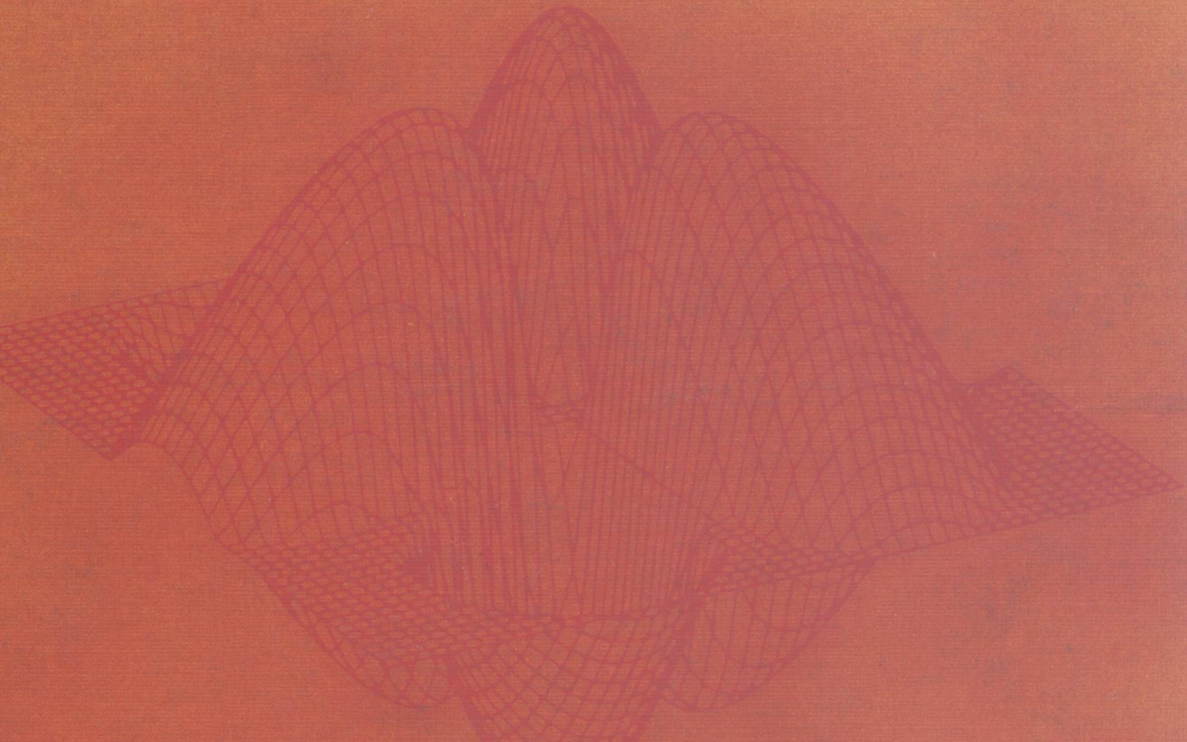
elementary organic chemistry

MOORE



ELEMENTARY ORGANIC CHEMISTRY

JAMES A. MOORE
University of Delaware

SAUNDERS GOLDEN SERIES

1974

W. B. SAUNDERS COMPANY Philadelphia • London • Toronto

W. B. Saunders Company: West Washington Square
Philadelphia, Pa. 19105

12 Dyott Street
London, WC1A 1DB

833 Oxford Street
Toronto, Ontario M8Z 5T9, Canada

Elementary Organic Chemistry ISBN 0-7216-6528-4

Made in the United States of America. Press of W. B. Saunders Company. Library of Congress catalog card number 73-86382.

Last digit is the print number: 9 8 7 6 5 4 3 2 1

preface

When another brief organic text is added to the lengthy list of those available, a statement of purpose is traditional. This book is intended for a one-semester or two-quarter course and is oriented primarily to the needs of students in health-related curricula. The importance of a basic knowledge of organic chemistry in these fields is fully recognized, but there seems to be less agreement on what is needed in a text.

Students using this book are likely to encounter a variety of organic compounds, as drugs, agricultural chemicals or biochemical entities, but will seldom if ever be called on to carry out syntheses. Preparative methods have accordingly been kept to a minimum, and traditional but archaic items, such as the synthesis of alkanes, have been avoided. Other time-worn topics that have been omitted are chemical tests, such as the Lucas, Hinsberg or Schiff reagents for characterizing functional groups. Spectroscopic methods for the identification of groups and structural elements are introduced in Chapter 8, and the use of spectral data is reinforced in subsequent chapters.

The sequence of material is for the most part traditional. An exception is the grouping of alcohols, amines and thiols, and a unified discussion of their amphoteric and nucleophilic properties. Phenols and aromatic amines are treated in a separate chapter, so that the chemistry common to both can be brought together.

The first eleven chapters contain the basic material on bonding, functional groups and reactions. The diversity and breadth of coverage has been restricted to permit adequate discussion of the topics that have been selected. Organic chemistry is a difficult subject for many students, mainly because unifying principles of bond-making and bond-breaking are lost in too large a body of facts. The student deserves a full explanation of the reactions that he is expected to know, and a minimum of distractions from minor asides and items of secondary importance.

Another reason for limiting the number of reactions and synthetic methods is to make it possible in a one-semester course to reach the later chapters, which are likely to be of most interest and importance to students in health- and biology-related programs. Four of these chapters cover the major groups of compounds in living systems.

Chapter 15 deals with biochemical processes, and emphasis is placed on the basic organic chemistry that underlies enzyme-catalyzed reactions.

The uses, occurrence and functions of organic compounds are a valid and important part of a nonmajor course, and should not be merely a diversion to heighten interest. With this in mind, a number of topics, including polymers, carbon resources, textile finishes and drugs, have been treated at some length to provide a meaningful discussion of the role of organic chemistry in these areas.

One of the most essential elements in an organic chemistry text is the solving of problems. In this book, a number of problems are presented throughout the text for "instant reinforcement," along with additional problems at the end of each chapter. These include both simple questions to aid in reviewing material covered, and problems that require application and extension of principles. An effort has been made to avoid vague or open-ended questions that do not have a clearly defined solution based on material presented in the book. Solutions to all problems are provided in the paperback text *Solutions to Problems in Elementary Organic Chemistry.*

It is a pleasure to thank Professors Roger Murray, John Swenton and Andrew Ternay, who reviewed the entire manuscript, and Professor Harold White and Dr. Everette May, who commented on several chapters. Thanks are due also to Mrs. Mary Ann Gregson for her able and expeditious typing of the manuscript.

JAMES A. MOORE

contents

introduction

The Nature of Organic Chemistry

The term **organic** was used by chemists of the early nineteenth century to describe compounds originating from plant or animal sources, as opposed to the metals, salts and oxides derived from minerals. The distinction between organic and inorganic substances was based, in part, on major differences in properties, but it also reflected the view that organic compounds possessed a vital quality which set them apart from the elements and compounds of the air, sea and earth. The notion of a vital force was gradually dispelled following a classic experiment in 1828 in which Wöhler demonstrated that the inorganic salt ammonium cyanate was converted by heat to urea, a compound present in the urine of all animals.

$$NH_4^+OCN^- \rightarrow NH_2\overset{\overset{O}{\|}}{C}NH_2$$

Ammonium cyanate Urea

Nevertheless, classification of compounds as organic or inorganic has persisted to the present, but with a different meaning. The term organic now refers to compounds of carbon, regardless of whether they have been isolated from natural sources or prepared by laboratory synthesis. Despite occasional claims that a "natural" compound such as a vitamin is somehow more authentic than or superior to the same substance prepared from "coal tar chemicals," samples isolated from food or prepared by synthesis are indistinguishable. In fact, the laboratory synthesis of a complex, naturally occurring molecule may provide the final proof of its structure.

Over three million different organic compounds are now known. The bulk of this vast catalog represents efforts to obtain more effective drugs, pesticides, dyes, fuels, textiles and other substances that contribute to the complex fabric of existence in the late twentieth century. Unfortunately, these contributions are seldom unmixed blessings. Thus, the chlorinated insecticides which provided the first means of malaria control also cause damage to higher organisms, and the use of these materials as agricultural chemicals has led to bitter controversy. It is clear that the attention of organic chemists and, indeed, all scientists in the next decades will be turned increasingly to problems arising from advancing technology and the accompanying environmental burdens. However, the same fundamental principles and search for basic knowledge and new structures of matter that led to stronger plastics and more potent insecticides will also be looked to for polymers and detergents that are more readily biodegradable, and drugs and pesticides with more selective biological activity.

one

atoms, molecules and bonds

Organic compounds were being isolated from natural sources and synthesized long before there was any significant understanding of molecular structure. It was recognized that carbon could be connected to as many as four other atoms, and that the same atoms could be assembled in more than one way to give different compounds. However, the nature of chemical bonding was confused and nebulous until about 1900, when physicists provided the concept of charged elementary particles and a model of atomic structure.

In this model, an atom is made up of a dense *positively charged* nucleus, surrounded by layers or shells of *negatively charged* electrons. The nucleus of a hydrogen atom consists of a single proton, and each succeeding element contains one additional proton, plus an equal or greater number of neutrons. Variation in the number of neutrons leads to **isotopes,** which are atoms of the same element with different mass. The nuclear charge, or atomic number, is balanced by electrons equal in number to the positive nuclear protons. Together with the periodic classification of the elements, this picture of atomic structure set the stage for a unified concept of chemical bonding.

1.1 Ionic and Covalent Bonds

Bonds can be classified into two broad types: **ionic** and **covalent.** Underlying both types of bonding is the fact that a *completely filled outer shell of electrons,* as in the inert gases helium and neon, is a particularly stable arrangement. One way to obtain a complete shell is *transfer* of electrons, giving negative or positive species called **ions.** As indicated in Figure 1.1, elements with one or two electrons in the outer shell, the metals, can *lose* electrons to form positively charged **cations.** As we move to the right of the periodic table, elements be-

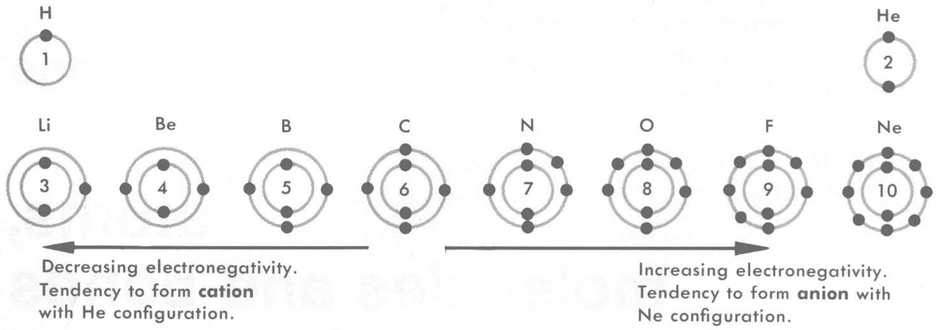
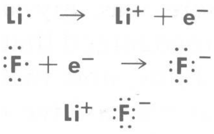


FIGURE 1.1 Atomic structures of first and second row elements.

come increasingly electronegative, and have a tendency to *add* electrons to complete the shell, giving negatively charged **anions.** An **ionic bond** is simply the electrostatic attraction of oppositely charged ions, as in the salt lithium fluoride. Ionic compounds exist in the solid state as a lattice with positive and negative ions distributed in a regular alternating pattern, as in Figure 1.2.



$$\mathrm{Li}\cdot \rightarrow \mathrm{Li}^+ + e^-$$

$$:\overset{..}{\underset{..}{\mathrm{F}}}\cdot + e^- \rightarrow :\overset{..}{\underset{..}{\mathrm{F}}}:^-$$

$$\mathrm{Li}^+ \;\; :\overset{..}{\underset{..}{\mathrm{F}}}:^-$$

Lithium fluoride

In the center of the periodic table, the elements boron, carbon and nitrogen have little tendency to form ions by gain or loss of electrons. A completely filled outer shell would require an ion with three or four charges, and the accumulation of like charges leads to very large electrostatic repulsion. An enormous amount of energy is required to obtain an ion such as C^{+4}, and carbon, therefore, forms covalent bonds.

Covalent bonds are formed by *sharing* pairs of electrons between two atoms. In 1916, G. N. Lewis suggested that the tendency of carbon to form four bonds in organic compounds could be explained by completing the electron shell of carbon with four electrons from other atoms. The resulting electron pairs are localized between the atoms

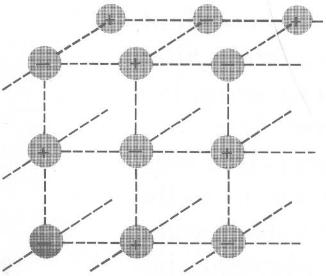
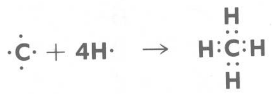


FIGURE 1.2 Ionic lattice.

and are attached by both nuclei. This type of bonding occurs with most other elements as well, and the concept of the electron-pair bond is one of the cornerstones of modern chemistry.



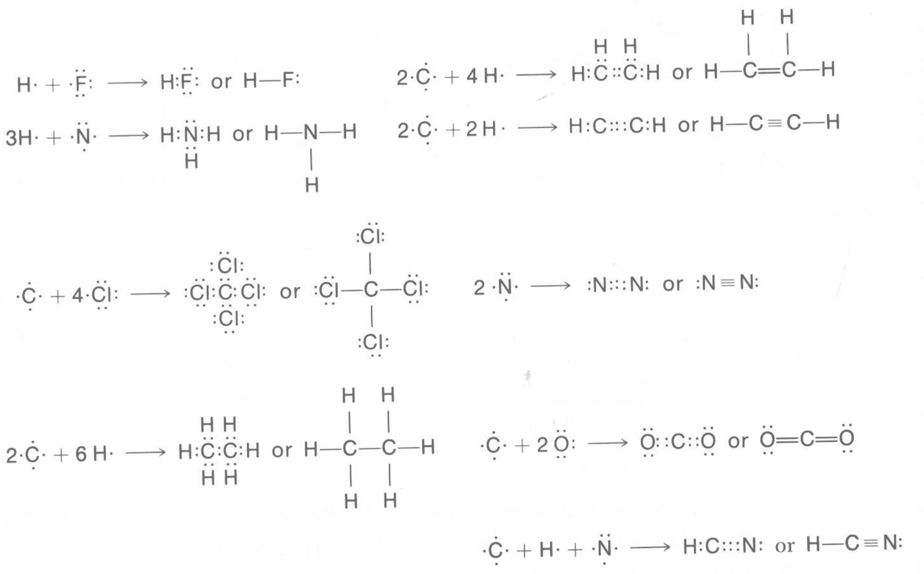
$$\cdot\underset{\cdot}{\dot{C}}\cdot + 4H\cdot \rightarrow H:\underset{\underset{H}{\cdot\cdot}}{\overset{\overset{H}{\cdot\cdot}}{C}}:H$$

Both ions and covalent molecules are conveniently depicted by "electron dot" formulas. The symbol of the element represents the nucleus plus all complete inner shells of electrons. Electrons in the outer shell are indicated by dots placed around this "kernel"; the pair of electrons in a covalent bond is often written as a dash. In writing these formulas, the kernels plus outer electrons are combined to give an arrangement in which each atom is surrounded as far as possible by a completed outer shell—*two* electrons around hydrogen and *eight* for the second-row elements. Electron pairs can be *shared* in a bond between atoms or remain *unshared*; two or three pairs can be shared, as required, giving *double* or *triple* bonds between atoms. Several examples of these formulas are shown in Table 1.1.

Problem 1.1 Write electron dot formulas for HCl, H_2O, NF_3, $CHCl_3$ and C_2F_4.

The atomic **kernel**, consisting of the nucleus and inner shells of electrons, has a net positive charge corresponding to the "missing"

TABLE 1.1 ELECTRON DOT FORMULAS



$$H\cdot + \cdot\underset{\cdot\cdot}{\ddot{F}}: \longrightarrow H:\underset{\cdot\cdot}{\ddot{F}}: \text{ or } H-F:$$

$$3H\cdot + \cdot\underset{\cdot}{\ddot{N}}\cdot \longrightarrow H:\underset{\underset{H}{\cdot\cdot}}{\ddot{N}}:H \text{ or } H-\underset{\underset{H}{|}}{N}-H$$

$$2\cdot\underset{\cdot}{\dot{C}}\cdot + 4H\cdot \longrightarrow H:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:H \text{ or } H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H$$

$$2\cdot\underset{\cdot}{\dot{C}}\cdot + 2H\cdot \longrightarrow H:C:::C:H \text{ or } H-C\equiv C-H$$

$$\cdot\underset{\cdot}{\dot{C}}\cdot + 4\cdot\underset{\cdot\cdot}{\ddot{Cl}}: \longrightarrow :\underset{\cdot\cdot}{\ddot{Cl}}:\underset{:\underset{\cdot\cdot}{\ddot{Cl}}:}{\overset{:\ddot{Cl}:}{\ddot{C}}}:\underset{\cdot\cdot}{\ddot{Cl}}: \text{ or } :\underset{\cdot\cdot}{\ddot{Cl}}-\underset{\underset{:\underset{\cdot\cdot}{Cl}:}{|}}{\overset{\overset{:\ddot{Cl}:}{|}}{C}}-\underset{\cdot\cdot}{\ddot{Cl}}:$$

$$2\cdot\underset{\cdot}{\ddot{N}}\cdot \longrightarrow :N:::N: \text{ or } :N\equiv N:$$

$$2\cdot\underset{\cdot}{\dot{C}}\cdot + 6H\cdot \longrightarrow H:\underset{H}{\overset{H}{\ddot{\underset{\cdot\cdot}{C}}}}:\underset{H}{\overset{H}{\ddot{\underset{\cdot\cdot}{C}}}}:H \text{ or } H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

$$\cdot\underset{\cdot}{\dot{C}}\cdot + 2\ddot{O}: \longrightarrow \underset{\cdot\cdot}{\ddot{O}}::C::\underset{\cdot\cdot}{\ddot{O}} \text{ or } \underset{\cdot\cdot}{\ddot{O}}=C=\underset{\cdot\cdot}{\ddot{O}}$$

$$\cdot\underset{\cdot}{\dot{C}}\cdot + H\cdot + \cdot\underset{\cdot}{\dot{N}}\cdot \longrightarrow H:C:::N: \text{ or } H-C\equiv N:$$

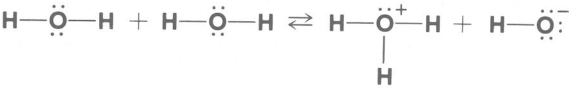
outer electrons. This kernel charge is equal to the atomic number minus the number of electrons in filled inner shells:

Element	H	B	C	N	O	S	F	Cl
Atomic Number	1	5	6	7	8	16	9	17
Inner Electrons	0	2	2	2	2	10	2	10
Kernel Charge	+1	+3	+4	+5	+6	+6	+7	+7

When the total number of outer shell electrons (shared and unshared) is equal to the total number of kernel charges, as in the examples in Table 1.1, the compound is neutral. If the total number of kernel charges and outer electrons differs, the formula represents a *charged* species. In calculating the charge on a given atom, each covalent bond between two atoms contributes one electron per atom and an unshared electron pair contributes two. The charge on an atom is the *algebraic sum of the kernel charge and the negative electron charge*, or:

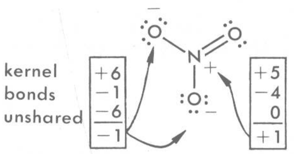
$$\text{atomic charge} = \text{kernel charge} - (\text{number of covalent bonds} + \text{unshared electrons}).$$

To illustrate, let us look at the self-dissociation of water in which a proton is transferred from one molecule to another, giving a **hydronium cation H_3O^+** and a **hydroxide anion HO^-**.

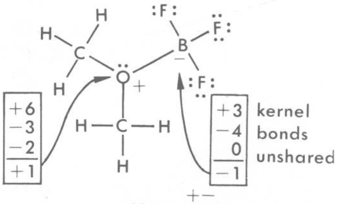


Kernel charge of oxygen	+6	+6	+6
Covalent bonds to oxygen	−2	−3	−1
Unshared electrons	−4	−2	−6
Net charge on oxygen	0	+1	−1

Two or more atoms in a formula may have charges, and the overall charge on the formula is the sum of these formal charges.



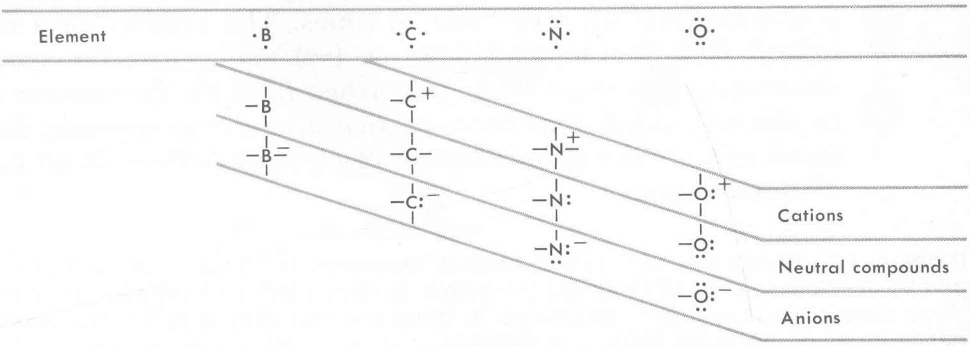
nitrate anion, NO_3^-
overall charge : 2(−1)+1=−1



$(CH_3)_2\overset{+}{O}\overset{-}{B}F_3$, overall charge: 0

Electron dot formulas and charges of several important ions and molecules of carbon and neighboring elements are given in Table 1.2. Dashes in these formulas represent covalent bonds to another atom such as hydrogen.

TABLE 1.2 IMPORTANT IONIC AND NEUTRAL SPECIES

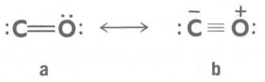


Problem 1.2 Write electron-dot formulas, showing all electrons and charges on atoms, for the following: (a) $HONO_2$ (nitric acid), (b) H_3CO^-, (c) CCl_3^-, (d) $H_3N—BF_3$ and (e) $(CH_3)_2NH_2^+$.

1.2 Resonance

Electron dot structures are not intended to represent a precise picture of electrons in molecules, but they do indicate the presence of bonds and unshared electrons associated with various atoms. In some cases, however, a single formula is inadequate. If two (or more) arrangements of electrons with equal or comparable stability can be written for a molecule, both of them will contribute to the structure. In this situation, which is called **resonance,** the molecule is a hybrid of the individual electronic structures and is *more stable* (lower in energy) than it would be if only one electron structure were contributing.

Carbon monoxide provides an example of resonance. Two arrangements of electrons, **a** and **b,** contribute significantly to the structure of CO (other electron structures are of much higher energy and can be ignored). In structure **a,** carbon does not have a completely filled outer shell of electrons. In **b,** the electron deficiency of carbon is overcome by the sharing of an additional electron pair, resulting in charges on both atoms.


$$:C{=}\ddot{O}: \longleftrightarrow :\overset{-}{C}{\equiv}\overset{+}{O}:$$

Neither structure **a** nor **b** adequately accounts for the properties of the very stable compound carbon monoxide. According to the resonance concept, the actual structure is *intermediate* between **a** and **b.** Electrons are not oscillating back and forth between **a** and **b,** but are **delocalized.** In structure **a** two electron pairs are located on oxygen; in structure **b** one of these pairs of electrons is present as a third bond between the atoms. Delocalization means that in the resonance hybrid, an electron pair is "spread out" in a cloud over the positions indicated by structures **a** and **b.**

The resonance concept is extremely useful in organic chemistry, and will come up a number of times. The symbol for a resonance hybrid is a double-headed arrow (↔) connecting the contributing structures. *This must be distinguished from the two arrows (⇄) used to denote equilibrium between two distinct compounds.* Resonance involves only the delocalization of electrons—there is no movement of atomic nuclei.

Problem 1.3 Nitrate ion, NO_3^-, is stabilized by resonance since the negative charge can be delocalized over all three oxygen atoms. a. Write electronic formulas for the three contributing resonance structures. b. Write electron structures for two resonance forms of nitrite ion, NO_2^-.

1.3 The Orbital Picture of Bonding

Soon after the idea of covalent bonding had been suggested, a more detailed view of atomic structure was developed from the principles of quantum theory and wave mechanics. These concepts provided a much more complete description of chemical bonds, and paved the way to major advances in the understanding of chemical properties and reactions. According to quantum theory, electrons are arranged around the nucleus of an atom in shells and subshells, each of which has a specific energy level. The main shells are numbered 1, 2, 3 . . . in order of increasing energy and increasing distance from the nucleus.

The shells are made up of **orbitals**, each of which can contain a maximum of two electrons. The first shell contains one orbital, called **1s**, and the second shell, four orbitals: **2s**, $\mathbf{2p_x}$, $\mathbf{2p_y}$ and $\mathbf{2p_z}$. The **2p** orbitals are equal in energy, and are a higher energy level than the **2s.** Higher shells contain larger numbers of orbitals, but these need not be discussed here.

Four rules govern the order in which orbitals are filled with electrons:

1. Only two electrons can occupy an atomic orbital.
2. The electrons in any orbital must have opposite (paired) spins.
3. Electrons occupy orbitals of lower energy first: **1s** before **2s**, and 2s before **2p.**
4. An orbital is not occupied by two electrons until all orbitals of equal energy each contain one electron. Thus the electron configuration of carbon is $\mathbf{1s^2\ 2s^2\ 2p_x\ 2p_y}$; the superscript indicates the number of electrons in the respective orbitals.

Problem 1.4 Write the electronic configurations for (a) H, (b) He, (c) Li^+, (d) Li, (e) B, (f) N and (g) Ne.

Orbitals have definitive shapes and spatial orientations. In precise terms, they represent regions of space around an atomic nucleus in which there is a high probability of finding electrons. As shown in

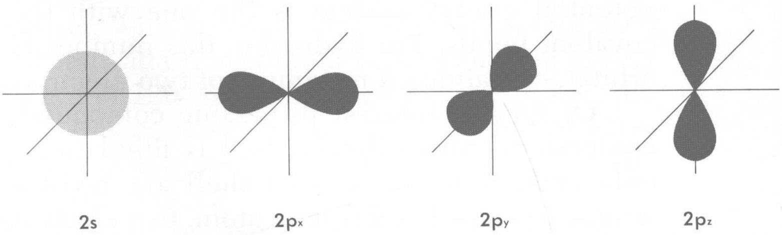


FIGURE 1.3 **2s** and **2p** orbitals.

Figure 1.3, s orbitals are spherical. In contrast, **p** orbitals are dumb-bell-shaped, with the lobes directed along three axes at right angles so that they are the maximum distance apart.

The purpose of any theory or model of chemical bonding is to provide insight into the central fact that *atoms have a strong tendency to combine into molecules.* If two hydrogen atoms are brought together, a chemical reaction occurs to give a hydrogen molecule, and *energy is released* in the process. Put another way, the H_2 molecule is more stable than two separate hydrogen atoms, and there is a binding force or bond energy holding the atoms together. The bond energy in a hydrogen molecule is 104 kcal. In the formation of H_2, this amount of energy is given off, and the heat of formation is written as $\Delta H = -104$ kcal. From the standpoint of the strength of bonding, however, bond energy is expressed as a positive value.

$$\mathrm{H\cdot + H\cdot \rightarrow H_2 \quad \Delta H = -104\ kcal}$$

Now what, precisely, is this attractive force that binds two hydrogen atoms together? When two hydrogens come within bonding distance, the **1s** atomic orbitals combine to form a **molecular orbital**[*] that encompasses both atoms. This molecular orbital is occupied by the two electrons, with spins paired. The resulting system of a *pair of electrons occupying a molecular orbital* is the modern picture of a covalent bond. For the simple diatomic hydrogen molecule, an exact mathematical expression corresponding to this bonding arrangement of two protons and two electrons can be derived from quantum theory. Complete calculations of larger molecules are not yet possible, but the agreement of theory and experimental measurements for the hydrogen molecule shows that the theory, even in approximate form, is a useful and dependable one.

1.4 Covalent Bonding of Carbon Hybrid Orbitals

The situation described for hydrogen extends to other elements and can be summed up in the statement that the most stable or lowest

---

[*] More accurately, two atomic orbitals combine to give *two* molecular orbitals. One of these is the bonding orbital, and is the only one we need consider.

potential energy system is the one with the *maximum number* of covalent bonds. For hydrogen, this number is one, since only the **1s** orbital, containing a maximum of two electrons, is available.

Of greater interest in organic compounds is bonding in carbon compounds. Since the **1s** shell is filled in all second row elements, only orbitals in the second shell are involved in bonding to other atoms. In an isolated carbon atom, two electrons occupy the **2s** orbital, and two of the **2p** orbitals each contain one electron. This arrangement would suggest that carbon can form only two covalent bonds, but as we have seen, carbon has *four* bonds in most compounds. To obtain four bonds, one electron is "promoted" from the **2s** to the $\mathbf{2p_z}$ atomic orbital, and the **2s** and **2p** orbitals then combine or "mix" to produce **hybrid orbitals.**

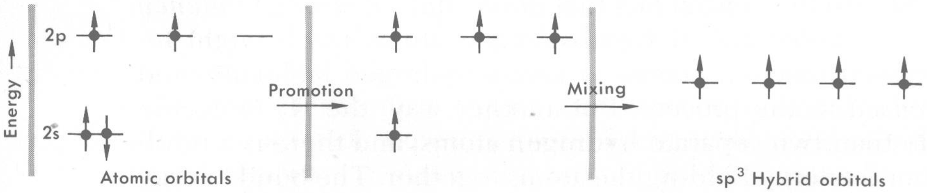


FIGURE 1.4 Formation of **sp^3** hybrid orbitals.

Hybridization of **s** orbitals can occur with all three, two or one of the **p** orbitals to produce, respectively, **four sp^3, three sp^2** or **two sp** hybrid orbitals. In each case the hybrid orbitals are directed in space to provide the maximum separation, as shown in Figure 1.5.

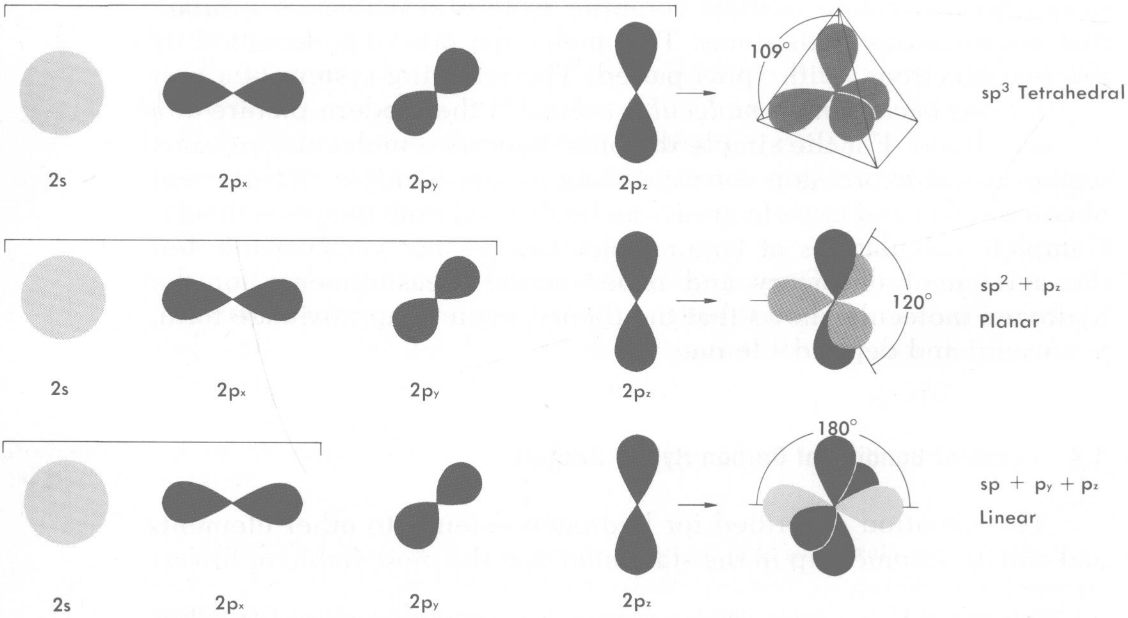


FIGURE 1.5 Hybridization of carbon orbitals.