach the class of giant molecules. A small segment of such a chain is pictured in figure 46.5. As a result of the study of the dimensions of

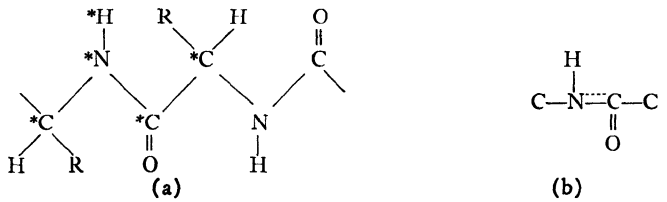


FIGURE 46.5. The polypeptide chain in proteins.

the amide group, it is known that, whereas the normal CN link has a length of 1.47 A, in the amide the length is 1.32 A. The CN link, therefore, has considerable double-bond character (see figure 18.5), which is illustrated graphically in part (b) of figure 46.5. The shortened bond is due to resonance. The double-bond character of the bond forces all the atoms in (b) into the same plane. These atoms are also shown in part (a) of the figure, indicated by the asterisks. It is believed that in most polypeptides the NH is *trans* to CO across the CN double bond.

Some proteins (such as muscle fibers) are elastic, showing ability to contract as much as 55 per cent. To account for the ease with which these fibers can be contracted and stretched, structural models of a helical type have recently been suggested. Figure 46.6 shows one view of such a model. The reader should study the top line of atoms in this model and pick out those which are indicated by the asterisks in part (a) of figure 46.5, in order to observe that these atoms are in one plane.

A side view of this same helical model is in figure 46.7. The model has 3.7 amino acid residues per turn, the helix being held together by hydrogen bonds between C=O and H–N groups (see the dotted bonds in the model). This is the contracted structure; stretching can be explained by the breaking of a certain number of the hydrogen bonds. The model described here is the α-helix. Other helixes have also been proposed, with different numbers of amino acid residues per turn, in an attempt to satisfy quantitative information obtained by X-ray and other methods.

These models illustrate only a portion of the protein problem. Certain properties of proteins demand structural models built of chains, sheets, and groups of chains and helixes in "rope" formation. In all these theories, however, the hydrogen bond between C=O and H–N is an important consideration.

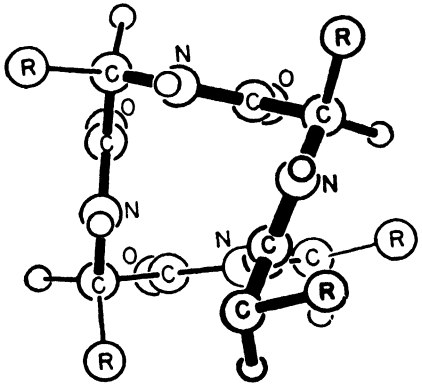


FIGURE 46.6. Polypeptide helix, looking through the cylindrical hole from one end [Adapted by permission from L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Nat. Acad. Sciences*, 37, 208 (1951)].

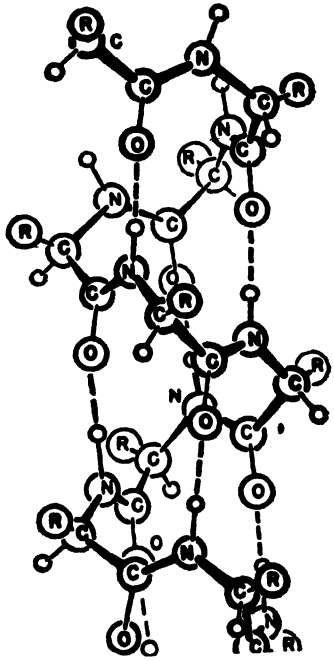


FIGURE 46.7. Polypeptide helix, side view [Adapted by permission from L. Pauling, R. B. Corey, and H. R. Branson, *Proc. Nat. Acad. Sciences*, 37, 207 (1951)].

46. 5. Rubber. This, also, consists of giant molecules, previously referred to in section 37.6, where the molecule was shown to be a long chain of isoprene units joined end to end. As is well known, the rubber molecule can be stretched. The ability to stretch is due to freedom of rotation around the single bonds, as stated in section 37.6, to give molecules of different lengths and degrees of packing.

46. 6. Structural Units. We have now described several important substances which are found in nature and are built up of smaller molecules discussed in considerable detail in this book. These smaller

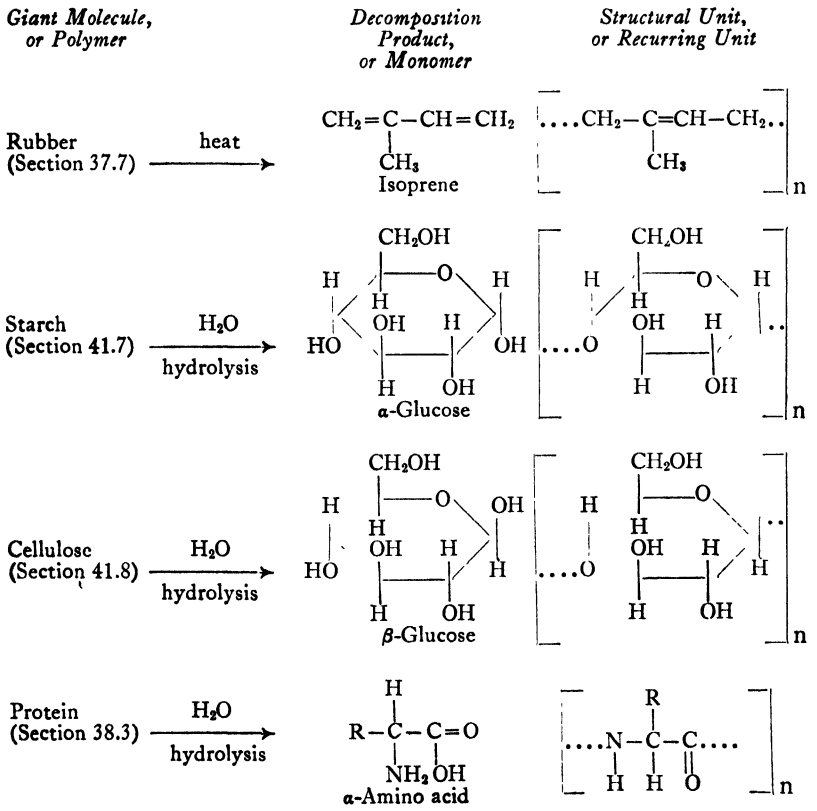


FIGURE 46.8. Structural units of certain giant molecules in nature.

molecules can be obtained from the natural substances by various methods as shown in figure 46.8.

The nature of the substance obtained by decomposing a giant molecule furnishes the clue to the structural units in the molecule; the giant molecule is built by joining n such units end to end as indicated by the dotted bonds. In the case of the native cellulose molecule, for example, it is claimed that n is at least 10,000.

Earlier in this book we defined isomer, dimer, and polymer, which mean, respectively, equal parts, two parts and many parts of the same thing. The giant molecules discussed here are often referred to as "high polymers" or "high polymeric substances" because they contain a great many of the same structural units. Structural units are also called "recurring" units or "repeating units." The simple molecule which yields the recurring unit of the giant molecule, by rearrangement of the valence bonds or by other methods to be described in the following sections, is referred to as the "monomer," meaning one part. We can, therefore, define a polymer as a substance containing recurring structural units, when the recurring unit corresponds to a simple molecule (monomer) from which the polymer may be formed or to which it may be decomposed.

46. 7. Association Polymers. A further examination of the preceding illustrations will show that the monomer of the rubber molecule has exactly the same composition as the structural unit, that is, C_5H_8. For that reason, the ratio of atoms in the final polymer is the same as in the monomer, although the value of n may vary as represented by $(C_5H_8)_n$. When a high polymer is made by the simple addition of molecules to each other, either by a shift in the double bonds as in the case of isoprene or by any other valence rearrangement, the phenomenon is called polymerization by association.

46. 8. Condensation Polymers. Chemists have not yet duplicated the processes used in nature for synthesizing molecules like starches and proteins. The process, in general, however, may be regarded as one in which two molecules are joined by elimination of one molecule of water, as shown in sections 38.3 and 41.7. This is known as polymerization by condensation. The structural unit in the resulting polymer does not have the same composition as the monomer. For example, the recurring unit of starch or cellulose contains one H_2O molecule less than the corresponding monomer, and the terminal units at the ends of the resulting long molecule may be different from the units inside the chain. This is illustrated in figure 46.9 by

the hypothetical formation of starch from α-glucose. The ratio of atoms in this condensation type of polymer is not the same as in the monomer.

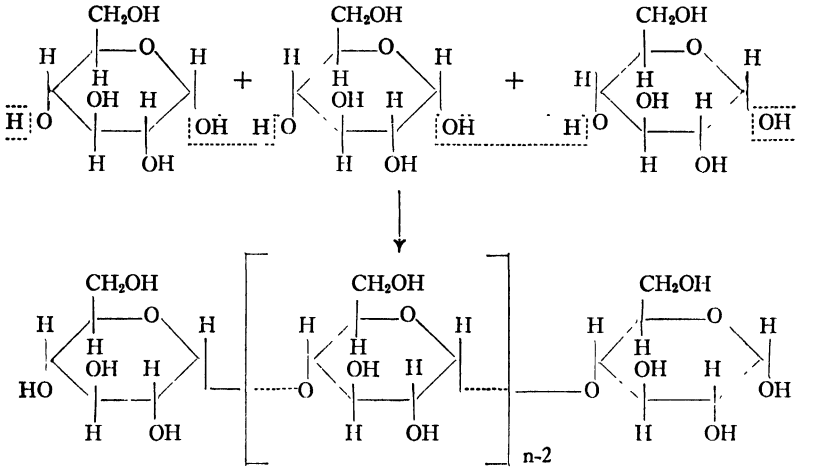


FIGURE 46.9. Hypothetical formation of starch from α-glucose.

46. 9. Synthetic Polymers. Although the chemist has not yet been able to synthesize starch and cellulose or duplicate natural rubber, he has been able to manufacture a large variety of giant molecules which not only compete with natural products, but also perform functions for which there is no competition from the natural products. These new compounds are conveniently classified as synthetic plastics, synthetic elastomers, and synthetic fibers, and will be described, with examples, in the following pages. First we shall consider rather briefly the chemistry of polymerization.

46. 9a. Polymerization by Condensation. This procedure for making high polymers follows common chemical experience. We generally expect molecules to interact by exchange of groups or radicals, or by removal of groups that form another compound. A very simple example of an *extended* reaction of this type, which results in a polymer, is the following:

$$HOCH_2CH_2OH + HOCH_2CH_2OH + HOCH_2CH_2OH \longrightarrow$$

Ethylene glycol
Ethene glycol
Ethanediol

$$2H_2O + HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

Triethylene glycol

The condensation, in this case, consists of the elimination of water. The reaction can be made to proceed to the formation of *polyethylene glycols* in the molecular weight range of 200 to 1,000, which are liquids, or to the range of 1,000 to 7,000 in which they are solids known as *Carbowax* compounds. They are used in ointments, hair dressings, etc. Because of its hygroscopic nature, triethylene glycol is used in air-conditioning systems and, in the form of an aerosol, it is an atmosphere disinfectant.

A related reaction was described in section 34.11*b*, in connection with the *silicones*, which, also, are condensation polymers. The silicones can be varied considerably in character by altering the R groups and by other means. They are generally more stable, especially to high temperature, than the carbon polymers and are used for gasket materials as well as for the manufacture of oils and elastomers.

Later, we shall refer again to the condensation polymers when we discuss Bakelite.

46. 9b. Polymerization by Association. The formation of addition polymers grew to be a vast industrial undertaking before the theoretical background was well advanced. The reaction may be represented, in general, by the transformation of an ethene (ethylene) type of structure to the normal single-bond type. The simplest process of this kind, at least on paper, is the manufacture of a Polythene polymer, which is accomplished by polymerizing ethene itself at a pressure of about 1,000 atmospheres (with a little oxygen as catalyst):

$$\underset{\text{Ethene}}{n\ CH_2{=}CH_2} \rightarrow \underset{\text{Polythene}}{\textit{end group}{-}(CH_2{-}CH_2)_{n-2}{-}\textit{end group}}$$

Polythene, or polyethylene, is a tough solid with a molecular weight of about 20,000. It is quite inert, because it is essentially a paraffin hydrocarbon (section 10.7) and is used as a lining for bottle caps, for collapsible tubes, plastic bottles, insulation on cables, etc. We shall return presently to the nature of the *end groups*, that is, the groups which terminate a long chain like this one. An end group is often different from the rest of the chain, but two molecules of monomer are generally used to make the end groups, leaving $n-2$ units inside the chain. This is illustrated by the starch molecule (figure 46.9), where it should also be observed that the terminal

unit on the right has a potential aldehyde group (section 40.2), but the one on the left does not.

The mechanism of addition polymerization has received much attention. It was just indicated that the catalyst in the manufacture of Polythene is oxygen; however, peroxides are almost universally used to catalyze this type of reaction, if a catalyst is employed at all. The mechanism of such additions has been described in this book in section 17.13 (the student should also review sections 17.3 and 17.12), where it was stated that peroxides cause formation of free radicals, the activation energy of which initiates chain reactions that can be carried by the excited C=C linkage. The following reactions should be compared with the corresponding steps shown in section 17.13:

$$\underset{\text{I}}{CH_2{::}CH_2} \rightarrow \underset{\text{II}}{\overset{-}{\underset{\cdot\cdot}{CH_2}} : \overset{+}{CH_2}} + R\cdot \rightarrow \underset{\text{III}}{RCH_2{-}\dot{C}H_2}$$

$$\underset{\text{III}}{RCH_2{-}\dot{C}H_2} + \underset{\text{II}}{\overset{-}{\underset{\cdot\cdot}{CH_2}} : \overset{+}{CH_2}} \rightarrow \underset{\text{IV}}{RCH_2{-}CH_2{-}CH_2{-}\dot{C}H_2} \text{ etc.}$$

The normal state of ethene is (I), but reaction probably takes place through the polarized structure (II) in which the π electrons are displaced as indicated. The introduction of a free radical into the system can be illustrated with acetyl peroxide:

$$CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \rightarrow CH_3{-}\overset{\overset{O}{\|}}{C}{-}O\cdot + CO_2 + \cdot CH_3$$

Either of the free radicals which result from this decomposition can be represented by R·. This fragment unites with (II) to give (III), which is now in turn a free radical and reacts with more of (II) to yield (IV). This chain formation continues until the activated chain, with its odd electron, pairs with another free-radical chain or with a free-radical fragment introduced by the catalyst. At the ends of the long chain, we may, therefore, have $-CH_3$ or $-O\overset{\overset{O}{\|}}{C}CH_3$.

In the case of Polythene, one of the terminal groups is probably CH_3, but the nature of the group at the other end is less certain. It probably contains oxygen in the form of a carbonyl radical, C=O. Peroxide-catalyzed polymerizations can be stopped by inhibitors (section 17.3).

We have indicated that a small amount of free radical introduced into the monomer system excites the C=C bond to the structure represented by (II). Some authorities prefer to write the polarized structure in the *diradical* form described in section 26.4, which can

$$CH_2 :: CH_2 \quad \rightarrow \quad \dot{C}H_2 : \dot{C}H_2$$

grow at either end.

The addition polymerization just described proceeds by what is known as a *free-radical* mechanism. Certain ethene derivatives can be polymerized by the catalytic effect of strong acids, and this type of reaction has been called polymerization by *ionic* mechanism. Either a strong acid, in its usual sense, can be used, or salts which are acid in the electronic sense (section 31.7) in that they are strongly electron-attractive. An example is boron trifluoride, BF_3 (see section 8.5), which is deficient in electrons. A compound like this can polarize an olefin double bond by displacing π electrons, to give a polarized intermediate analogous to (III) previously illustrated:

$$F : \underset{\cdot\cdot}{\overset{F}{\underset{F}{B}}} \quad + \quad CH_2 :: CHR \quad \rightarrow \quad \underset{\cdot\cdot}{CH_2} : CHR \quad (\text{with } BF_3 \text{ on } CH_2;\ -\text{ on } CH_2,\ +\text{ on } CHR)$$

This new molecule is in an activated state, but is highly polar rather than being a free radical. It can excite and react with more olefin double bonds, as described before in the reaction between fragments (III) and (II) to give (IV).

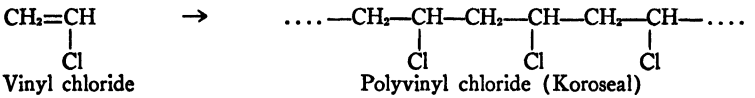
$$\underset{\cdot\cdot}{CH_2}\text{—}CHR \quad + \quad \underset{\cdot\cdot}{CH_2}\text{—}CHR \quad \rightarrow \quad \underset{\cdot\cdot}{CH_2}\text{—}CHR\text{—}CH_2\text{—}CHR$$

(BF_3 on the first CH_2; $-$ on the first CH_2, $+$ on the last CHR)

$$\rightarrow \quad BF_2\text{—}[CH_2\text{—}CHR]_n\text{—}CH{=}CHR \quad + \quad HF$$

Derivatives of styrene (the formula of which is given in section 46.10a) can be polymerized in this way. At the termination of its growth, at least one end of the long chain will be saltlike in character. Much less is known about ionic polymerizations than about free-radical polymerizations, but the student should observe that the reaction principles are similar to those used to explain the "ionic" reactons of the benzene ring in chapter 20.

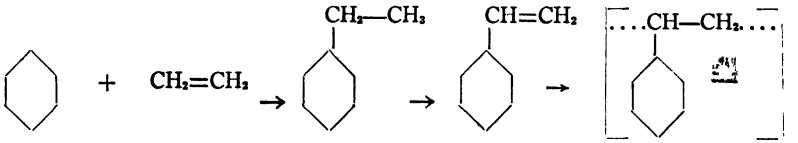
Another factor of importance in addition polymerization is the regularity with which monomers add to each other. An illustration is the polymerization of vinyl chloride (section 25.3),



where the monomers add in head-to-tail fashion. More explicitly, this is head-tail-head-tail, etc. Another possible arrangement with certain polymers is head-head-tail-tail-head-head, etc.

46. 10. Plastics. Synthetic *plastics* are also known as synthetic *resins*, from the similarity of the manufactured raw materials to the natural resins, a familiar example of which is shellac. The synthetic plastics have many uses and can be molded into many shapes for purposes ranging from cigarette holders to airplane bodies.

46. 10a. Thermoplastics. These polymers have chain structures as distinguished from three-dimensional network polymers to be described in section 46.10*b*. A good example is *Styron*, a polymer made from styrene:



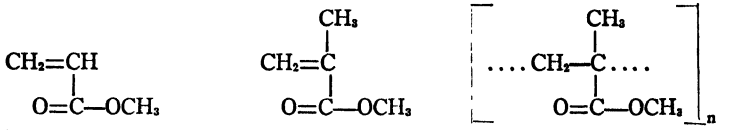
The polystyrene plastics are examples of association polymers, in which there is a simple union between monomer molecules to form the giant molecule. It is claimed that polystyrene molecules reach a molecular weight of more than 600,000.

This class of polymers also includes copolymers in which several different molecules are combined in the chain to form the high polymer. An example is the copolymer of vinyl acetate, $CH_2{=}CH$, and vinyl chloride, $CH_2{=}CH$, from which the *vinylite* $\quad\quad\quad

a swelling and then complete solution. The polystyrenes can also be heated above the melting point and then cooled back to the solid state with little change in the chain length. Because polymers built up from linear molecules of this type can be so readily melted (are fusible) without decomposition, they are called *thermoplastics.*

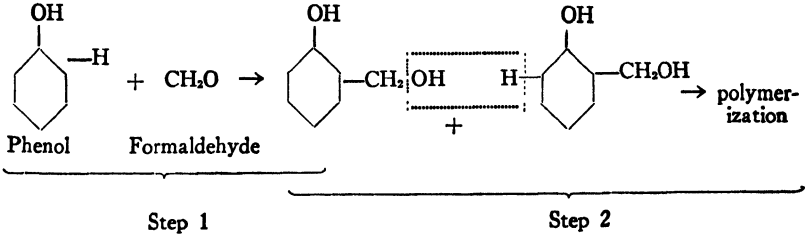
The linear giant molecules should not be considered as necessarily *straight* chains. They may wander into various directions and probably are not arranged in such an ordered manner as the molecules indicated in figure 12.10.

The very important plastic known as *Lucite* and as *Plexiglas* is an association polymer made from methyl methacrylate, a derivative



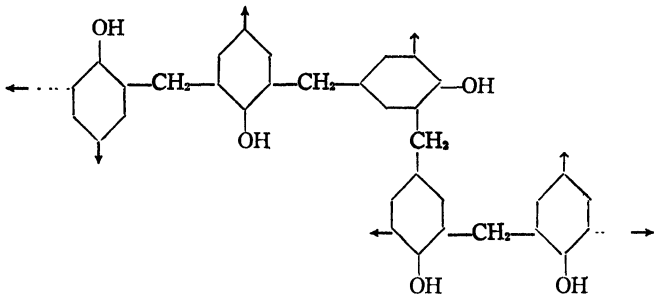
of acrylic acid, $CH_2{=}CH{-}COOH$. Lucite and Plexiglas, when heated, can be shaped into many useful objects, such as umbrella handles, airplane windows, etc. A copolymer of the acrylate and the methacrylate is known as *Acryloid,* which forms a viscous solution in certain solvents and is used as an adhesive.

46. 10b. Thermosetting Plastics. These consist of giant chains which are *cross-linked* into a three-dimensional network. An example is *Bakelite.* This is a condensation polymer, and one of the first important commercial plastics. The reactions in the formation of Bakelite are complex, but it is believed that the first step is the simple addition of phenol to formaldehyde, and the initial product then condenses to form the giant molecule by elimination of water:



The student should observe that the styrene chain, which was described previously, can grow by adding only one unit at a time at

either end. It, therefore, grows at a perfectly steady rate. This linear growth is also characteristic of the Bakelite reaction:



The union between adjacent molecules to form a chain (although a crooked one) is shown here as taking place through positions in the benzene ring which are *ortho* or *para* to the –OH group. Since other *o*- and *p*- positions are still available as reactive points (indicated by arrows), the chain still has possibilities for growth, at an angle to this line.

When this linear type of polymer is heated with the proper catalysts, and with proper proportions of formaldehyde to furnish more $-CH_2-$ groups, it becomes a hard, infusible plastic due to cross-linking between adjacent chains. Each molecule that adds to this structure offers new attachment points for other molecules so that the structure grows faster as it gets bigger. The molecular weight of a structure of this kind increases at a geometric rate.

A plastic of the cross-linked type is insoluble in most solvents because the solvent molecules cannot penetrate the solid material to separate the molecules of the polymer. This is due to their tangled, three-dimensional nature, even if, in fact, the entire solid structure is not one molecule. Three-dimensional polymers are quite hard and infusible. They often decompose if heated to the point where fusion would be expected.

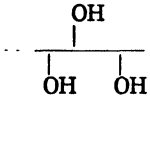
In manufacturing operations, these plastics are usually made directly into the shape of the finished product by placing the incompletely polymerized ingredients in position, in a mold, for example, and heating until reaction is complete. The time required to finish the operation is the "set time." The mold can then be opened while still hot to remove the solid finished article. Because these polymers

are set by heat, they are called *thermosetting* plastics. When making articles from *thermoplastics,* the plastic itself is run into the mold while molten, then must be cooled to the solid state before opening the mold.

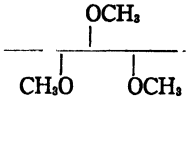
The thermosetting plastics, because of their resistance to melting and to solvents, have a very wide use. A typical application is in lacquers to be employed as protective linings in chemical reaction vessels. By contrast, thermoplastics can be used to thicken many liquids, a high viscosity being obtainable with a relatively small concentration of the plastic in the liquid.

Cellulose was described earlier in this chapter (section 46.3) as a high polymer used by nature in the structural parts of plants. It is appropriate to consider it again in this section because of its three-dimensional character. The molecule is an extended chain (figure 46.1), but each glucose unit has three –OH groups which can form hydrogen bonds (section 27.7) with the –OH groups in adjoining chain molecules. Although hydrogen bonds are weaker than primary valence bonds, the cumulative effect of many such hydrogen bonds results in a strong union between adjacent cellulose chains. The chains may be looked on as cross-linked. When cellulose is treated with concentrated alkali solution, the chain molecules are separated and dispersed in solution because of the modification of the –OH groups to –ONa groups with consequent destruction of the hydrogen bonds.

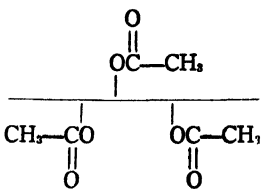
The conversion of cellulose on a commercial scale to thermoplastic plastics makes use of this principle of eliminating the hydrogen bond and making the chain molecules essentially independent of each other. This is done by converting the –OH groups of cellulose chains to ether or ester groups:



Three —OH groups in each glucose unit of cellulose



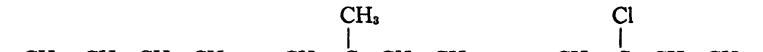
Methocel
Methyl ether of cellulose



Cellulose acetate
Acetic acid ester of cellulose

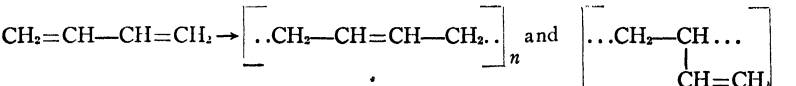
The properties of the products can be varied by replacing one, two, or all three of the –OH groups. Methyl cellulose (*Methocel*) is used as a thickening agent, for example, for ice cream. The plastic known as *Tenite* is a cellulose acetate. A *rayon* is made from cellulose acetate by dissolving it in acetone and extruding the viscous solution through spinerettes, countercurrent to warm air to evaporate the solvent.

46. 11. Elastomers. The synthetic elastomers are plastics which can return rapidly to essentially their original shape and size after having been stretched to many times their original dimensions. These substances have properties which we normally associate with natural rubber. We have already discussed the chemistry of isoprene, the building unit of rubber, and have shown that it contains a conjugate system of double and single bonds (section 18.1). The structures of isoprene and a few related compounds are as follows:



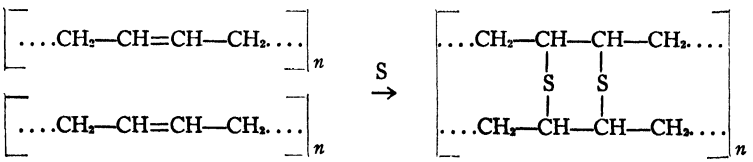
Butadiene (section 18.1) | Isoprene (section 37.1) | Chloroprene (section 37.6)

A property of the conjugate system is the tendency to give 1,4 as well as 1,2 addition; both mechanisms occur in the self-addition which we call polymerization by association:



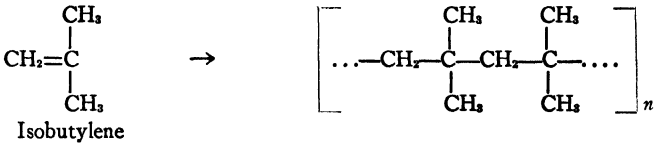
Butadiene | 1, 4-Polymer | 1, 2-Polymer

In either case the high polymer still retains double bonds. The presence of these double bonds is responsible for the ability of certain polymers to be *vulcanized;* the properties of the polymers can be modified by partially cross-linking adjacent chains. When sulphur is used as vulcanizing agent, the sulphur atoms probably act as connecting links. The mechanism is not well understood, but in the case of sulphur it is usually represented thus:



The ability to be vulcanized is a highly desirable feature of most of the commonly used elastomers.

An especially easily polymerizable olefin is isobutylene (isobutene), which yields a polymer with a head-to-tail structure:

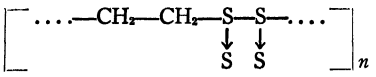


Isobutylene

One of the commercial polyisobutylenes is called *Vistanex.* A copolymer of isobutylene and isoprene is *Butyl* rubber. The presence of isoprene units in the copolymer means the presence of double bonds, and Butyl rubber is, therefore, vulcanizable.

A copolymer of styrene and butadiene became famous in World War II as GR-S rubber (Government rubber type S). The *Buna* rubbers, originating from Germany, are so named because sodium is used as a polymerization catalyst (Bu for butadiene and Na for sodium).

One group of the early successful elastomers is the family of polymers called *Thiokols.* They are condensation polymers made by the action of a sodium polysulphide, such as Na_2S_4, on compounds like ethylene chloride, CH_2Cl–CH_2Cl, or dichloroethyl ether (section 34.4). In the case of ethylene chloride, the repeating unit in the polymer is



Thiokols are so stable that they have found many applications where rubber cannot be used because of its sensitivity to sunlight, gasoline, etc.

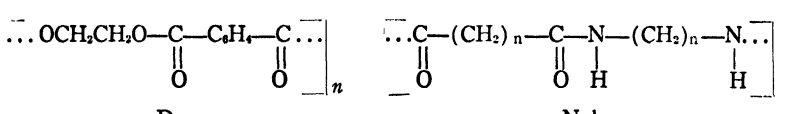
Vinylite, briefly mentioned in section 46.10*a,* and *Koroseal* (section 46.9*b*) are classed under elastomers. A closely related material is *Saran,* a copolymer of vinyl chloride, $CH_2{=}CHCl$, and vinylidine chloride, $CH_2{=}CCl_2$. Saran is inert to most chemical reagents and is popular in the laboratory in the form of tubing. Even more inert is *Teflon,* a polymer of tetrafluoroethene, $CF_2{=}CF_2$.

46. 12. Fibers. Synthetic fibers can be obtained from certain plastics, generally by dissolving them in suitable solvents and extrud-

ing the solutions through openings to give fibers of definite thickness. Saran, which has just been described, is an exception in that the fibers are extruded directly from the molten plastic. In all cases, the fibers are treated chemically and physically immediately after extrusion, to make them suitable for the intended purposes; the fibers may be spun into yarn for manufacture of fabrics or they may be coarse enough for use as bristles.

Vinyon is so inert chemically that it is woven into filter cloths for use in the chemical laboratory. It is a copolymer of vinyl chloride with a small amount of vinyl acetate. *Dynel* is a copolymer of vinyl chloride ($CH_2=CH-Cl$) and vinyl cyanide ($CH_2=CH-CN$); the second is more commonly known as acrylonitrile. This fiber can be made into furry materials for liners of winter garments or covers for roller-type paint applicators. *Orlon* is a polymer of vinyl cyanide. Its uses are similar to those of nylon, since the fibers can be processed to yield fabrics which resemble either silk or wool.

Dacron is a polyester, a condensation polymer in which the unit



Dacron Nylon

structure is the ethylene glycol (section 27.5) ester of terephthalic acid (section 31.13). *Nylons* have a peptide linkage similar to that in the proteins of silk and wool, and are condensation polymers. An example is the nylon made by heating equimolecular quantities of adipic acid, $HOOC(CH_2)_4COOH$, and hexamethylenediamine, $H_2N(CH_2)_6NH_2$. The condensation takes place with elimination of water.

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