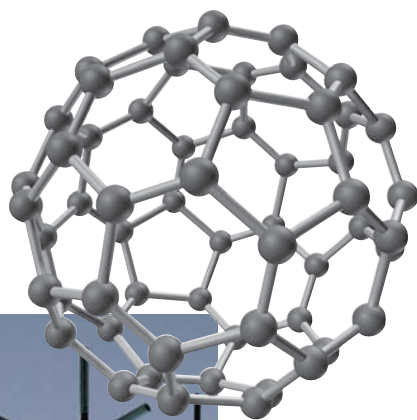# Covalent Bonding and Shapes of Molecules

A model of the structure of diamond, one form of pure carbon. Each carbon atom in diamond is bonded to four other carbon atoms at the corners of a tetrahedron. Inset: A model of buckyball, a form of carbon with a molecular formula of C_{60}. (Charles D. Winters)

KEY QUESTIONS

ACCORDING TO the simplest definition, **organic chemistry** is the study of the compounds of carbon. As you study this text, you will realize that organic compounds are everywhere around us—in our foods, flavors, and fragrances; in our medicines, toiletries, and cosmetics; in our plastics, films, fibers, and resins; in our paints and varnishes; in our glues and adhesives; and, of course, in our bodies and in all living things.

Perhaps the most remarkable feature of organic chemistry is that it is the chemistry of carbon and only a few other elements—chiefly hydrogen, oxygen, and nitrogen. Chemists

have discovered or made well over 10 million organic compounds. While the majority of them contain carbon and just those three elements, many also contain sulfur, phosphorus, and a halogen (fluorine, chlorine, bromine, or iodine).

Let us begin our study of organic chemistry with a review of how carbon, hydrogen, oxygen, and nitrogen combine by sharing electron pairs to form molecules.

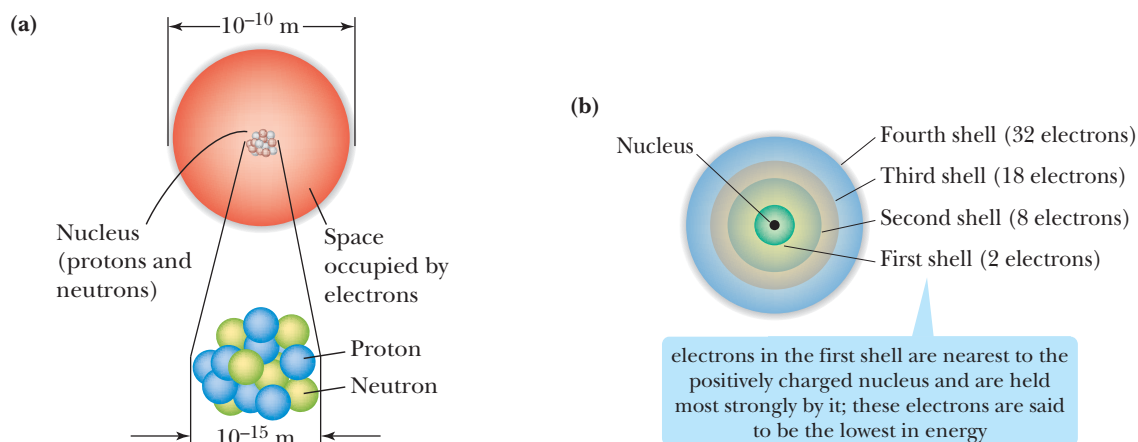**Shell**   A region of space around a nucleus where electrons are found.

Orbital   A region of space where an electron or pair of electrons spends 90 to 95% of its time.

1.1   How Do We Describe the Electronic Structure of Atoms?

You are already familiar with the fundamentals of the electronic structure of atoms from a previous study of chemistry. Briefly, an atom contains a small, dense nucleus made of neutrons and positively charged protons (Figure 1.1a).

Electrons do not move freely in the space around a nucleus, but rather are confined to regions of space called **principal energy levels** or, more simply, **shells**. We number these shells 1, 2, 3, and so forth from the inside out (Figure 1.1b).

Shells are divided into subshells designated by the letters s, p, d, and f, and within these subshells, electrons are grouped in orbitals (Table 1.1). An **orbital** is a region of space that can hold 2 electrons. In this course, we focus on compounds of carbon with hydrogen, oxygen, and nitrogen, all of which use only electrons in s and p orbitals for covalent bonding. Therefore, we are concerned primarily with s and p orbitals.

(a)

Nucleus (protons and neutrons)

Space occupied by electrons

10^{-10} m

Proton

Neutron

10^{-15} m

(b)

Nucleus

Fourth shell (32 electrons)

Third shell (18 electrons)

Second shell (8 electrons)

First shell (2 electrons)

electrons in the first shell are nearest to the positively charged nucleus and are held most strongly by it; these electrons are said to be the lowest in energy

FIGURE 1.1
A schematic view of an atom. (a) Most of the mass of an atom is concentrated in its small, dense nucleus, which has a diameter of 10^{-14} to 10^{-15} meter (m). (b) Each shell can contain up to $2n^2$ electrons, where n is the number of the shell. Thus, the first shell can hold 2 electrons, the second 8 electrons, the third 18, the fourth 32, and so on. (Table 1.1).

the first shell contains a single orbital called a $1s$ orbital. The second shell contains one $2s$ orbital and three $2p$ orbitals. All p orbitals come in sets of three and can hold up to 6 electrons. The third shell contains one $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals. All d orbitals come in sets of five and can hold up to 10 electrons. All f orbitals come in sets of seven and can hold up to 14 electrons

TABLE 1.1   Distribution of Orbitals within Shells

Shell	Orbitals Contained in Each Shell	Maximum Number of Electrons Shell Can Hold	Relative Energies of Electrons in Each Shell
4	One $4s$, three $4p$, five $4d$, and seven $4f$ orbitals	$2 + 6 + 10 + 14 = 32$	Higher
3	One $3s$, three $3p$, and five $3d$ orbitals	$2 + 6 + 10 = 18$	
2	One $2s$ and three $2p$ orbitals	$2 + 6 = 8$	
1	One $1s$ orbital	2	Lower

TABLE 1.2   **Ground-State Electron Configurations for Elements 1–18***

First Period	H	1	$1s^1$	
	He	2	$1s^2$	
Second Period	Li	3	$1s^2s^1$	$[He]2s^1$
	Be	4	$1s^22s^2$	$[He]2s^2$
	B	5	$1s^22s^22p_x^1$	$[He]2s^22p_x^1$
	C	6	$1s^22s^22p_x^12p_y^1$	$[He]2s^22p_x^12p_y^1$
	N	7	$1s^22s^22p_x^12p_y^12p_z^1$	$[He]2s^22p_x^12p_y^12p_z^1$
	O	8	$1s^22s^22p_x^22p_y^12p_z^1$	$[He]2s^22p_x^22p_y^12p_z^1$
	F	9	$1s^22s^22p_x^22p_y^22p_z^1$	$[He]2s^22p_x^22p_y^22p_z^1$
	Ne	10	$1s^22s^22p_x^22p_y^22p_z^2$	$[He]2s^22p_x^22p_y^22p_z^2$
Third Period	Na	11	$1s^22s^22p_x^22p_y^22p_z^23s^1$	$[Ne]3s^1$
	Mg	12	$1s^22s^22p_x^22p_y^22p_z^23s^2$	$[Ne]3s^2$
	Al	13	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^1$	$[Ne]3s^23p_x^1$
	Si	14	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^1$	$[Ne]3s^23p_x^13p_y^1$
	P	15	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$	$[Ne]3s^23p_x^13p_y^13p_z^1$
	S	16	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^13p_z^1$	$[Ne]3s^23p_x^23p_y^13p_z^1$
	Cl	17	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^33p_z^1$	$[Ne]3s^23p_x^23p_y^23p_z^1$
	Ar	18	$1s^22s^22p_x^22p_y^22p_z^23s^23p_x^23p_y^23p_z^2$	$[Ne]3s^23p_x^23p_y^23p_z^2$

*Elements are listed by symbol, atomic number, ground-state electron configuration, and shorthand notation for the ground-state electron configuration, in that order.

Rule 1. Orbitals in these elements fill in the order $1s$, $2s$, $2p$, $3s$, and $3p$.

Rule 2. Notice that each orbital contains a maximum of two electrons. In neon. there are six additional electrons after the $1s$ and $2s$ orbitals are filled. These are written as $2p_x^22p_y^22p_z^2$. Alternatively, we can group the three filled $2p$ orbitals and write them in a condensed form as $2p^6$.

Rule 3. Because the p_x, p_y, and p_z orbitals are equal in energy, we fill each with one electron before adding a second electron. That is, only after each $3p$ orbital contains one electron do we add a second electron to the $3p_x$ orbital.
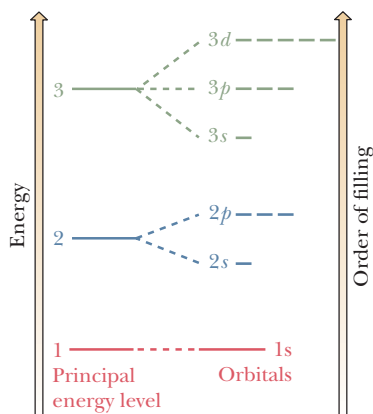
A.   Electron Configuration of Atoms

The electron configuration of an atom is a description of the orbitals the electrons in the atom occupy. Every atom has an infinite number of possible electron configurations. At this stage, we are concerned only with the **ground-state electron configuration—the** electron configuration of lowest energy. Table 1.2 shows ground-state electron configurations for the first 18 elements of the Periodic Table. We determine the ground-state electron con-figuration of an atom with the use of the following three rules:
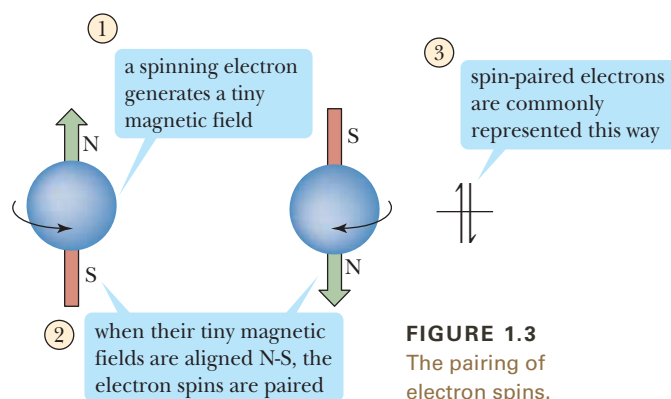
Ground-state electron configuration The electron configuration of lowest energy for an atom, molecule, or ion.

    Rule 1. *Orbitals fill in order of increasing energy from lowest to highest* (Figure 1.2).

    Rule 2. *Each orbital can hold up to two electrons with their spins paired. Spin pairing* means that each electron spins in a direction opposite that of its partner (Figure 1.3). We show this pairing by writing two arrows, one with its head up and the other with its head down.

    Rule 3. *When orbitals of equivalent energy are available, but there are not enough electrons to fill them completely, then we add one electron to each equivalent orbital before we add a second electron to any one of them.*

FIGURE 1.2
Relative energies and order of filling of orbitals through the $3d$ orbitals.

① a spinning electron generates a tiny magnetic field

② when their tiny magnetic fields are aligned N-S, the electron spins are paired

③ spin-paired electrons are commonly represented this way

FIGURE 1.3
The pairing of electron spins.

EXAMPLE   1.1

Write ground-state electron configurations for these elements:

(a) Lithium   **(b)** Oxygen   **(c)** Chlorine

STRATEGY

Locate each atom in the Periodic Table and determine its atomic number. The order of filling of orbitals is $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, and so on.

SOLUTION

(a) Lithium (atomic number 3): $1s^2 2s^1$. Alternatively, we can write the ground-state electron configuration as [He] $2s^1$.

(b) Oxygen (atomic number 8): $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$. Alternatively, we can group the four electrons of the $2p$ orbitals together and write the ground-state electron configuration as $1s^2 2s^2 2p^4$. We can also write it as [He] $2s^2 2p^4$.

(c) Chlorine (atomic number 17): $1s^2 2s^2 2p^6 3s^2 3p^5$. Alternatively, we can write it as [Ne] $3s^2 3p^5$.

See problems 1.17–1.20

PROBLEM   1.1

Write and compare the ground-state electron configurations for the elements in each set. What can be said about the outermost shell of orbitals for each pair of elements?

(a) Carbon and silicon
(b) Oxygen and sulfur
(c) Nitrogen and phosphorus

B.   Lewis Structures

In discussing the physical and chemical properties of an element, chemists often focus on the outermost shell of its atoms, because electrons in this shell are the ones involved in the formation of chemical bonds and in chemical reactions. We call outer-shell electrons **valence electrons**, and we call the energy level in which they are found the **valence shell**. Carbon, for example, with a ground-state electron configuration of $1s^2 2s^2 2p^2$, has four valence (outer-shell) electrons.

To show the outermost electrons of an atom, we commonly use a representation called a **Lewis structure**, after the American chemist Gilbert N. Lewis (1875–1946), who devised this notation. A Lewis structure shows the symbol of the element, surrounded by a number of dots equal to the number of electrons in the outer shell of an atom of that element. In Lewis structures, the atomic symbol represents the nucleus and all filled inner shells. Table 1.3 shows Lewis structures for the first 18 elements of the Periodic Table. As you study the entries in the table, note that, with the exception of helium, the number of valence electrons of the element corresponds to the group number of the element in the Periodic Table; for example, oxygen, with six valence electrons, is in Group 6A.

At this point, we must say a word about the numbering of the columns (families or groups) in the Periodic Table. Dmitri Mendeleev gave them numerals and added the letter A for some columns and B for others. This pattern remains in common use in the United

Valence electrons
Electrons in the valence (outermost) shell of an atom.

Valence shell   The outermost electron shell of an atom.

Lewis structure of an atom   The symbol of an element surrounded by a number of dots equal to the number of electrons in the valence shell of the atom.

TABLE 1.3   **Lewis Structures for Elements 1–18 of the Periodic Table**

1A	2A	3A	4A	5A	6A	7A	8A
H·							He:
Li·	Be:	B:	·C:	·N:	:O:	:F:	:Ne:
Na·	Mg:	Al:	·Si:	·P:	:S:	:Cl:	:Ar:

helium and neon have filled valence shells

neon and argon have in common an electron configuration in which the s and p orbitals of their valence shells are filled with eight electrons

States today. In 1985, however, the International Union of Pure and Applied Chemistry (IUPAC) recommended an alternative system in which the columns are numbered 1 to 18 beginning on the left and without added letters. Although we use the original Mendeleev system in this text, the Periodic Table on the inside back cover of the text shows both.

Notice from Table 1.3 that, for C, N, O, and F in period 2 of the Periodic Table, the valence electrons belong to the second shell. It requires 8 electrons to fill this shell. For Si, P, S, and Cl in period 3 of the Periodic Table, the valence electrons belong to the third shell. With 8 electrons, this shell is only partially filled: The $3s$ and $3p$ orbitals are fully occupied, but the five $3d$ orbitals can accommodate an additional 10 valence electrons. Because of the differences in number and kind of valence shell orbitals available to elements of the second and third periods, significant differences exist in the covalent bonding of oxygen and sulfur and of nitrogen and phosphorus. For example, although oxygen and nitrogen can accommodate no more than 8 electrons in their valence shells, many phosphorus-containing compounds have 10 electrons in the valence shell of phosphorus, and many sulfur-containing compounds have 10 and even 12 electrons in the valence shell of sulfur.
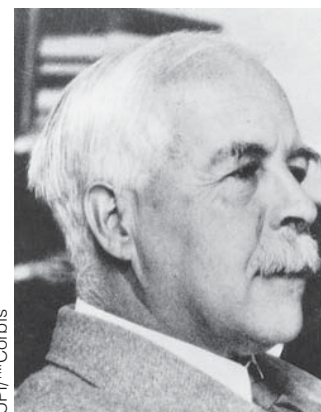
Gilbert N. Lewis (1875–1946) introduced the theory of the electron pair that extended our understanding of covalent bonding and of the concept of acids and bases. It is in his honor that we often refer to an "electron dot" structure as a Lewis structure.

1.2 What Is the Lewis Model of Bonding?

A. Formation of Ions

In 1916, Lewis devised a beautifully simple model that unified many of the observations about chemical bonding and reactions of the elements. He pointed out that the chemical inertness of the noble gases (Group 8A) indicates a high degree of stability of the electron configurations of these elements: helium with a valence shell of two electrons ($1s^2$), neon with a valence shell of eight electrons ($2s^2 2p^6$), argon with a valence shell of eight electrons ($3s^2 3p^6$), and so forth.

Noble Gas	Noble Gas Notation
He	$1s^2$
Ne	[He] $2s^2 2p^6$
Ar	[Ne] $3s^2 3p^6$
Kr	[Ar] $4s^2 4p^6 3d^{10}$
Xe	[Kr] $5s^2 5p^6 4d^{10}$

The tendency of atoms to react in ways that achieve an outer shell of eight valence electrons is particularly common among elements of Groups 1A–7A (the main-group elements). We give this tendency the special name, the **octet rule**. An atom with almost eight valence electrons tends to gain the needed electrons to have eight electrons in its valence shell and an electron configuration like that of the noble gas nearest it in atomic number. In gaining electrons, the atom becomes a negatively charged ion called an **anion**. An atom with only one or two valence electrons tends to lose the number of electrons required to have the same electron configuration as the noble gas nearest it in atomic number. In losing one or more electrons, the atom becomes a positively charged ion called a **cation**.

Octet rule The tendency among atoms of Group 1A–7A elements to react in ways that achieve an outer shell of eight valence electrons.

Anion An atom or group of atoms bearing a negative charge.

Cation An atom or group of atoms bearing a positive charge.

EXAMPLE   1.2

Show how the loss of one electron from a sodium atom to form a sodium ion leads to a stable octet:

$$\text{Na} \longrightarrow \text{Na}^+ + e^-$$

A sodium atom   A sodium ion   An electron
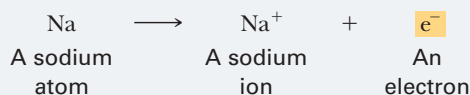
STRATEGY

To see how this chemical change leads to a stable octet, write the condensed ground-state electron configuration for a sodium atom and for a sodium ion, and then compare the two to that of neon, the noble gas nearest to sodium in atomic number.

SOLUTION

A sodium atom has one electron in its valence shell. The loss of this one valence electron changes the sodium atom to a sodium ion, Na^+, which has a complete octet of electrons in its valence shell and the same electron configuration as neon, the noble gas nearest to it in atomic number.

Na (11 electrons): $1s^2 2s^2 2p^6\ 3s^1$

Na^+ (10 electrons): $1s^2 2s^2 2p^6$

Ne (10 electrons): $1s^2 2s^2 2p^6$

See problems 1.22, 1.23

PROBLEM   1.2

Show how the gain of two electrons by a sulfur atom to form a sulfide ion leads to a stable octet:

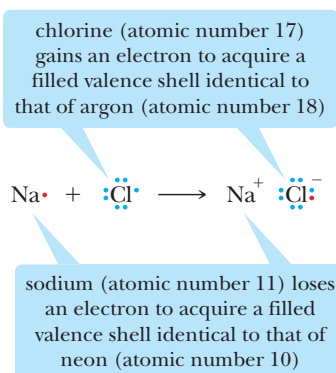$$S + \boxed{2e^-} \longrightarrow S^{2-}$$

B.   Formation of Chemical Bonds

According to the Lewis model of bonding, atoms interact with each other in such a way that each atom participating in a chemical bond acquires a valence-shell electron configuration the same as that of the noble gas closest to it in atomic number. Atoms acquire completed valence shells in two ways:
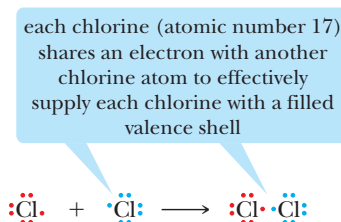
1. An atom may lose or gain enough electrons to acquire a filled valence shell. An atom that gains electrons becomes an anion, and an atom that loses electrons becomes a cation. A chemical bond between an anion and a cation is called an **ionic bond**.

Ionic bond   A chemical bond resulting from the electrostatic attraction of an anion and a cation.

chlorine (atomic number 17) gains an electron to acquire a filled valence shell identical to that of argon (atomic number 18)

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

sodium (atomic number 11) loses an electron to acquire a filled valence shell identical to that of neon (atomic number 10)

2. An atom may share electrons with one or more other atoms to acquire a filled valence shell. A chemical bond formed by sharing electrons is called a **covalent bond**.

Covalent bond   A chemical bond resulting from the sharing of one or more pairs of electrons.

each chlorine (atomic number 17) shares an electron with another chlorine atom to effectively supply each chlorine with a filled valence shell

$$:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!\cdot \ + \ \cdot\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!: \ \longrightarrow \ :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!\cdot\!\cdot\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!:$$

Electronegativity   A measure of the force of an atom's attraction for electrons it shares in a chemical bond with another atom.

We now ask how we can find out whether two atoms in a compound are joined by an ionic bond or a covalent bond. One way to answer this question is to consider the relative positions of the two atoms in the Periodic Table. Ionic bonds usually form between a metal and a nonmetal. An example of an ionic bond is that formed between the metal sodium and the nonmetal chlorine in the compound sodium chloride, Na^+Cl^-. By contrast, when two nonmetals or a metalloid and a nonmetal combine, the bond between them is usually covalent. Examples of compounds containing covalent bonds between nonmetals include Cl_2, H_2O, CH_4, and NH_3. Examples of compounds containing covalent bonds between a metalloid and a nonmetal include BF_3, $SiCl_4$, and AsH_4.

Another way to identify the type of bond is to compare the electronegativities of the atoms involved, which is the subject of the next subsection.

C.   Electronegativity and Chemical Bonds

Electronegativity is a measure of the force of an atom's attraction for electrons that it shares in a chemical bond with another atom. The most widely used scale of electronegativities (Table 1.4) was devised by Linus Pauling in the 1930s. On the Pauling scale, fluorine, the most electronegative element, is assigned an electronegativity of 4.0, and all other elements are assigned values in relation to fluorine.

As you study the electronegativity values in this table, note that they generally increase from left to right within a period of the Periodic Table and generally increase from bottom to top within a group. Values increase from left to right because of the increasing positive charge on the nucleus, which leads to a stronger attraction for electrons in the valence shell. Values increase going up a column because of the decreasing distance of the valence electrons from the nucleus, which leads to stronger attraction between a nucleus and its valence electrons.

Note that the values given in Table 1.4 are only approximate. The electronegativity of a particular element depends not only on its position in the Periodic Table, but also on its oxidation state. The electronegativity of Cu(I) in Cu_2O, for example, is 1.8, whereas the electronegativity of Cu(II) in CuO is 2.0. In spite of these variations, electronegativity is still a useful guide to the distribution of electrons in a chemical bond.

UPI/™Corbis

Linus Pauling (1901–1994) was the first person ever to receive two unshared Nobel Prizes. He received the Nobel Prize for Chemistry in 1954 for his contributions to the nature of chemical bonding. He received the Nobel Prize for Peace in 1962 for his efforts on behalf of international control of nuclear weapons and against nuclear testing.

TABLE 1.4   Electronegativity Values for Some Atoms (Pauling Scale)

																H 2.1								

1A	2A						8B			1B	2B	3A	4A	5A	6A	7A
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	3B	4B	5B	6B	7B				1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2

■ <1.0   ■ 1.5 – 1.9   ■ 2.5 – 2.9
■ 1.0 – 1.4   ■ 2.0 – 2.4   ■ 3.0 – 4.0

H

Electronegativity increases →

Li	Be		B	C	N	O	F
Na	Mg		Al	Si	P	S	Cl
K	Ca						Br
							I

Electronegativity increases ↑

Partial Periodic Table showing commonly encountered elements in organic chemistry. Electronegativity generally increases from left to right within a period and from bottom to top within a group. Hydrogen is less electronegative than the elements in red and more electronegative than those in blue. Hydrogen and phosphorus have the same electronegativity on the Pauling scale.

Ionic Bonds

An ionic bond forms by the transfer of electrons from the valence shell of an atom of lower electronegativity to the valence shell of an atom of higher electronegativity. The more electronegative atom gains one or more valence electrons and becomes an anion; the less electronegative atom loses one or more valence electrons and becomes a cation.
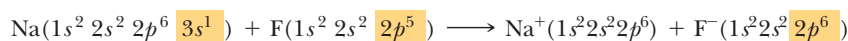
EXAMPLE   1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?
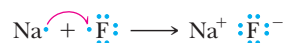
(a) Lithium or carbon   **(b)** Nitrogen or oxygen

(c) Carbon or oxygen

STRATEGY

Determine whether the pair resides in the same period (row) or group (column) of the Periodic Table. For those in the same period, electronegativity increases from left to right. For those in the same group, electronegativity increases from bottom to top.

SOLUTION

The elements in these pairs are all in the second period of the Periodic Table. Electronegativity in this period increases from left to right.

(a) C > Li   **(b)** O > N   **(c)** O > C

See problem 1.24

PROBLEM   1.3

Judging from their relative positions in the Periodic Table, which element in each pair has the larger electronegativity?

(a) Lithium or potassium

(b) Nitrogen or phosphorus

(c) Carbon or silicon

As a guideline, we say that this type of electron transfer to form an ionic compound is most likely to occur if the difference in electronegativity between two atoms is approximately 1.9 or greater. A bond is more likely to be covalent if this difference is less than 1.9. Note that the value 1.9 is somewhat arbitrary: Some chemists prefer a slightly larger value, others a slightly smaller value. The essential point is that the value 1.9 gives us a guidepost against which to decide whether a bond is more likely to be ionic or more likely to be covalent.

An example of an ionic bond is that formed between sodium (electronegativity 0.9) and fluorine (electronegativity 4.0). The difference in electronegativity between these two elements is 3.1. In forming Na^+F^-, the single $3s$ valence electron of sodium is transferred to the partially filled valence shell of fluorine:

$$\text{Na}(1s^2\, 2s^2\, 2p^6\, \boxed{3s^1}\,) \;+\; \text{F}(1s^2\, 2s^2\, \boxed{2p^5}\,) \longrightarrow \text{Na}^+(1s^2 2s^2 2p^6) \;+\; \text{F}^-(1s^2 2s^2\, \boxed{2p^6}\,)$$

As a result of this transfer of one electron, both sodium and fluorine form ions that have the same electron configuration as neon, the noble gas closest to each in atomic number. In the following equation, we use a single-headed curved arrow to show the transfer of one electron from sodium to fluorine:

$$\text{Na·} + \text{·}\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{\text{F}}}\text{:} \longrightarrow \text{Na}^+ \;\; \text{:}\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{\text{F}}}\text{:}^-$$

Covalent Bonds

A covalent bond forms when electron pairs are shared between two atoms whose difference in electronegativity is 1.9 or less. According to the Lewis model, an electron pair in a covalent bond functions in two ways simultaneously: It is shared by two atoms, and, at the same time, it fills the valence shell of each atom.

The simplest example of a covalent bond is that in a hydrogen molecule, H_2. When two hydrogen atoms bond, the single electrons from each atom combine to form an electron pair with the release of energy. A bond formed by sharing a pair of electrons is called a *single bond* and is represented by a single line between the two atoms. The electron pair shared between the two hydrogen atoms in H_2 completes the valence shell of each hydrogen. Thus, in H_2, each hydrogen has two electrons in its valence shell and an electron configuration like that of helium, the noble gas nearest to it in atomic number:

$$\text{H·} + \text{·H} \longrightarrow \text{H—H} \qquad \Delta H^0 \;=\; -435 \text{ kJ/mol } (-104 \text{ kcal/mol})$$
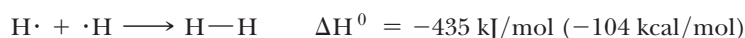
The Lewis model accounts for the stability of covalently bonded atoms in the following way: In forming a covalent bond, an electron pair occupies the region between two nuclei and serves to shield one positively charged nucleus from the repulsive force of the other positively charged nucleus. At the same time, an electron pair attracts both nuclei. In other words, an electron pair in the space between two nuclei bonds them together and fixes the internuclear distance to within very narrow limits. The distance between nuclei participating in a chemical bond is called a **bond length**. Every covalent bond has a definite bond length. In H—H, it is 74 pm, where 1 pm $= 10^{-12}$ m.

Although all covalent bonds involve the sharing of electrons, they differ widely in the degree of sharing. We classify covalent bonds into two categories—nonpolar covalent and polar covalent—depending on the difference in electronegativity between the bonded atoms. In a **nonpolar covalent bond**, electrons are shared equally. In a **polar covalent bond**, they are shared unequally. It is important to realize that no sharp line divides these two categories, nor, for that matter, does a sharp line divide polar covalent bonds and ionic bonds. Nonetheless, the rule-of-thumb guidelines in Table 1.5 will help you decide whether a given bond is more likely to be nonpolar covalent, polar covalent, or ionic.

A covalent bond between carbon and hydrogen, for example, is classified as nonpolar covalent because the difference in electronegativity between these two atoms is $2.5 - 2.1 = 0.4$ unit. An example of a polar covalent bond is that of H—Cl. The difference in electronegativity between chlorine and hydrogen is $3.0 - 2.1 = 0.9$ unit.

Nonpolar covalent bond
A covalent bond between atoms whose difference in electronegativity is less than approximately 0.5.

Polar covalent bond
A covalent bond between atoms whose difference in electronegativity is between approximately 0.5 and 1.9.

TABLE 1.5 Classification of Chemical Bonds

Difference in Electronegativity between Bonded Atoms	Type of Bond	Most Likely Formed Between
Less than 0.5	Nonpolar covalent	Two nonmetals or a nonmetal and a metalloid
0.5 to 1.9	Polar covalent	
Greater than 1.9	Ionic	A metal and a nonmetal

EXAMPLE   1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic:
(a) O—H
(b) N—H
(c) Na—F
(d) C—Mg

STRATEGY

Use the difference in electronegativity between the two atoms and compare this value with the range of values given in Table 1.5.

SOLUTION

On the basis of differences in electronegativity between the bonded atoms, three of these bonds are polar covalent and one is ionic:

Bond	Difference in Electronegativity	Type of Bond
(a) O—H	$3.5 - 2.1 = 1.4$	polar covalent
(b) N—H	$3.0 - 2.1 = 0.9$	polar covalent
(c) Na—F	$4.0 - 0.9 = 3.1$	ionic
(d) C—Mg	$2.5 - 1.2 = 1.3$	polar covalent

See problem 1.25

PROBLEM   1.4

Classify each bond as nonpolar covalent, polar covalent, or ionic:
(a) S—H   **(b)** P—H   **(c)** C—F   **(d)** C—Cl

FIGURE 1.4

An electron density model of HCl. Red indicates a region of high electron density, and blue indicates a region of low electron density.

red represents high electron density

blue represents low electron density

$$\overset{\delta+\ \ \ \delta-}{\underset{H-Cl}{\longrightarrow}}$$
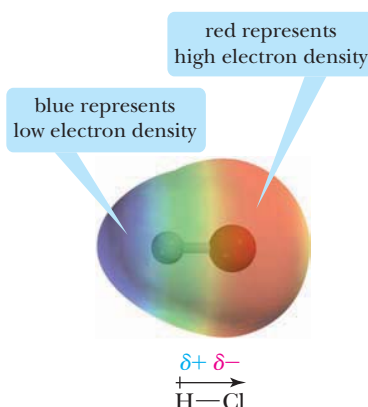
An important consequence of the unequal sharing of electrons in a polar covalent bond is that the more electronegative atom gains a greater fraction of the shared electrons and acquires a partial negative charge, which we indicate by the symbol $\delta-$ (read "delta minus"). The less electronegative atom has a lesser fraction of the shared electrons and acquires a partial positive charge, which we indicate by the symbol $\delta+$ (read "delta plus"). This separation of charge produces a **dipole** (two poles). We can also show the presence of a bond dipole by an arrow, with the head of the arrow near the negative end of the dipole and a cross on the tail of the arrow near the positive end (Figure 1.4).

We can display the polarity of a covalent bond by a type of molecular model called an *electron density model.* In this type of model, a blue color shows the presence of a $\delta+$ charge, and a red color shows the presence of a $\delta-$ charge. Figure 1.4 shows an electron density model of HCl. The ball-and-stick model in the center shows the orientation of the two atoms in space. The transparent surface surrounding the ball-and-stick model shows the relative sizes of the atoms (equivalent to the size shown by a space-filling model). Colors on the surface show the distribution of electron density. We see by the blue color that hydrogen bears a $\delta+$ charge and by the red color that chlorine bears a $\delta-$ charge.

EXAMPLE   1.5

Using a bond dipole arrow and the symbols $\delta-$ and $\delta+$, indicate the direction of polarity in these polar covalent bonds:

(a) C—O   **(b)** N—H   **(c)** C—Mg

STRATEGY

To determine the polarity of a covalent bond and the direction of the polarity, compare the electronegativities of the bonded atoms. Remember that a bond dipole arrow always points toward the more electronegative atom.

SOLUTION

For (a), carbon and oxygen are both in period 2 of the Periodic Table. Because oxygen is farther to the right than carbon, it is more electronegative. For (b), nitrogen is more electronegative than hydrogen. For (c), magnesium is a metal located at the far left of the Periodic Table, and carbon is a nonmetal located at the right. All nonmetals, including hydrogen, have a greater electronegativity than do the metals in columns 1A and 2A. The electronegativity of each element is given below the symbol of the element:

(a) $\overset{\delta+\ \ \ \delta-}{C-O}$ **(b)** $\overset{\delta-\ \ \ \delta+}{N-H}$ **(c)** $\overset{\delta-\ \ \ \delta+}{C-Mg}$

    2.5 3.5   3.0 2.1   2.5   1.2
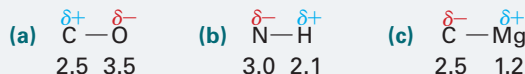
See problems 1.26, 1.38, 1.40

PROBLEM   1.5

Using a bond dipole arrow and the symbols $\delta-$ and $\delta+$, indicate the direction of polarity in these polar covalent bonds:

(a) C—N   **(b)** N—O   **(c)** C—Cl

In summary, the twin concepts of electronegativity and the polarity of covalent bonds will be very helpful in organic chemistry as a guide to locating centers of chemical reactions. In many of the reactions we will study, reaction is initiated by the attraction between a center of partial positive charge and a center of partial negative charge.

Draw Lewis Structures of Molecules and Ions

HOW TO 1.1

The ability to draw Lewis structures for molecules and ions is a fundamental skill in the study of organic chemistry. The following steps will help you to do this (as you study these steps look at the examples in Table 1.6). As an example, let us draw a Lewis structure of acetic acid, molecular formula $C_2H_4O_2$. Its structural formula, CH_3COOH, gives a hint of the connectivity.

STEP 1: Determine the number of valence electrons in the molecule or ion. To do so, add the number of valence electrons contributed by each atom. For ions, add one electron for each negative charge on the ion, and subtract one electron for each positive charge on the ion. For example, the Lewis structure of the water molecule, H_2O, must show eight valence electrons: one from each hydrogen and six from oxygen. The Lewis structure for the hydroxide ion, OH^-, must also show eight valence electrons: one from hydrogen, six from oxygen, plus one for the negative charge on the ion. For acetic acid the molecular formula is $C_2H_4O_2$. The Lewis structure must show 8(2 carbons) + 4(4 hydrogens) + 12(2 oxygens) = 24 valence electrons.

STEP 2: Determine the arrangement of atoms in the molecule or ion. This step is the most difficult part of drawing a Lewis structure. Fortunately, the structural formula of a compound can provide valuable information about connectivity. The order in which the atoms are listed in a structural formula is a guide. For example, the CH_3 part of the structural formula of acetic acid tells you that three hydrogen atoms are bonded to the carbon written on the left, and the COOH part tells you that both oxygens are bonded to the same carbon and a hydrogen is bonded to one of the oxygens.
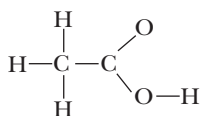
Except for the simplest molecules and ions, the connectivity must be determined experimentally. For some molecules and ions we give as examples, we ask you to propose a connectivity of the atoms. For most, however, we give you the experimentally determined arrangement.

STEP 3: Arrange the remaining electrons in pairs so that each atom in the molecule or ion has a complete outer shell. Show a pair of *bonding electrons* as a single line between the bonded atoms; show a pair of *nonbonding electrons* as a pair of Lewis dots. To accomplish this, connect the atoms with single bonds. Then arrange the remaining electrons in pairs so that each atom in the molecule or ion has a complete outer shell. Each hydrogen atom must be surrounded by two electrons. Each atom of carbon, oxygen, and nitrogen, as well as each halogen, must be surrounded by eight electrons (per the octet rule). Recall that each neutral carbon atom has four valence electrons and each neutral oxygen atom has six valence electrons. The structure here shows the required 24 valence electrons. The left carbon has four single bonds and a complete valence shell. Each hydrogen also has a complete valence shell. The lower oxygen has two single bonds and two unshared pairs of electrons and, therefore, has a complete valence shell. The original six valence electrons of the upper oxygen are accounted for, but it does not yet have a filled valence shell. Similarly, the original four valence electrons of the right carbon atom are accounted for but it still does not have a complete valence shell.
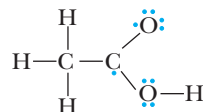
Notice that in the structure so far, we have accounted for all valence electrons, but two atoms do not yet have completed valence shells. Furthermore, one carbon atom and one oxygen atom each have a single unpaired electron.

STEP 4: Use multiple bonds where necessary to eliminate unpaired electrons. In a **single bond**, two atoms share one pair of electrons. It is sometimes necessary for atoms to share more than one pair of electrons. In a **double bond**, they share two pairs of electrons; we show a double bond by drawing two parallel lines between the bonded atoms. In a **triple bond**, two atoms share three pairs of electrons; we show a triple bond by three parallel lines between the bonded atoms. The following structure combines the unpaired electrons on carbon and oxygen and creates a double bond (C=O) between these two atoms. The Lewis structure is now complete.
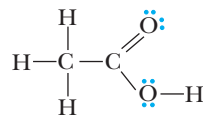
TABLE 1.6 Lewis Structures for Several Compounds. The number of valence electrons in each molecule is given in parentheses after the molecule's molecular formula.

$H—\ddot{O}—H$	$H—\overset{H}{\underset{H}{N}}—H$	$H—\overset{H}{\underset{H}{C}}—H$	$H—\ddot{\underset{..}{Cl}}:$
H_2O (8) Water	NH_3 (8) Ammonia	CH_4 (8) Methane	HCl (8) Hydrogen chloride
$\underset{H}{\overset{H}{\diagdown}}C=C\underset{\diagup H}{\overset{H\diagdown}{}}$	$H—C≡C—H$	$\underset{H}{\overset{H}{\diagdown}}C=\ddot{O}$	$\underset{H}{\overset{:O:}{\underset{\diagup}{C}}}\underset{H}{\overset{..}{\diagdown}}$
C_2H_4 (12) Ethylene	C_2H_2 (10) Acetylene	CH_2O (12) Formaldehyde	H_2CO_3 (24) Carbonic acid

Bonding electrons Valence electrons shared in a covalent bond.

Nonbonding electrons Valence electrons not involved in forming covalent bonds, that is, unshared electrons.

From the study of the compounds in Table 1.6 and other organic compounds, we can make the following generalizations: In neutral (uncharged) organic compounds,

- H has one bond.
- C has four bonds.
- N has three bonds and one unshared pair of electrons.
- O has two bonds and two unshared pair of electrons.
- F, Cl, Br, and I have one bond and three unshared pairs of electrons.

EXAMPLE 1.6

Draw Lewis structures, showing all valence electrons, for these molecules:

(a) H_2O_2 (b) CH_3OH (c) CH_3Cl

STRATEGY

Determine the number of valence electrons and the connectivity of the atoms in each molecule. Connect the bonded atoms by single bonds and then arrange the remaining valence electrons so that each atom has a filled valence shell.

SOLUTION

(a) A Lewis structure for hydrogen peroxide, H_2O_2, must show 6 valence electrons from each oxygen and 1 from each hydrogen, for a total of $12 + 2 = 14$ valence electrons. We know that hydrogen forms only one covalent bond, so the connectivity of the atoms must be as follows:

$$H—O—O—H$$
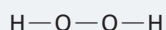
The three single bonds account for 6 valence electrons. We place the remaining 8 valence electrons on the oxygen atoms to give each a complete octet:

$$H—\ddot{O}—\ddot{O}—H$$
Lewis structure
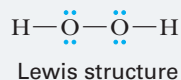
Ball-and-stick models show only nuclei and covalent bonds; they do not show unshared pairs of electrons

(b) A Lewis structure for methanol, CH_3OH, must show 4 valence electrons from carbon, 1 from each hydrogen, and

6 from oxygen, for a total of $4 + 4 + 6 = 14$ valence electrons. The connectivity of the atoms in methanol is given on the left. The five single bonds in this partial structure account for 10 valence electrons. We place the remaining 4 valence electrons on oxygen as two Lewis dot pairs to give it a complete octet.

$$H—\overset{H}{\underset{H}{C}}—O—H \qquad H—\overset{H}{\underset{H}{C}}—\ddot{O}—H$$

The order of attachment of atoms | Lewis structure
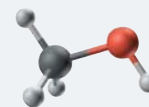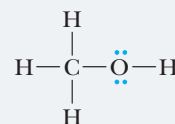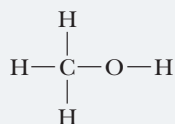
(c) A Lewis structure for chloromethane, CH_3Cl, must show 4 valence electrons from carbon, 1 from each hydrogen, and 7 from chlorine, for a total of $4 + 3 + 7 = 14$. Carbon has four bonds, one to each of the hydrogens and one to chlorine. We place the remaining 6 valence electrons on chlorine as three Lewis dot pairs to complete its octet.

$$H—\overset{H}{\underset{H}{C}}—\ddot{\underset{..}{Cl}}:$$

Lewis structure

See problems 1.27, 1.28

PROBLEM 1.6

Draw Lewis structures, showing all valence electrons, for these molecules:
(a) C_2H_6 **(b)** CS_2 **(c)** HCN

E. Formal Charge

Throughout this course, we deal not only with molecules, but also with polyatomic cations and polyatomic anions. Examples of polyatomic cations are the hydronium ion, H_3O^+, and the ammonium ion, NH_4^+. An example of a polyatomic anion is the bicarbonate ion, HCO_3^-. It is important that you be able to determine which atom or atoms in a molecule or polyatomic ion bear the positive or negative charge. The charge on an atom in a molecule or polyatomic ion is called its **formal charge**. To derive a formal charge,

Formal charge The charge on an atom in a molecule or polyatomic ion.

Step 1: *Write a correct Lewis structure for the molecule or ion.*

Step 2: *Assign to each atom all its unshared (nonbonding) electrons and one-half its shared (bonding) electrons.*

Step 3: *Compare the number arrived at in Step 2 with the number of valence electrons in the neutral, unbonded atom.* If the number of electrons assigned to a bonded atom is less than that assigned to the unbonded atom, then more positive charges are in the nucleus than counterbalancing negative charges, and the atom has a positive formal charge. Conversely, if the number of electrons assigned to a bonded atom is greater than that assigned to the unbonded atom, then the atom has a negative formal charge.

$$\text{Formal charge} = \begin{matrix} \text{Number of valence} \\ \text{electrons in neutral} \\ \text{unbonded atom} \end{matrix} - \left(\begin{matrix} \text{All unshared} \\ \text{electrons} \end{matrix} + \begin{matrix} \text{One-half of all} \\ \text{shared electrons} \end{matrix} \right)$$

EXAMPLE 1.7

Draw Lewis structures for these ions, and show which atom in each bears the formal charge:
(a) H_3O^+ **(b)** CH_3O^-

STRATEGY

Draw a correct Lewis structure molecule showing all valence electrons on each atom. Then determine the location of the formal charge.

SOLUTION

(a) The Lewis structure for the hydronium ion must show 8 valence electrons: 3 from the three hydrogens, 6 from oxygen, minus 1 for the single positive charge. A neutral, unbonded oxygen atom has 6 valence electrons. To the oxygen atom in H_3O^+, we assign two unshared electrons and one from each shared pair of electrons, giving it a formal charge of $6 - (2 + 3) = +1$.

assigned 5 valence electrons:
formal charge of +1

$$H-\overset{\overset{\displaystyle ..}{+}}{\underset{\underset{\displaystyle H}{|}}{O}}-H$$
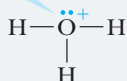
(b) The Lewis structure for the methoxide ion, CH_3O^-, must show 14 valence electrons: 4 from carbon, 6 from oxygen, 3 from the hydrogens, plus 1 for the single negative charge. To carbon, we assign 1 electron from each shared pair, giving it a formal charge of $4 - 4 = 0$. To oxygen, we assign 7 valence electrons, giving it a formal charge of $6 - 7 = -1$.

assigned 7 valence electrons:
formal charge of −1

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{..}{\underset{..}{O}}{:}^-$$
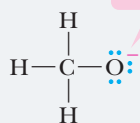
See problems 1.30–1.32, 1.34

PROBLEM 1.7

Draw Lewis structures for these ions, and show which atom in each bears the formal charge(s):
(a) $CH_3NH_3^+$ **(b)** CH_3^+

In writing Lewis structures for molecules and ions, you must remember that elements of the second period, including carbon, nitrogen, and oxygen, can accommodate no more than eight electrons in the four orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$) of their valence shells. Following are two Lewis structures for nitric acid, HNO_3, each with the correct number of valence electrons, namely, 24; one structure is acceptable and the other is not:

An acceptable
Lewis structure

Not an acceptable
Lewis structure

10 electrons in the
valence shell of nitrogen

The structure on the left is an acceptable Lewis structure. It shows the required 24 valence electrons, and each oxygen and nitrogen has a completed valence shell of 8 electrons. Further, the structure on the left shows a positive formal charge on nitrogen and a negative formal charge on one of the oxygens. An acceptable Lewis structure must show these formal charges. The structure on the right is *not* an acceptable Lewis structure. Although it shows the correct number of valence electrons, it places 10 electrons in the valence shell of nitrogen, yet the four orbitals of the second shell ($2s$, $2p_x$, $2p_y$, and $2p_z$) can hold no more than 8 valence electrons!

The Lewis structure of HNO_3 shows the negative formal charge localized on one of the oxygen atoms. The electron density model, on the other hand, shows that the negative charge is distributed equally over the two oxygen atoms on the right. The concept of resonance can explain this phenomenon and will be discussed in Section 1.6. Notice also the intense blue color on nitrogen, which is due to its positive formal charge.

1.3 How Do We Predict Bond Angles and the Shapes of Molecules?

In Section 1.2, we used a shared pair of electrons as the fundamental unit of a covalent bond and drew Lewis structures for several small molecules containing various combinations of single, double, and triple bonds. (See, for example, Table 1.6.) We can predict bond angles in these and other molecules in a very straightforward way by using the concept of **valence-shell electron-pair repulsion (VSEPR)**. According to this concept, the valence electrons of an atom may be involved in the formation of single, double, or triple bonds, or they may be unshared. Each combination creates a region of electron density that, because it is occupied by electrons, is negatively charged. Because like charges repel each other, the various regions of electron density around an atom spread so that each is as far away from the others as possible.

Recall from your prior studies in chemistry that VSEPR can be used to predict the shapes of molecules. This can be demonstrated in a very simple way by using balloons. Imagine that a balloon represents a region of electron density. If you tie two balloons together by their ends, they assume the shapes shown in Figure 1.5. The point where they are tied together represents the atom about which you want to predict a bond angle, and the balloons represent regions of electron density about that atom.

FIGURE 1.5
Balloon models used to predict bond angles. (a) Two balloons assume a linear shape with a bond angle of 180° about the tie point. (b) Three balloons assume a trigonal planar shape with bond angles of 120° about the tie point. (c) Four balloons assume a tetrahedral shape with bond angles of 109.5° about the tie point.

the point where the balloons are tied together represents (EA) the atom

each balloon represents a region of electron density, which could be a single bond, a double bond, a triple bond, or a lone pair of electrons

Charles D. Winters

Charles D. Winters

Charles D. Winters

Linear
(a)

Trigonal planar
**(b)**

Tetrahedral
(c)

(a)

(b)

109.5°

109.5°
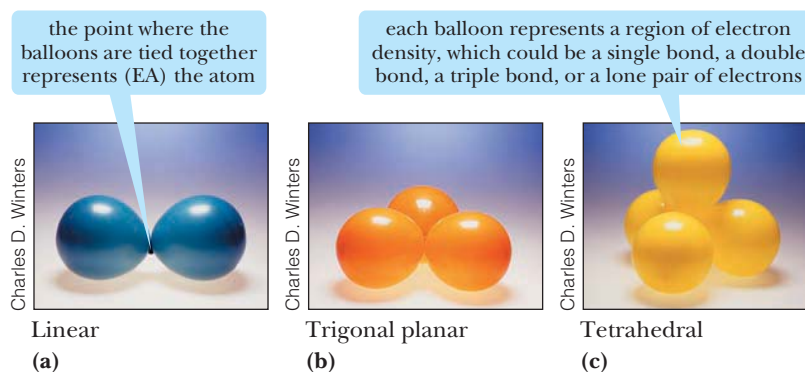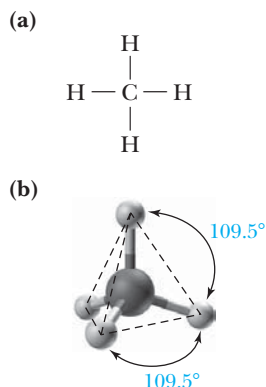
FIGURE 1.6
The shape of a methane molecule, CH_4. (a) Lewis structure and (b) ball-and-stick model. The single bonds occupy four regions of electron density, causing the molecule to be **tetrahedral**. The hydrogens occupy the four corners of a regular tetrahedron, and all H—C—H bond angles are 109.5°.

(a)

unshared pairs of electrons

(b)

107.3°

107.3°
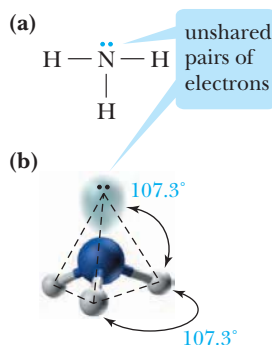
FIGURE 1.7
The shape of an ammonia molecule, NH_3. (a) Lewis structure and (b) ball-and-stick model. The three single bonds and one lone pair of electrons create four regions of electron density. This allows the lone pair and the three hydrogens to occupy the four corners of a tetrahedron. However, we do not take lone pairs of electrons into account when describing the shape of the molecule. For this reason, we describe the geometry of an ammonia molecule as **pyramidal**; that is, the molecule has a shape like a triangular-based pyramid with the three hydrogens at the base and nitrogen at the apex. The observed bond angles are 107.3°. We account for this small difference between the predicted and observed angles by proposing that the unshared pair of electrons on nitrogen repels adjacent electron pairs more strongly than bonding pairs repel each other.

(a)

(b)
Unshared electron pairs

104.5°
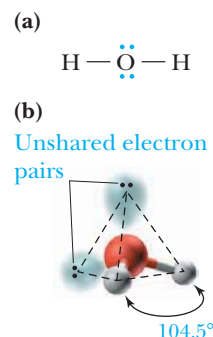
FIGURE 1.8
The shape of a water molecule, H_2O. (a) A Lewis structure and (b) a ball-and-stick model. Using VSEPR, we predict that the four regions of electron density around oxygen are arranged in a tetrahedral manner and that the H–O–H bond angle is 109.5°. Experimental measurements show that the actual H–O–H bond angle is 104.5°, a value smaller than that predicted. We explain this difference between the predicted and observed bond angle by proposing, as we did for NH_3, that unshared pairs of electrons repel adjacent pairs more strongly than do bonding pairs. Note that the distortion from 109.5° is greater in H_2O, which has two unshared pairs of electrons, than it is in NH_3, which has only one unshared pair. We describe the shape of water as **bent**.

We can use the example of the balloons to model the shapes that methane (CH_4), ammonia (NH_3), and water (H_2O) assume. As you look at each of these molecules in Figures 1.6–1.8, take note of (1) the number of regions of electron density shown by the Lewis structure, (2) the geometry that is required to maximize the separation of these regions of electron density, and (3) the names of the shapes that result from this treatment using VSEPR.

A general prediction emerges from this discussion of the shapes of CH_4, NH_3, and H_2O molecules. If a Lewis structure shows four regions of electron density around an atom, then VSEPR predicts a tetrahedral distribution of electron density and bond angles of approximately 109.5°.

In many of the molecules we encounter, an atom is surrounded by three regions of electron density. Figure 1.9 shows Lewis structures for formaldehyde (CH_2O) and ethylene

Formaldehyde

a double bond is treated as a single region of electron density

116.5°

121.8°

Top view

Side view

Ethylene

121.4°

117.2°

Top view

Side view
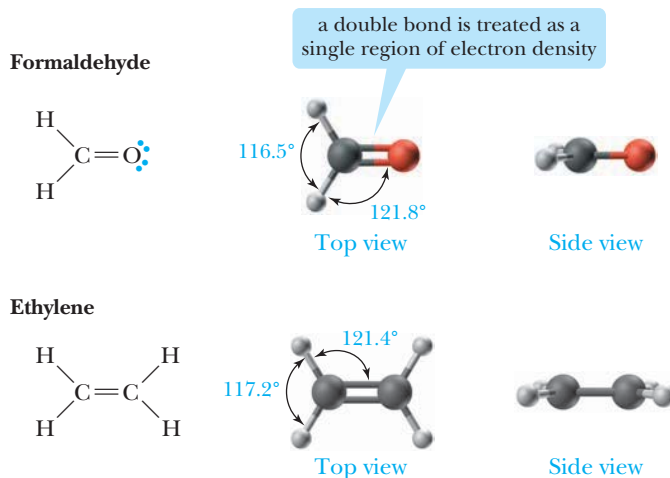
FIGURE 1.9
Shapes of formaldehyde (CH_2O) and ethylene (C_2H_4). In each molecule, the carbons are surrounded by three regions of electron density. Three regions of electron density about an atom are farthest apart when they lie in a plane and make angles of 120° with each other. We describe the geometry about each carbon atom as **trigonal planar**.

(a) **Carbon dioxide**

$$\ddot{\text{O}}\!=\!\text{C}\!=\!\ddot{\text{O}}$$

a triple bond is treated as a single region of electron density

Side view   End view

(b) **Acetylene**

$$\text{H}\!-\!\text{C}\!\equiv\!\text{C}\!-\!\text{H}$$

Side view   End view
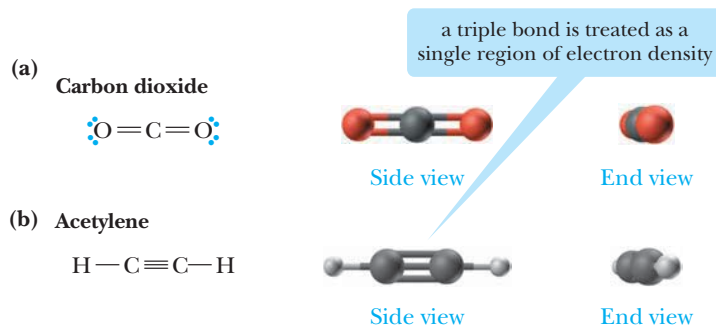
FIGURE 1.10
Shapes of (a) carbon dioxide (CO_2) and (b) acetylene (C_2H_2). In each case, the two regions of electron density are farthest apart if they form a straight line through the central atom and create an angle of 180°. Both carbon dioxide and acetylene are referred to as **linear** molecules.

(C_2H_4). As you look at these two molecules, take note of (1) the number of regions of electron density shown by the Lewis structure, (2) the geometry that is required to maximize the separation of these regions of electron density, and (3) the names of the shapes that result from this treatment using VSEPR. Also notice that using VSEPR, we treat a double bond as a single region of electron density.

In still other types of molecules, a central atom is surrounded by only two regions of electron density. Figure 1.10 shows Lewis structures and ball-and-stick models of carbon dioxide (CO_2) and acetylene (C_2H_2). As with double bonds, VSEPR treats triple bonds as one region of electron density.

Table 1.7 summarizes the predictions of VSEPR.

TABLE 1.7   **Predicted Molecular Shapes (VSEPR)**

Regions of Electron Density around Central Atom	Predicted Distribution of Electron Density about the Central Atom	Predicted Bond Angles	Examples (Shape of the Molecule)
4	Tetrahedral	109.5°	a solid wedge-shaped bond represents a bond extending out of the plane of the page / a dashed wedge-shaped bond represents a bond extending behind the plane of the page Methane (tetrahedral) Ammonia (pyramidal) Water (bent)
3	Trigonal planar	120°	Ethylene (planar) Formaldehyde (planar)
2	Linear	180°	$\ddot{\text{O}}\!=\!\text{C}\!=\!\ddot{\text{O}}$ Carbon dioxide (linear) H—C≡C—H Acetylene (linear)

EXAMPLE 1.8

Predict all bond angles in these molecules:
(a) CH_3Cl **(b)** $CH_2{=}CHCl$

STRATEGY

To predict bond angles, first draw a correct Lewis structure for the molecule. Be certain to show all unpaired electrons. Then determine the number of regions of electron density (either 2, 3, or 4) around each atom and use that number to predict bond angles (either 180°, 120°, or 109.5°).

SOLUTION

(a) The Lewis structure for CH_3Cl shows carbon surrounded by four regions of electron density. Therefore, we predict that the distribution of electron pairs about carbon is tetrahedral, that all bond angles are 109.5°, and that the shape of CH_3Cl is tetrahedral:
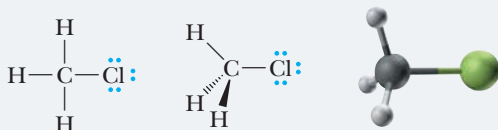
(b) The Lewis structure for $CH_2{=}CHCl$ shows each carbon surrounded by three regions of electron density. Therefore, we predict that all bond angles are 120°.

(Top view)   (Viewed along the $C{=}C$ bond)
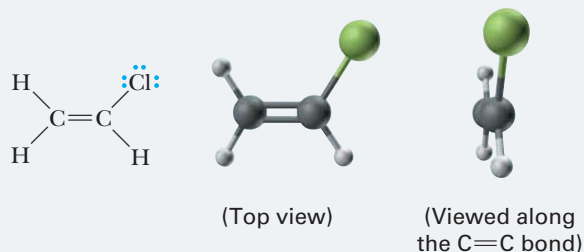
See problems 1.41–1.43

PROBLEM 1.8

Predict all bond angles for these molecules:
(a) CH_3OH **(b)** CH_2Cl_2 **(c)** H_2CO_3 (carbonic acid)

Chemical Connections 1A

BUCKYBALL: A NEW FORM OF CARBON

Many elements in the pure state can exist in different forms. We are all familiar with the fact that pure carbon is found in two forms: graphite and diamond. These forms have been known for centuries, and it was generally believed that they were the only forms of carbon having extended networks of C atoms in well-defined structures.

But that is not so! The scientific world was startled in 1985 when Richard Smalley of Rice University and Harry W. Kroto of the University of Sussex, England, and their co-workers announced that they had detected a new form of carbon with a molecular formula C_{60}. They suggested that the molecule has a structure resembling a soccer ball: 12 five-membered rings and 20 six-membered rings arranged such that each five-membered ring is surrounded by six-membered rings. This structure reminded its discoverers of a geodesic dome, a structure invented by the innovative American engineer and philosopher R. Buckminster Fuller. Therefore, the official name of the new allotrope of carbon has become fullerene. Kroto, Smalley, and Robert F. Curl were awarded the Nobel Prize for Chemistry in 1996 for their work with fullerenes. Many higher fullerenes, such as C_{70} and C_{84}, have also been isolated and studied.
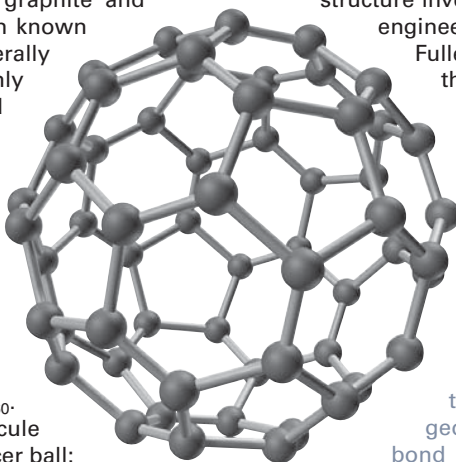
Question

Predict the bond angles about the carbon atoms in C_{60}. What geometric feature distinguishes the bond angles about each carbon in C_{60} from the bond angles of a compound containing typical carbon–carbon bonds?

1.4   How Do We Predict If a Molecule Is Polar or Nonpolar?

In Section 1.2C, we used the terms *polar* and *dipole* to describe a covalent bond in which one atom bears a partial positive charge and the other bears a partial negative charge. We also saw that we can use the difference in electronegativity between bonded atoms to determine the polarity of a covalent bond and the direction of its polarity. We can now combine our understanding of bond polarity and molecular geometry (Section 1.3) to predict the polarity of molecules.

A molecule will be polar if (1) it has polar bonds and (2) the vector sum of its bond dipoles is zero (i.e., the bond dipoles cancel each other). Consider first carbon dioxide, CO_2, a molecule with two polar carbon–oxygen double bonds. Because carbon dioxide is a linear molecule, the vector sum of its two bond dipoles is zero; therefore, this molecule is nonpolar.

two bond dipoles of equal strength will cancel when oriented in opposite directions

$\delta-$ $\delta+$ $\delta-$

$:O=C=O:$
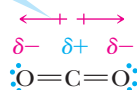
Carbon dioxide
(a nonpolar molecule)
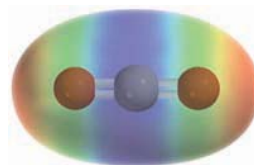
In a water molecule, each O—H bond is polar, with oxygen, the more electronegative atom, bearing a partial negative charge and each hydrogen bearing a partial positive charge. Because water is a bent molecule, the center of its partial positive charge is between the two hydrogen atoms, and the center of its partial negative charge is on oxygen. Thus, water has polar bonds and, because of its geometry, it is a polar molecule.

the vector sum (red) of the bond dipoles (blue) situates the center of partial positive charge (δ^+) in between the two hydrogen atoms

$\delta-$

O

H   H

$\delta+$
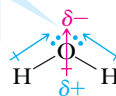
Water
(a polar molecule)
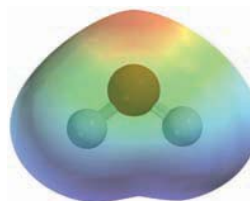
Ammonia has three polar N—H bonds, and because of its geometry, the vector sum of their bond dipoles does not equal zero. Thus, ammonia is a polar molecule.

the center of partial positive charge ($\delta+$) is midway between the three hydrogen atoms

$\delta-$

N

H   H

$\delta+$ H
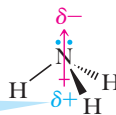
Ammonia
(a polar molecule)
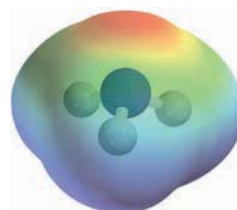
EXAMPLE 1.9

Which of these molecules are polar? For each that is polar, specify the direction of its polarity.
(a) CH_3Cl **(b)** CH_2O **(c)** C_2H_2

STRATEGY

To determine whether a molecule is polar, first determine if it has polar bonds, and if it does, determine whether the vector sum of the bond dipoles is zero. If the vector sum of the bond dipoles is not zero, the molecule is polar.

SOLUTION

Both chloromethane (CH_3Cl) and formaldehyde (CH_2O) have polar bonds and, because of their geometry, are polar molecules. Because acetylene (C_2H_2) is linear, and each of its C—H bonds is nonpolar covalent, the molecule is nonpolar.

Chloromethane
(polar)

Formaldehyde
(polar)

Acetylene
(nonpolar)
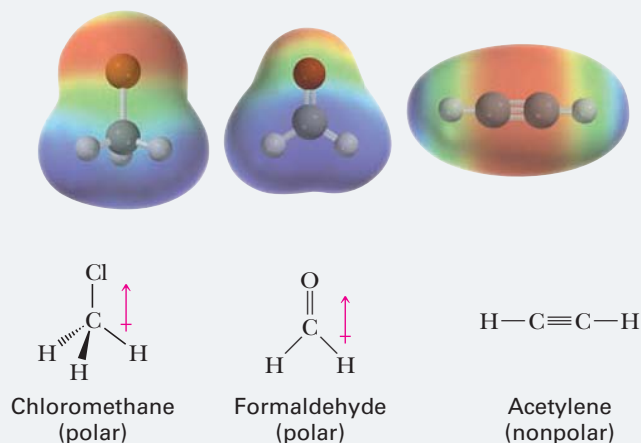
See problems 1.44, 1.46

PROBLEM 1.9

Both carbon dioxide (CO_2) and sulfur dioxide (SO_2) are triatomic molecules. Account for the fact that carbon dioxide is a nonpolar molecule, whereas sulfur dioxide is a polar molecule.

1.5 What Is Resonance?

As chemists developed a better understanding of covalent bonding in organic compounds, it became obvious that, for a great many molecules and ions, no single Lewis structure provides a truly accurate representation. For example, Figure 1.11 shows three Lewis structures for the carbonate ion, $CO_3{}^{2-}$, each of which shows carbon bonded to three oxygen atoms by a combination of one double bond and two single bonds. Each Lewis structure implies that one carbon–oxygen bond is different from the other two. This, however, is not the case; it has been shown that all three carbon–oxygen bonds are identical.

To describe the carbonate ion, as well as other molecules and ions for which no single Lewis structure is adequate, we turn to the theory of resonance.

A. The Theory of Resonance

The theory of resonance was developed by Linus Pauling in the 1930s. According to this theory, many molecules and ions are best described by writing two or more Lewis structures and considering the real molecule or ion to be a composite of these structures. We call

(a)

(b)

(c)
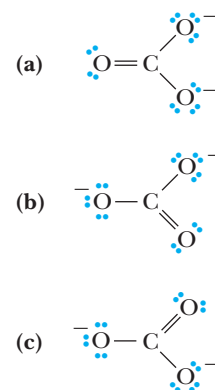
FIGURE 1.11
Three Lewis structures for the carbonate ion.

curved arrows always originate from electrons, either from bonds...

...or from unshared pairs of electrons
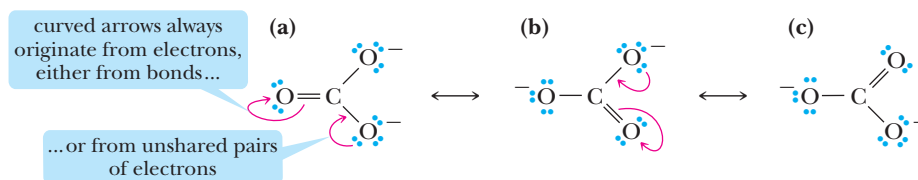
FIGURE 1.12

The carbonate ion represented as a hybrid of three equivalent contributing structures. Curved arrows show the redistribution of valence electrons between one contributing structure and the next.

Resonance contributing structures   Representations of a molecule or ion that differ only in the distribution of valence electrons.

Resonance hybrid   A molecule or ion that is best described as a composite of a number of contributing structures.

Double-headed arrow   A symbol used to connect contributing structures.

individual Lewis structures **resonance contributing structures**. We show that the real molecule or ion is a **resonance hybrid** of the various contributing structures by interconnecting them with **double-headed arrows**.

Figure 1.12 shows three resonance contributing structures for the carbonate ion. The three are equivalent, meaning that they have identical patterns of covalent bonding (each contributing structure has one double bond and two single bonds) and are of equal energy.

Use of the term *resonance* for this theory of covalent bonding might suggest to you that bonds and electron pairs constantly change back and forth from one position to another over time. This notion is not at all correct. The carbonate ion, for example, has one and only one real structure. The problem is ours: How do we draw that one real structure? The resonance method is a way to describe the real structure and at the same time retain Lewis structures with electron-pair bonds. Thus, although we realize that the carbonate ion is not accurately represented by any one contributing structure shown in Figure 1.12, we continue to represent it as one of these for convenience. We understand, of course, that what is intended is the resonance hybrid.

A final note. Do not confuse resonance contributing structures with equilibration among different species. A molecule described as a resonance hybrid is not equilibrating among individual electron configurations. Rather, the molecule has only one structure, which is best described as a hybrid of its various contributing structures. The colors of the color wheel provide a good analogy. Green is not a primary color; the colors yellow and blue are mixed to make green. You can think of molecules represented by resonance hybrids as being green. Green is not sometimes yellow and sometimes blue. Green is green! In an analogous way, a molecule described as a resonance hybrid is not sometimes one contributing structure and sometimes another. It is a single structure all of the time—the resonance hybrid.

B.   Curved Arrows and Electron Pushing

Curved arrow   A symbol used to show the redistribution of valence electrons.

Notice in Figure 1.12 that the only change from resonance contributing structure (a) to (b) and then from (b) to (c) is a redistribution of valence electrons. To show how this redistribution of valence electrons occurs, chemists use a symbol called a **curved arrow**, which shows the repositioning of an electron pair from its origin (the tail of the arrow) to its destination (the head of the arrow). The repositioning may be from an atom to an adjacent bond or from a bond to an adjacent atom.

A curved arrow is nothing more than a bookkeeping symbol for keeping track of electron pairs or, as some call it, **electron pushing**. Do not be misled by its simplicity. Electron pushing will help you see the relationship between contributing structures. Furthermore, it will help you follow bond-breaking and bond-forming steps in organic reactions. Understanding this type of electron pushing is a survival skill in organic chemistry; your success in this course depends on it.
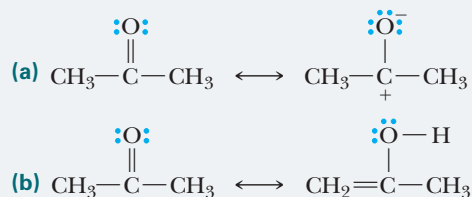
C. Rules for Writing Acceptable Resonance Contributing Structures

You must follow these four rules in writing acceptable resonance contributing structures:

1. All contributing structures must have the same number of valence electrons.
2. All contributing structures must obey the rules of covalent bonding; thus, no contributing structure may have more than 2 electrons in the valence shell of hydrogen or more than 8 electrons in the valence shell of a second-period element. Third-period elements, such as sulfur and phosphorus, may have up to 12 electrons in their valence shells.
3. The positions of all nuclei must be the same; that is, contributing structures differ only in the distribution of valence electrons.
4. All contributing structures must have the same total number of paired and unpaired electrons.

EXAMPLE   1.10

Which sets are pairs of acceptable resonance contributing structures?

(a) $CH_3-C(=O)-CH_3 \longleftrightarrow CH_3-\overset{+}{C}(-\overset{..}{\overset{..}{O}}{}^-)-CH_3$

(b) $CH_3-C(=O)-CH_3 \longleftrightarrow CH_2=C(-\overset{..}{O}-H)-CH_3$

STRATEGY

The concept being examined here is that resonance involves the redistribution of valence electrons; the connectivity of atoms does not change.

SOLUTION

(a) A pair of resonance contributing structures. They differ only in the distribution of valence electrons.

(b) Not a pair of resonance contributing structures. They differ in the arrangement of their atoms. Oxygen is bonded to a hydrogen atom in the Lewis structure on the right, but the other structure contains no such bond.

See problem 1.47

PROBLEM   1.10

Which sets are pairs of resonance contributing structures?

(a) $CH_3-C(=\overset{..}{O}:)(-\overset{..}{O}:^-) \longleftrightarrow CH_3-\overset{+}{C}(-\overset{..}{O}:^-)(-\overset{..}{O}:^-)$

(b) $CH_3-C(=\overset{..}{O}:)(-\overset{..}{O}:^-) \longleftrightarrow CH_3-C(-\overset{..}{O}:^-)(-\overset{..}{O}:)$
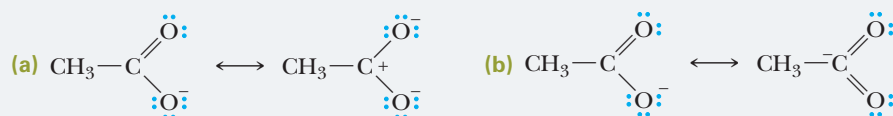
EXAMPLE   1.11

Draw the resonance contributing structure indicated by the curved arrows. Be certain to show all valence electrons and all formal charges.

(a) $CH_3-C(=\overset{..}{O}:)-H \longleftrightarrow$

(b) $H-\overset{|}{\underset{H}{C}}-C(=\overset{..}{O}:)-H \longleftrightarrow$

(c) $CH_3-\overset{..}{O}-\overset{+}{\underset{H}{C}}-H \longleftrightarrow$
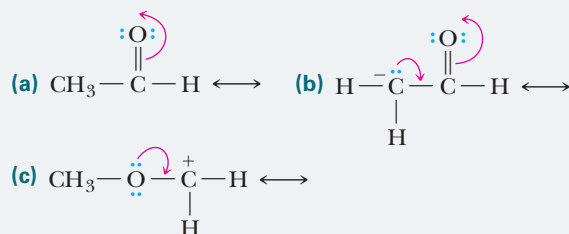
STRATEGY

Any curved arrow that points to an atom will generate a lone pair of electrons. Any curved arrow that points to a

bond will result in an additional bond on top of the original bond. That is, a single bond will become a double bond and a double bond will become a triple bond.
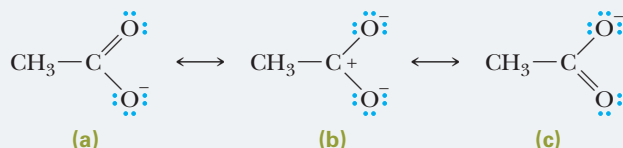
SOLUTION

(a) $CH_3-\overset{+}{C}(-\overset{..}{\overset{..}{O}}:^-)-H$

(b) $H-C(-\overset{..}{\overset{..}{O}}:^-)=\overset{|}{\underset{H}{C}}-H$

(c) $CH_3-\overset{+}{\overset{..}{O}}=C(-H)-H$ with H below
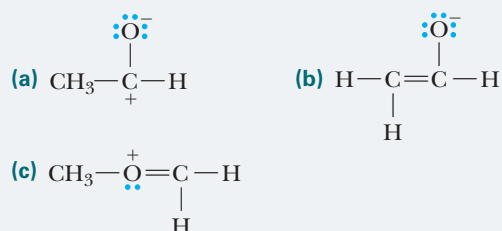
See problems 1.48, 1.50

PROBLEM　1.11

Use curved arrows to show the redistribution of valence electrons in converting resonance contributing structure (a) to (b) and then (b) to (c). Also show, using curved arrows, how (a) can be converted to (c) without going through (b).

(a)　　　　　　　(b)　　　　　　　(c)

1.6　What Is the Orbital Overlap Model of Covalent Bonding?

As much as the Lewis and VSEPR models help us to understand covalent bonding and the geometry of molecules, they leave many questions unanswered. The most important of these questions is the relation between molecular structure and chemical reactivity. For example, carbon–carbon double bonds are different in chemical reactivity from carbon–carbon single bonds. Most carbon–carbon single bonds are quite unreactive but carbon–carbon double bonds, as we will see in Chapter 5, react with a wide variety of reagents. The Lewis model and VSEPR give us no way to account for these differences. Therefore, let us turn to a newer model of covalent bonding, namely, the formation of covalent bonds by the overlap of atomic orbitals.

A.　Shapes of Atomic Orbitals
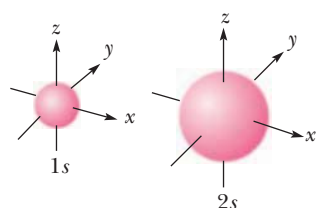
FIGURE 1.13

Shapes of 1s and 2s atomic orbitals.

One way to visualize the electron density associated with a particular orbital is to draw a boundary surface around the region of space that encompasses some arbitrary percentage of the negative charge associated with that orbital. Most commonly, we draw the boundary surface at 95%. Drawn in this manner, all s orbitals have the shape of a sphere with its center at the nucleus (Figure 1.13). Of the various s orbitals, the sphere representing the 1s orbital is the smallest. A 2s orbital is a larger sphere, and a 3s orbital is an even larger sphere.

Figure 1.14 shows the three-dimensional shapes of the three 2p orbitals, combined in one diagram to illustrate their relative orientations in space. Each 2p orbital consists of two
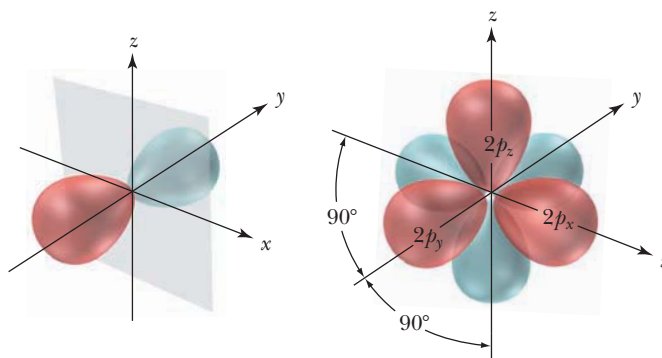
FIGURE 1.14

Shapes of $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The three 2p orbitals are mutually perpendicular. One lobe of each orbital is shown in red, the other in blue.

lobes arranged in a straight line with the nucleus in the middle. The three $2p$ orbitals are mutually perpendicular and are designated $2p_x$, $2p_y$, and $2p_z$.

B. Formation of a Covalent Bond by the Overlap of Atomic Orbitals

According to the orbital overlap model, a covalent bond is formed when a portion of an atomic orbital of one atom overlaps a portion of an atomic orbital of another atom. In forming the covalent bond in H_2, for example, two hydrogens approach each other so that their $1s$ atomic orbitals overlap to form a sigma covalent bond (Figure 1.15). A **sigma (σ) bond** is a covalent bond in which orbitals overlap along the axis joining the two nuclei.

C. Hybridization of Atomic Orbitals

The formation of a covalent bond between two hydrogen atoms is straightforward. The formation of covalent bonds with second-period elements, however, presents the following problem: In forming covalent bonds, atoms of carbon, nitrogen, and oxygen (all second-period elements) use $2s$ and $2p$ atomic orbitals. The three $2p$ atomic orbitals are at angles of 90° to one another (Figure 1.14), and if atoms of second-period elements used these orbitals to form covalent bonds, the bond angles around each would be approximately 90°. Bond angles of 90°, however, are rarely observed in organic molecules. What we find, instead, are bond angles of approximately 109.5° in molecules with only single bonds, 120° in molecules with double bonds, and 180° in molecules with triple bonds:

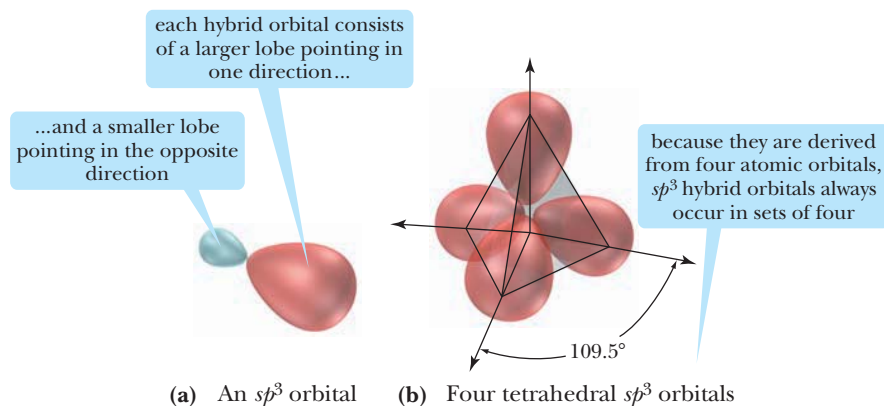**Sigma (σ) bond** A covalent bond in which the overlap of atomic orbitals is concentrated along the bond axis.

FIGURE 1.15 Formation of the covalent bond in H_2 by the overlap of the $1s$ atomic orbitals of each hydrogen.
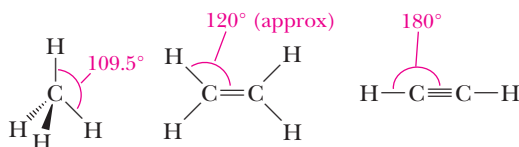
To account for these observed bond angles, Pauling proposed that atomic orbitals combine to form new orbitals, called **hybrid orbitals.** In your introductory chemistry course, you learned about several types of hybrid orbitals made up from s, p, and even d atomic orbitals. In organic chemistry, because we deal almost exclusively with elements of the first and second periods of the Periodic Table, we are mostly concerned with the hybrid orbitals that result from the combination of s and p atomic orbitals. These are aptly named the sp-type hybrid orbitals, of which there are three types. The type and number of hybrid orbitals formed are equal to the number of atomic orbitals combined. Elements of the second period form these three types of hybrid orbitals, designated sp^3, sp^2, and sp, each of which can contain up to two electrons. We review these hybrid orbitals for you here. Keep in mind that superscripts in the designation of hybrid orbitals tell you how many atomic orbitals have been combined to form the hybrid orbitals. The designation sp^3, for example, tells you that *one s* atomic orbital and *three p* atomic orbitals are combined in forming the hybrid orbital. Do not confuse this use of superscripts with how we use superscripts in writing a ground-state electron configuration—for example, $1s^2 2s^2 2p^5$ for fluorine. In the case of an electron configuration, superscripts tell you the number of electrons in each orbital or set of orbitals.

As you review each type of hybrid orbital in the following subsections, take note of (1) the number and types of atomic orbitals that were combined to make the hybrid orbitals, (2) the number of p orbitals that remain uncombined, and (3) the three-dimensional arrangement in space of the hybrid orbitals and any uncombined p orbitals. In particular, you will find that these three-dimensional arrangements will retain the names (tetrahedral, trigonal planar, linear) and bond angles (109.5°, 120°, and 180°) used to describe the shapes of molecules in our section on VSEPR (Section 1.3).
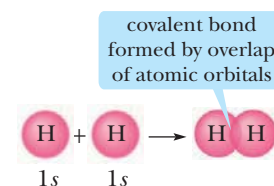
Hybrid orbital An orbital produced from the combination of two or more atomic orbitals.

FIGURE 1.16
sp^3 Hybrid orbitals. (a) Representation of a single sp^3 hybrid orbital showing two lobes of unequal size. (b) Three-dimensional representation of four sp^3 hybrid orbitals, which point toward the corners of a regular tetrahedron. The smaller lobes of each sp^3 hybrid orbital are hidden behind the larger lobes.

each hybrid orbital consists of a larger lobe pointing in one direction...

...and a smaller lobe pointing in the opposite direction

because they are derived from four atomic orbitals, sp^3 hybrid orbitals always occur in sets of four

109.5°

(a) An sp^3 orbital   **(b)** Four tetrahedral sp^3 orbitals

D. sp^3 Hybrid Orbitals: Bond Angles of Approximately 109.5°

sp^3 **Hybrid orbital**   An orbital produced by the combination of one s atomic orbital and three p atomic orbitals.

The combination of one $2s$ atomic orbital and three $2p$ atomic orbitals forms four equivalent sp^3 **hybrid orbitals** (Figure 1.16).

In Section 1.2, we described the covalent bonding in CH_4, NH_3, and H_2O in terms of the Lewis model, and in Section 1.3 we used VSEPR to predict bond angles of approximately 109.5° in each molecule. Figure 1.17 shows the bonding in these molecules in terms of the overlap of orbitals. Notice that the central atom in each compound uses four sp^3 hybrid orbitals to either form a sigma (σ) bond with a hydrogen atom or to hold unshared pairs of electrons. In each case, the orbitals are arranged tetrahedrally, while the shape that describes each molecule is based only on the arrangement of atoms.

an sp^3 hybrid orbital from carbon and a $1s$ atomic orbital from hydrogen combine to form a σ bond

unshared electron pairs occupy sp^3 hybrid orbitals that are not used for bonding

	Orbital overlap model	Orbital overlap model	Orbital overlap model
	Methane	**Ammonia**	**Water**
Arrangement of orbitals:	Tetrahedral	Tetrahedral	Tetrahedral
Shape of molecule:	Tetrahedral	Pyramidal	Bent

FIGURE 1.17
Orbital overlap models of methane, ammonia, and water.

E. sp^2 Hybrid Orbitals: Bond Angles of Approximately 120°

sp^2 **Hybrid orbital**   An orbital produced by the combination of one s atomic orbital and two p atomic orbitals.

The combination of one $2s$ atomic orbital and two $2p$ atomic orbitals forms three equivalent sp^2 **hybrid orbitals** (Figure 1.18). Because they are derived from three atomic orbitals, sp^2 hybrid orbitals always occur in sets of three. The third $2p$ atomic orbital (remember $2p_x$, $2p_y$, and $2p_z$) is not involved in hybridization and consists of two lobes lying perpendicular to the plane of the hybrid orbitals [Figure 1.18(c)].

(a) An sp^2 orbital   **(b)** Three sp^2 orbitals   **(c)**
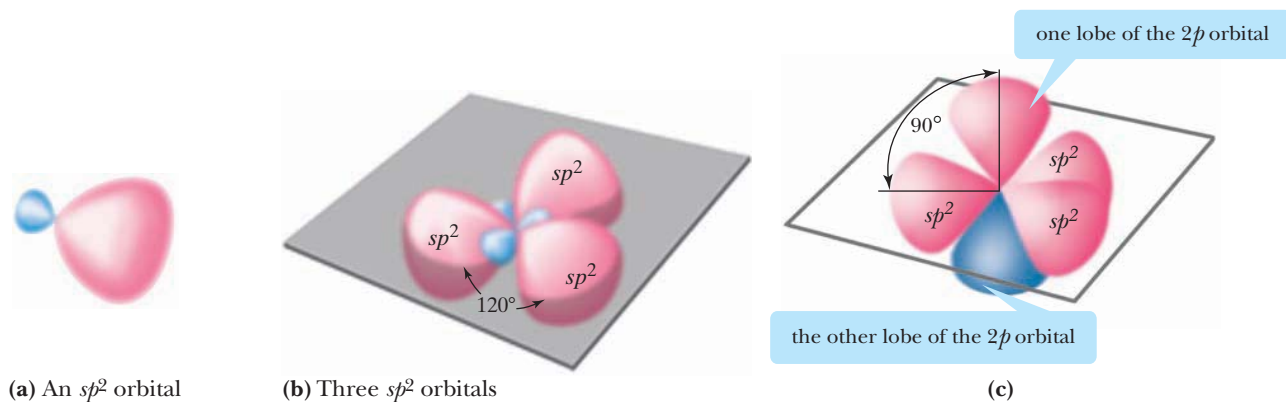
FIGURE 1.18
sp^2 Hybrid orbitals. (a) A single sp^2 hybrid orbital showing two lobes of unequal size. (b) The three sp^2 hybrid orbitals with their axes in a plane at angles of 120°. (c) The unhybridized $2p$ atomic orbital perpendicular to the plane created by the three sp^2 hybrid orbitals.

Second-period elements use sp^2 hybrid orbitals to form double bonds. Figure 1.19(a) shows a Lewis structure for ethylene, C_2H_4. A sigma bond between the carbons in ethylene forms by the overlap of sp^2 hybrid orbitals along a common axis [Figure 1.19(b)]. Each carbon also forms sigma bonds to two hydrogens. The remaining $2p$ orbitals on adjacent carbon atoms lie parallel to each other and overlap to form a pi bond [Figure 1.19(c)]. A **pi (π) bond** is a covalent bond formed by the overlap of parallel p orbitals. Because of the lesser degree of overlap of orbitals forming pi bonds compared with those forming sigma bonds, pi bonds are generally weaker than sigma bonds.

Pi (π) bond A covalent bond formed by the overlap of parallel p orbitals.

(a)   **(b)**   **(c)**
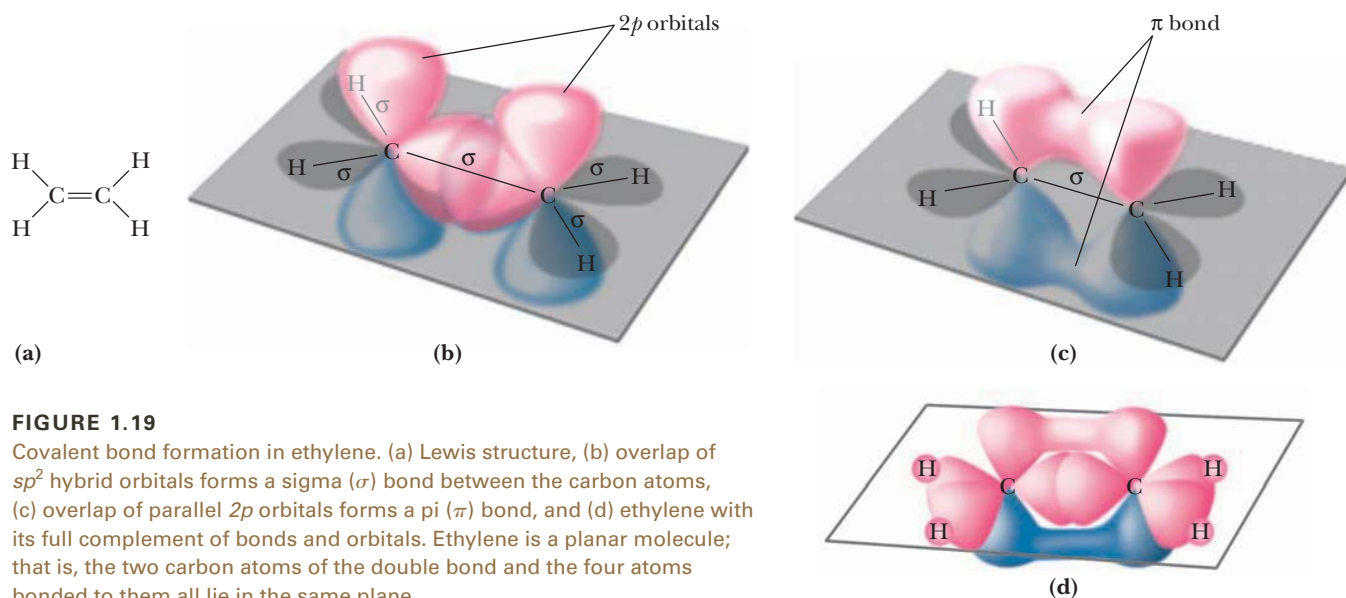
FIGURE 1.19
Covalent bond formation in ethylene. (a) Lewis structure, (b) overlap of sp^2 hybrid orbitals forms a sigma (σ) bond between the carbon atoms, (c) overlap of parallel $2p$ orbitals forms a pi (π) bond, and (d) ethylene with its full complement of bonds and orbitals. Ethylene is a planar molecule; that is, the two carbon atoms of the double bond and the four atoms bonded to them all lie in the same plane.

(d)

The orbital overlap model describes all double bonds in the same way that we have described a carbon–carbon double bond. In formaldehyde, CH_2O, the simplest organic molecule containing a carbon–oxygen double bond, carbon forms sigma bonds to two hydrogens by the overlap of an sp^2 hybrid orbital of carbon and the $1s$ atomic orbital of

Formaldehyde

$$\begin{array}{c} H \\ \diagdown \\ C = \ddot{O}: \\ \diagup \\ H \end{array}$$

(a) (b) (c) (d)
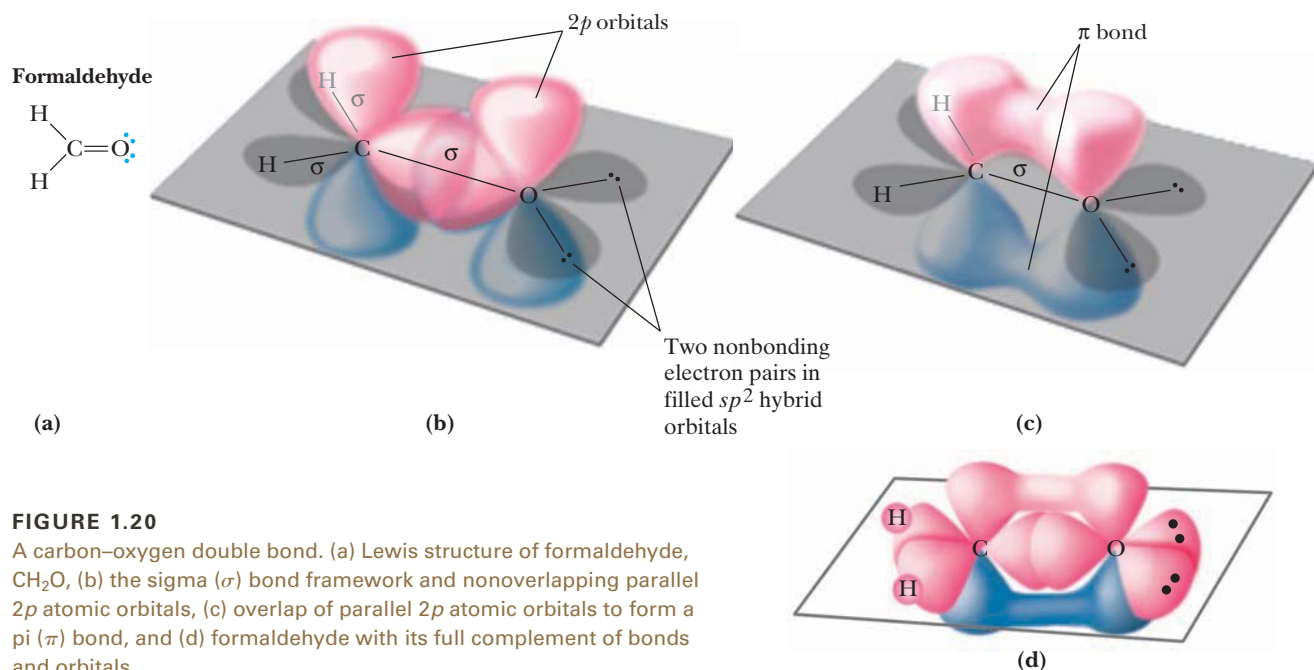
FIGURE 1.20
A carbon–oxygen double bond. (a) Lewis structure of formaldehyde, CH_2O, (b) the sigma (σ) bond framework and nonoverlapping parallel $2p$ atomic orbitals, (c) overlap of parallel $2p$ atomic orbitals to form a pi (π) bond, and (d) formaldehyde with its full complement of bonds and orbitals.

each hydrogen. Carbon and oxygen are joined by a sigma bond formed by the overlap of sp^2 hybrid orbitals and a pi bond formed by the overlap of unhybridized $2p$ atomic orbitals (Figure 1.20).

_sp_ Hybrid orbital A hybrid atomic orbital produced by the combination of one s atomic orbital and one p atomic orbital.

F. _sp_ Hybrid Orbitals: Bond Angles of Approximately 180°

The combination of one $2s$ atomic orbital and one $2p$ atomic orbital forms two equivalent **_sp_ hybrid orbitals**. Because they are derived from two atomic orbitals, _sp_ hybrid orbitals always occur in sets of two (Figure 1.21).

(a) (b) (c) (d)
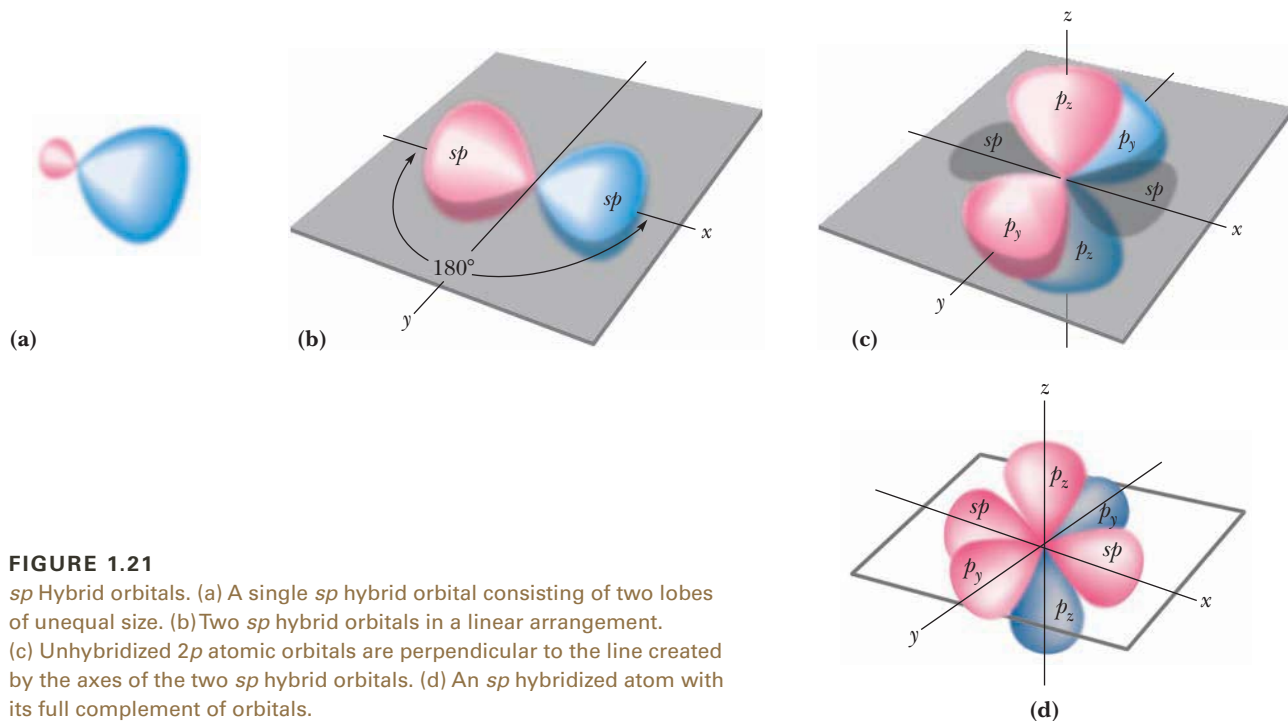
FIGURE 1.21
_sp_ Hybrid orbitals. (a) A single _sp_ hybrid orbital consisting of two lobes of unequal size. (b) Two _sp_ hybrid orbitals in a linear arrangement. (c) Unhybridized $2p$ atomic orbitals are perpendicular to the line created by the axes of the two _sp_ hybrid orbitals. (d) An _sp_ hybridized atom with its full complement of orbitals.

Acetylene

$H-C{\equiv}C-H$

(a)

(b)

(c)
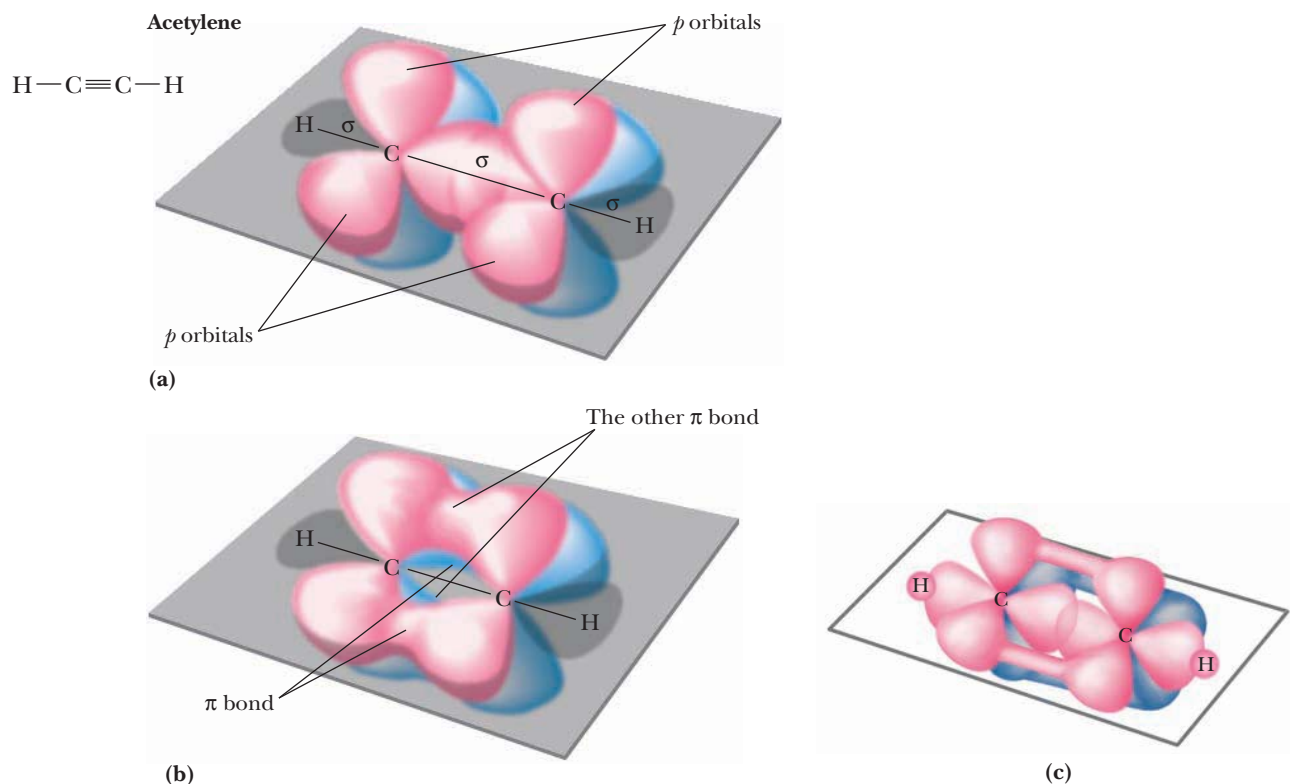
FIGURE 1.22
Covalent bonding in acetylene. (a) The sigma bond framework shown along with nonoverlapping 2p atomic orbitals. (b) Formation of two pi bonds by overlap of two sets of parallel 2p atomic orbitals. (c) Acetylene with its full complement of bonds and orbitals.

Figure 1.22 shows a Lewis structure and an orbital overlap diagram for acetylene, C_2H_2. A carbon–carbon triple bond consists of one sigma bond and two pi bonds. The sigma bond is formed by the overlap of sp hybrid orbitals. One pi bond is formed by the overlap of a pair of parallel 2p atomic orbitals. The second pi bond is formed by the overlap of a second pair of parallel 2p atomic orbitals.

Table 1.8 summarizes the relationship among the number of groups bonded to carbon, orbital hybridization, and the types of bonds involved.

TABLE 1.8 **Covalent Bonding of Carbon**

Groups Bonded to Carbon	Orbital Hybridization	Predicted Bond Angles	Types of Bonds to Carbon	Example	Name
4	sp^3	109.5°	four sigma bonds		ethane
3	sp^2	120°	three sigma bonds and one pi bond		ethylene
2	sp	180°	two sigma bonds and two pi bonds	$H-C{\equiv}C-H$	acetylene

EXAMPLE   1.12

Describe the bonding in acetic acid, CH_3COOH, in terms of the orbitals involved, and predict all bond angles.

STRATEGY

First draw a Lewis structure for acetic acid and then determine the number of regions of electron density about each atom.

SOLUTION

The following are three identical Lewis structures. Labels on the first structure point to atoms and show hybridization. Labels on the second structure point to bonds and show the type of bond, either sigma or pi.

Labels on the third structure point to atoms and show bond angles about each atom as predicted by valence-shell electron-pair repulsion.
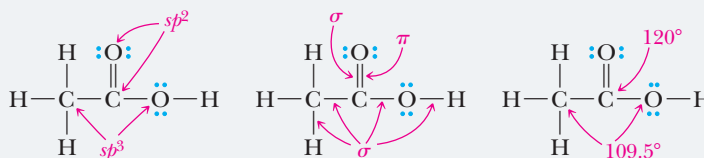
See problem 1.51

PROBLEM   1.12

Describe the bonding in these molecules in terms of the atomic orbitals involved, and predict all bond angles:

(a) $CH_3CH{=}CH_2$
(b) CH_3NH_2

1.7   What Are Functional Groups?

Over 10 million organic compounds have been discovered or made by organic chemists! Surely it would seem to be an almost impossible task to learn the physical and chemical properties of this many compounds. Fortunately, the study of organic compounds is not as formidable a task as you might think. While organic compounds can undergo a wide variety of chemical reactions, only certain portions of their structure are changed in any particular reaction. The part of an organic molecule that undergoes chemical reactions is called a **functional group**, and, as we will see, the same functional group, in whatever organic molecule we find it, undergoes the same types of chemical reactions. Therefore, you do not have to study the chemical reactions of even a fraction of the 10 million known organic compounds. Instead you need only to identify a few characteristic types of functional groups and then study the chemical reactions that each undergoes.

Functional group   An atom or a group of atoms within a molecule that shows a characteristic set of physical and chemical properties.

Functional groups are also important because they are the units by which we divide organic compounds into families of compounds. For example, we group those compounds which contain an —OH (hydroxyl) group bonded to a tetrahedral carbon into a family called alcohols, and compounds containing a —COOH (carboxyl) group into a family called carboxylic acids. In Table 1.9, we introduce five of the most common functional groups. A complete list of all functional groups we will study is on the inside front cover of the text.

At this point, our concern is only pattern recognition—that is, how to recognize these five functional groups when you see them and how to draw structural formulas of molecules containing them.

Finally, functional groups serve as the basis for naming organic compounds. Ideally, each of the 10 million or more organic compounds must have a name that is different from every other compound.

To summarize, functional groups

- are sites of chemical reaction; a particular functional group, in whatever compound we find it, undergoes the same types of chemical reactions.
- determine, in large measure, the physical properties of a compound.
- are the units by which we divide organic compounds into families.
- serve as a basis for naming organic compounds.

TABLE 1.9 **Five Common Functional Groups**

Functional Group	Name of Group	Present In	Example	Name of Example
$-OH$	hydroxyl	alcohols	CH_3CH_2OH	Ethanol
$-NH_2$	amino	amines	$CH_3CH_2NH_2$	Ethanamine
$-\overset{\overset{\displaystyle O}{\|\|}}{C}-H$	carbonyl	aldehydes	$CH_3\overset{\overset{\displaystyle O}{\|\|}}{C}H$	Ethanal
$-\overset{\overset{\displaystyle O}{\|\|}}{C}-$	carbonyl	ketones	$CH_3\overset{\overset{\displaystyle O}{\|\|}}{C}CH_3$	Acetone
$-\overset{\overset{\displaystyle O}{\|\|}}{C}-OH$	carboxyl	carboxylic acids	$CH_3\overset{\overset{\displaystyle O}{\|\|}}{C}OH$	Acetic acid

A. Alcohols

The functional group of an **alcohol** is an **—OH (hydroxyl)** group bonded to a tetrahedral (sp^3 hybridized) carbon atom. In the general formula that follows, we use the symbol R to indicate either a hydrogen or another carbon group. The important point in the general structure is that the —OH group is bonded to a tetrahedral carbon atom:

Hydroxyl group An —OH group.

Functional group (R=H or carbon group) · Structural formula · Condensed structural formula
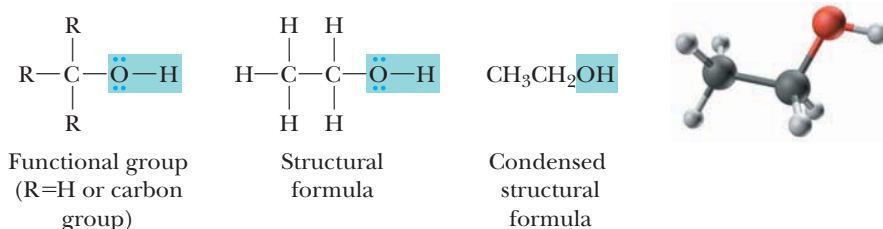
The rightmost representation of this alcohol is a **condensed structural formula**, CH_3CH_2OH. In a condensed structural formula, CH_3 indicates a carbon bonded to three hydrogens, CH_2 indicates a carbon bonded to two hydrogens, and CH indicates a carbon bonded to one hydrogen. We generally do not show unshared pairs of electrons in a condensed structural formula.

Alcohols are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)**, depending on the number of carbon atoms bonded to the carbon bearing the —OH group:

A 1° alcohol · A 2° alcohol · A 3° alcohol
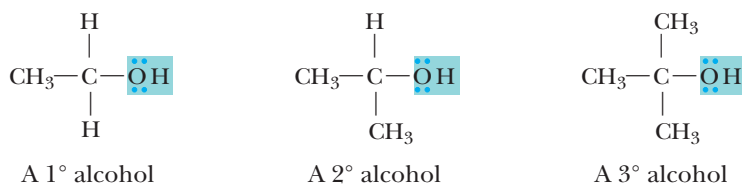
EXAMPLE 1.13

Write condensed structural formulas for the two alcohols with the molecular formula C_3H_8O. Classify each as primary, secondary, or tertiary.

STRATEGY

First, bond the three carbon atoms in a chain with the —OH (hydroxyl) group bonded to either an end carbon or the middle carbon of the chain. Then, to complete each structural formula, add seven hydrogens so that each carbon has four bonds to it.
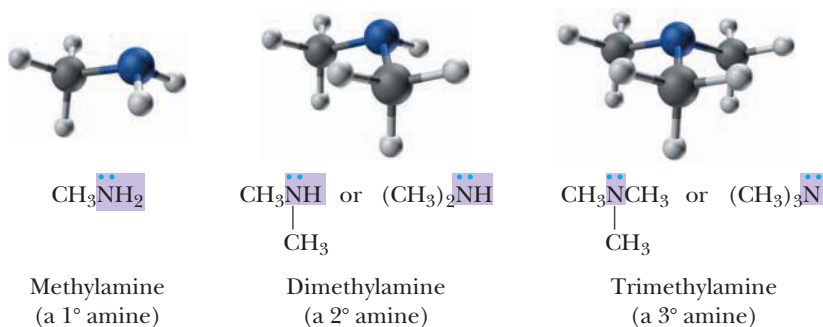
SOLUTION

a 1° alcohol: the carbon bearing the —OH group is bonded to just one carbon

$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{..}{\underset{..}{O}}-H$ or $CH_3CH_2CH_2OH$

a 2° alcohol: the carbon bearing the —OH group is bonded to two other carbons

$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$ or $CH_3\overset{OH}{\underset{|}{C}}HCH_3$
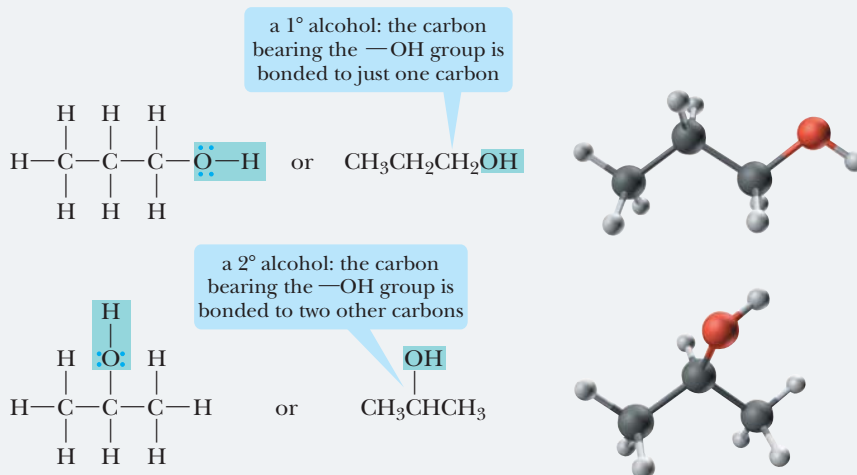
See problems 1.53–1.56, 1.58, 1.59

PROBLEM 1.13

Write condensed structural formulas for the four alcohols with the molecular formula $C_4H_{10}O$. Classify each as primary, secondary, or tertiary.

B. Amines

Amino group An sp^3 hybridized nitrogen atom bonded to one, two, or three carbon groups.

The functional group of an amine is an **amino group**—a nitrogen atom bonded to one, two, or three carbon atoms. In a **primary (1°) amine**, nitrogen is bonded to one carbon atom. In a **secondary (2°) amine**, it is bonded to two carbon atoms, and in a **tertiary (3°) amine**, it is bonded to three carbon atoms. The second and third structural formulas below can be written in a more abbreviated form by collecting the CH_3 groups and writing them as $(CH_3)_2NH$ and $(CH_3)_3N$, respectively.

$CH_3\overset{..}{N}H_2$

$CH_3\overset{..}{\underset{\underset{\displaystyle CH_3}{|}}{N}}H$ or $(CH_3)_2\overset{..}{N}H$

$CH_3\overset{..}{\underset{\underset{\displaystyle CH_3}{|}}{N}}CH_3$ or $(CH_3)_3\overset{..}{N}$

Methylamine
(a 1° amine)

Dimethylamine
(a 2° amine)

Trimethylamine
(a 3° amine)

EXAMPLE 1.14

Write condensed structural formulas for the two primary (1°) amines with the molecular formula C_3H_9N.

STRATEGY

For a primary amine, draw a nitrogen atom bonded to two hydrogens and one carbon. The nitrogen may be bonded to the three-carbon chain in two different ways. Then add the seven hydrogens to give each carbon four bonds and give the correct molecular formula.

SOLUTION

$CH_3CH_2CH_2NH_2$

$\overset{NH_2}{\underset{}{CH_3CHCH_3}}$
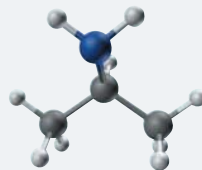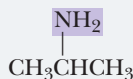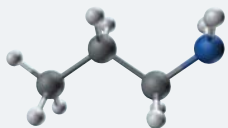
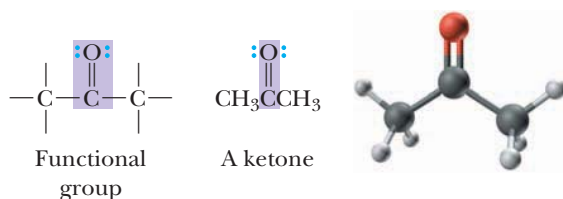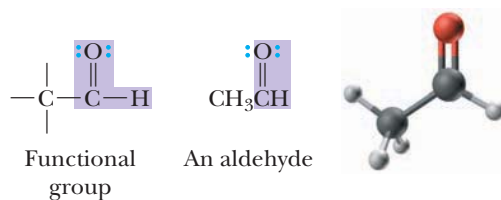**PROBLEM   1.14**

Write condensed structural formulas for the three secondary amines with molecular formula $C_4H_{11}N$.

C. Aldehydes and Ketones

Both aldehydes and ketones contain a **C=O (carbonyl)** group. The **aldehyde** functional group contains a carbonyl group bonded to a hydrogen. In formaldehyde, CH_2O, the simplest aldehyde, the carbonyl carbon is bonded to two hydrogen atoms. In a condensed structural formula, the aldehyde group may be written showing the carbon–oxygen double bond as CH=O, or, alternatively, it may be written —CHO. The functional group of a **ketone** is a carbonyl group bonded to two carbon atoms.

Carbonyl group   A C=O group.

$$-\overset{\overset{\displaystyle :O:}{\|}}{\underset{}{C}}-\overset{}{\underset{}{C}}-H$$

Functional
group

$$CH_3\overset{\overset{\displaystyle :O:}{\|}}{CH}$$

An aldehyde

$$-\overset{}{\underset{}{C}}-\overset{\overset{\displaystyle :O:}{\|}}{\underset{}{C}}-\overset{}{\underset{}{C}}-$$

Functional
group

$$CH_3\overset{\overset{\displaystyle :O:}{\|}}{C}CH_3$$

A ketone

EXAMPLE   1.15

Write condensed structural formulas for the two aldehydes with the molecular formula C_4H_8O.

STRATEGY

First, draw the functional group of an aldehyde and add the remaining carbons, which in this case may be bonded in two different ways. Then, add seven hydrogens to complete the four bonds of each carbon and give the correct molecular formula: Note that the aldehyde group may be written showing the carbon–oxygen double bond as C=O, or, alternatively, it may be written —CHO.

SOLUTION

$$CH_3CH_2CH_2\overset{\overset{\displaystyle :O:}{\|}}{CH}$$

or

$$CH_3CH_2CH_2\overset{..}{C}\overset{..}{H}\overset{..}{O}$$

$$CH_3\overset{\overset{\displaystyle :O:}{\|}}{\underset{\underset{CH_3}{|}}{CH}}CH$$

or

$$(CH_3)_2CHC\overset{..}{H}\overset{..}{O}$$
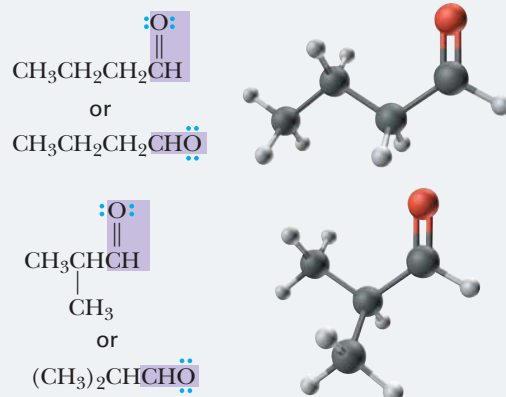
PROBLEM   1.15

Write condensed structural formulas for the three ketones with the molecular formula $C_5H_{10}O$.

D.   Carboxylic Acids

Carboxyl group   A —COOH group.

The functional group of a carboxylic acid is a —**COOH** (**carboxyl**: *carb*onyl + hydr*oxyl*) group:

Functional group   Acetic acid
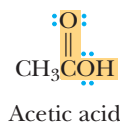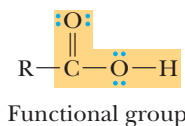
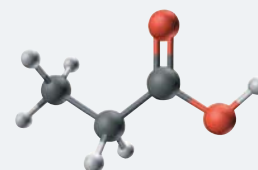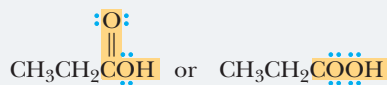
EXAMPLE   1.16

Write a condensed structural formula for the single carboxylic acid with the molecular formula $C_3H_6O_2$.

STRATEGY

First draw the carboxyl group and add the two remaining carbons. Finally, add the five remaining hydrogens in such a way that each carbon in the molecule has four bonds to it.

SOLUTION

CH_3CH_2COH or CH_3CH_2COOH

See problems 1.53–1.56, 1.58, 1.59

PROBLEM   1.16

Write condensed structural formulas for the two carboxylic acids with the molecular formula $C_4H_8O_2$.

SUMMARY OF KEY QUESTIONS

1.1   How Do We Describe the Electronic Structure of Atoms?

- An atom consists of a small, dense nucleus and electrons concentrated about the nucleus in regions of space called **shells**.
- Each shell can contain as many as $2n^2$ electrons, where n is the number of the shell. Each shell is subdivided into regions of space called **orbitals**.
- The first shell ($n = 1$) has a single s orbital and can hold $2 \times 1^2 = 2$ electrons.

- The second shell ($n = 2$) has one s orbital and three p orbitals and can hold $2 \times 2^2 = 8$ electrons.
- The **Lewis structure** of an element shows the symbol of the element surrounded by a number of dots equal to the number of electrons in its **valence shell**.

1.2   What Is the Lewis Model of Bonding?

- According to the **Lewis model of bonding**, atoms bond together in such a way that each atom participating in a chemical bond acquires a completed valence-shell electron configuration resembling that of the noble gas nearest it in atomic number.
- Atoms that lose sufficient electrons to acquire a completed valence shell become **cations**; atoms that gain sufficient electrons to acquire a completed valence shell become **anions**.

- An **ionic bond** is a chemical bond formed by the attractive force between an anion and a cation.
- A **covalent bond** is a chemical bond formed by the sharing of electron pairs between atoms.
- The tendency of main-group elements (those of Groups 1A–7A) to achieve an outer shell of eight **valence electrons** is called the **octet rule**.

- **Electronegativity** is a measure of the force of attraction by an atom for electrons it shares in a chemical bond with another atom. Electronegativity increases from left to right and from bottom to top in the Periodic Table.
- A **Lewis structure** for a molecule or an ion must show (1) the correct arrangement of atoms, (2) the correct num-

ber of valence electrons, (3) no more than two electrons in the outer shell of hydrogen, (4) no more than eight electrons in the outer shell of any second-period element, and (5) all formal charges.
- **Formal charge** is the charge on an atom in a molecule or polyatomic ion.

1.3   How Do We Predict Bond Angles and the Shapes of Molecules?

- **Valence-shell electron pair repulsion (VSEPR)** predicts bond angles of 109.5° about atoms surrounded by four regions of electron density, bond angles of 120° about atoms surrounded by three regions of electron density,

and bond angles of 180° about atoms surrounded by two regions of electron density.
- The common shapes of small molecules include **tetrahedral, pyramidal, linear**, and **bent**.

1.4   How Do We Predict If a Molecule Is Polar or Nonpolar?

- As a rough guideline, we say that a **nonpolar covalent bond** is a covalent bond in which the difference in electronegativity between the bonded atoms is less than 0.5 unit.
- A **polar covalent bond** is a covalent bond in which the difference in electronegativity between the bonded atoms is

between 0.5 and 1.9 units. In a polar covalent bond, the more electronegative atom bears a partial negative charge ($\delta-$) and the less electronegative atom bears a partial positive charge ($\delta+$).
- A molecule is polar if the vector sum of its bond **dipoles** equals zero.

1.5   What Is Resonance?

- According to the **theory of resonance**, a molecule or ion for which no single Lewis structure is adequate is best described by writing two or more **resonance contributing structures** and considering the real molecule or ion to be a **hybrid** of the various contributing structures.
- Resonance contributing structures are interconnected by **double-headed arrows**.

- We show how valence electrons are redistributed from one contributing structure to the next by **curved arrows**. A curved arrow extends from where the electrons are initially shown (on an atom or in a covalent bond) to their new location (an adjacent atom or an adjacent covalent bond).
- The use of curved arrows in this way is commonly referred to as **electron pushing**.

1.6   What Is the Orbital Overlap Model of Covalent Bonding?

- According to the **orbital overlap model**, the formation of a covalent bond results from the overlap of **atomic orbitals**.
- The greater the overlap, the stronger is the resulting covalent bond.
- The combination of atomic orbitals is called **hybridization**, and the resulting orbitals are called **hybrid orbitals**.
- The combination of one 2*s* atomic orbital and three 2*p* atomic orbitals produces four equivalent **sp^3 hybrid orbitals**, each pointing toward a corner of a regular tetrahedron at angles of 109.5°.
- The combination of one 2*s* atomic orbital and two 2*p* atomic orbitals produces three equivalent **sp^2 hybrid orbitals**, the axes of which lie in a plane at angles of 120°.

Most C═C, C═O, and C═N **double bonds** are a combination of one **sigma (σ) bond** formed by the overlap of **sp^2 hybrid orbitals** and one **pi (π) bond** formed by the overlap of parallel 2*p* atomic orbitals.
- The combination of one 2*s* atomic orbital and one 2*p* atomic orbital produces two equivalent **sp hybrid orbitals**, the axes of which lie in a plane at an angle of 180°.
- All C≡C triple bonds are a combination of one sigma bond formed by the overlap of *sp* hybrid orbitals and two pi bonds formed by the overlap of two pairs of parallel 2*p* atomic orbitals.
- Hybrid orbitals can be arranged in tetrahedral, **trigonal planar**, and linear geometries.

1.7   What Are Functional Groups?

- **Functional groups** are characteristic structural units by which we divide organic compounds into classes and that serve as a basis for nomenclature. They are also sites of chemical reactivity; a particular functional group, in whatever compound we find it, undergoes the same types of reactions.
- Important functional groups for us at this stage in the course are

- the **hydroxyl group** of **1°, 2°**, and **3° alcohols**
- the **amino group** of **1°, 2°**, and **3° amines**
- the **carbonyl group** of **aldehydes** and **ketones**
- the **carboxyl group** of **carboxylic acids**

QUICK QUIZ

Answer true or false to the following questions to assess your general knowledge of the concepts in this chapter. If you have difficulty with any of them, you should review the appropriate section in the chapter (shown in parentheses) before attempting the more challenging end-of-chapter problems.

1. These bonds are arranged in order of increasing polarity $C-H < N-H < O-H$. (1.2)

2. All atoms in a contributing structure must have complete valence shells. (1.5)

3. An electron in a $1s$ orbital is held closer to the nucleus than an electron in a $2s$ orbital. (1.1)

4. A sigma bond and a pi bond have in common that each can result from the overlap of atomic orbitals. (1.6)

5. The molecular formula of the smallest aldehyde is C_3H_6O, and that of the smallest ketone is also C_3H_6O. (1.7)

6. To predict whether a covalent molecule is polar or nonpolar, you must know both the polarity of each covalent bond and the geometry (shape) of the molecule. (1.4)

7. An orbital is a region of space that can hold two electrons. (1.1)

8. In the ground-state electron configuration of an atom, only the lowest-energy orbitals are occupied. (1.1)

9. Electronegativity generally increases with atomic number. (1.2)

10. Paired electron spins means that the two electrons are aligned with their spins North Pole to North Pole and South Pole to South Pole. (1.1)

11. According to the Lewis model of bonding, atoms bond together in such a way that each atom participating in the bond acquires an outer-shell electron configuration matching that of the noble gas nearest it in atomic number. (1.2)

12. A primary amine contains one $N-H$ bond, a secondary amine contains two $N-H$ bonds, and a tertiary amine contains three $N-H$ bonds. (1.7)

13. All bond angles in sets of resonance contributing structures must be the same. (1.5)

14. Electronegativity is a measure of an atom's attraction for electrons it shares in a chemical bond with another atom. (1.2)

15. An orbital can hold a maximum of two electrons with their spins paired. (1.1)

16. Fluorine in the upper right corner of the Periodic Table is the most electronegative element; hydrogen, in the upper left corner, is the least electronegative element. (1.2)

17. A primary alcohol has one $-OH$ group, a secondary alcohol has two $-OH$ groups, and a tertiary alcohol has three $-OH$ groups. (1.7)

18. H_2O and NH_3 are polar molecules, but CH_4 is nonpolar. (1.4)

19. Electronegativity generally increases from top to bottom in a column of the Periodic Table. (1.2)

20. All contributing structures must have the same number of valence electrons. (1.5)

21. A carbon–carbon double bond is formed by the overlap of sp^2 hybrid orbitals, and a triple bond is formed by the overlap of sp^3 hybrid orbitals. (1.6)

22. A covalent bond formed by sharing two electrons is called a double bond. (1.2)

23. The functional groups of an alcohol, an aldehyde, and a ketone have in common the fact that each contains a single oxygen atom. (1.7)

24. Electrons in atoms are confined to regions of space called principal energy levels. (1.1)

25. In a single bond, two atoms share one pair of electrons; in a double bond, they share two pairs of electrons; and in a triple bond, they share three pairs of electrons. (1.2)

26. The Lewis structure for ethene, C_2H_4, must show eight valence electrons. (1.2)

27. The Lewis structure for formaldehyde, CH_2O, must show eight valence electrons. (1.2)

28. The letters VSEPR stand for valence-shell electron pair repulsion. (1.3)

29. In predicting bond angles about a central atom in a covalent bond, VSEPR considers only shared pairs (pairs of electrons involved in forming covalent bonds). (1.3)

30. An sp hybrid orbital may contain a maximum of four electrons, an sp^2 hybrid orbital may contain a maximum of six valence electrons, and an sp^3 hybrid orbital may contain a maximum of eight electrons. (1.6)

31. For a central atom surrounded by three regions of electron density, VSEPR predicts bond angles of $360°/3 = 120°$. (1.3)

32. The three $2p$ orbitals are aligned parallel to each other. (1.1)

33. All molecules with polar bonds are polar. (1.4)

34. Electronegativity generally increases from left to right across a period of the Periodic Table. (1.2)

35. A compound with the molecular formula C_3H_6O may be an aldehyde, a ketone, or a carboxylic acid. (1.7)

36. Dichloromethane, CH_2Cl_2 is polar, but tetrachloromethane, CCl_4, is nonpolar. (1.4)

37. A covalent bond is formed between atoms whose difference in electronegativity is less than 1.9. (1.2)

38. Each principal energy level can hold two electrons. (1.1)

39. Atoms that share electrons to achieve filled valence shells form covalent bonds. (1.2)

40. Contributing structures differ only in the distribution of valence electrons. (1.5)

41. In creating hybrid orbitals (sp, sp^2, and sp^3), the number of hybrid orbitals created is equal to the number of atomic orbitals hybridized. (1.6)

42. VSEPR treats the two electron pairs of a double bond and the three electron pairs of a triple bond as one region of electron density. (1.3)

43. If the difference in electronegativity between two atoms is zero (they have identical electronegativities), then the two atoms will not form a covalent bond. (1.2)

44. A carbon–carbon triple bond is a combination of one sigma bond and two pi bonds. (1.6)

45. A carbon–carbon double bond is a combination of two sigma bonds. (1.6)

46. An s orbital has the shape of a sphere with the center of the sphere at the nucleus. (1.1)

47. A functional group is a group of atoms in an organic molecule that undergoes a predictable set of chemical reactions. (1.7)

48. In a polar covalent bond, the more electronegative atom has a partial negative charge ($\delta-$) and the less electronegative atom has a partial positive charge ($\delta+$). (1.2)

49. Electronegativity depends on both the nuclear charge and the distance of the valence electrons from the nucleus. (1.2)

50. There are two alcohols with the molecular formula C_3H_8O. (1.7)

51. In methanol, CH_3OH, the O—H bond is more polar than the C—O bond. (1.4)

52. The molecular formula of the smallest carboxylic acid is $C_2H_6O_2$. (1.7)

53. Each $2p$ orbital has the shape of a dumbbell with the nucleus at the midpoint of the dumbbell. (1.1)

54. Atoms that lose electrons to achieve a filled valence shell become cations and form ionic bonds with anions. (1.1)

55. There are three amines with the molecular formula C_3H_9N. (1.7)

Answers: (1) T (2) F (3) T (4) T (5) F (6) T (7) T (8) T (9) T (10) F
(11) T (12) F (13) T (14) T (15) T (16) T (17) F (18) T (19) T (20) T
(21) F (22) F (23) T (24) T (25) T (26) T (27) F (28) T (29) F (30) F
(31) T (32) T (33) F (34) T (35) F (36) T (37) T (38) T (39) T (40) T
(41) T (42) T (43) T (44) T (45) T (46) F (47) T (48) T (49) T (50) T
(51) T (52) T (53) T (54) T (55) F

Detailed explanations for many of these answers can be found in the accompanying Solutions Manual.

PROBLEMS

A problem marked with an asterisk indicates an applied "real-world" problem. Answers to problems whose numbers are printed in blue are given in Appendix D.

Section 1.1 Electronic Structure of Atoms

1.17 Write the ground-state electron configuration for each element: **(See Example 1.1)**

(a) Sodium   (e) Potassium
(b) Magnesium   (f) Aluminum
(c) Oxygen   (g) Phosphorus
(d) Nitrogen   (h) Argon

1.18 Write the ground-state electron configuration for each ion: **(See Example 1.1)**

(a) Na^+ (e) H^-
(b) Cl^- (f) K^+
(c) Mg^{2+} (g) Br^+
(d) H^+ (h) Li^+

1.19 Which element has the ground-state electron configuration **(See Example 1.1)**

(a) $1s^22s^22p^63s^23p^4$
(b) $1s^22s^22p^4$

1.20 Which element or ion does not have the ground-state electron configuration $1s^22s^22p^63s^23p^6$? **(See Example 1.1)**

(a) S^{2-} (b) Cl^- (c) Ar
(d) Ca^{2+} (e) K

1.21 Define *valence shell* and *valence electron*. Why are valence electrons more important to bonding than other types of electrons?

1.22 How many electrons are in the valence shell of each element? **(See Example 1.2)**

(a) Carbon   (b) Nitrogen   (c) Chlorine
(d) Aluminum   (e) Oxygen

1.23 How many electrons are in the valence shell of each ion? **(See Example 1.2)**

(a) H^+ (b) H^- (c) F^- (d) Cl^+

Section 1.2 Lewis Structures

1.24 Judging from their relative positions in the Periodic Table, which element in each set is more electronegative? **(See Example 1.3)**

(a) Carbon or nitrogen   (b) Chlorine or bromine
(c) Oxygen or sulfur   (d) Oxygen or phosphorus

1.25 Which compounds have nonpolar covalent bonds, which have polar covalent bonds, and which have ionic bonds? **(See Example 1.4)**

(a) LiF   (b) CH_3F (c) $MgCl_2$ (d) HCl

1.26 Using the symbols $\delta-$ and $\delta+$, indicate the direction of polarity, if any, in each covalent bond: **(See Example 1.5)**

(a) C—Cl   (b) S—H   (c) C—S   (d) P—H

1.27 Write Lewis structures for each of the following compounds, showing all valence electrons (none of the compounds contains a ring of atoms): **(See Example 1.6)**

(a) Hydrogen peroxide, H_2O_2
(b) Hydrazine, N_2H_4
(c) Methanol, CH_3OH
(d) Methanethiol, CH_3SH
(e) Methanamine, CH_3NH_2
(f) Chloromethane, CH_3Cl
(g) Dimethyl ether, CH_3OCH_3
(h) Ethane, C_2H_6
(i) Ethylene, C_2H_4
(j) Acetylene, C_2H_2
(k) Carbon dioxide, CO_2
(l) Formaldehyde, CH_2O
(m) Acetone, CH_3COCH_3
(n) Carbonic acid, H_2CO_3
(o) Acetic acid, CH_3COOH

1.28 Write Lewis structures for these ions: **(See Example 1.6)**

(a) Bicarbonate ion, HCO_3^-
(b) Carbonate ion, CO_3^{2-}
(c) Acetate ion, CH_3COO^-
(d) Chloride ion, Cl^-

1.29 Why are the following molecular formulas impossible?

(a) CH_5 (b) C_2H_7 (c) H_2^{2+}

1.30 Following the rule that each atom of carbon, oxygen, and nitrogen reacts to achieve a complete outer shell of eight valence electrons, add unshared pairs of electrons as necessary to complete the valence shell of each atom in the following ions.

Then, assign formal charges as appropriate: **(See Example 1.7)**
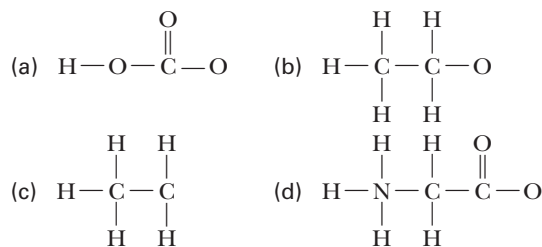
1.31 The following Lewis structures show all valence electrons. Assign formal charges in each structure as appropriate. **(See Example 1.7)**
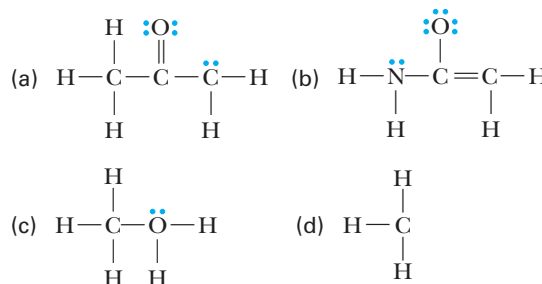
1.32 Each compound contains both ionic and covalent bonds. Draw a Lewis structure for each, and show by charges which bonds are ionic and by dashes which bonds are covalent. **(See Example 1.7)**

(a) NaOH   (b) $NaHCO_3$ (c) NH_4Cl
(d) CH_3COONa (e) CH_3ONa

1.33 Silver and oxygen can form a stable compound. Predict the formula of this compound, and state whether the compound consists of ionic or covalent bonds.

1.34 Draw Lewis structures for the following molecule and ions: **(See Example 1.7)**

(a) NH_3 (b) NH_4^+ (c) NH_2^-

Section 1.2   Polarity of Covalent Bonds

1.35 Which statement is true about electronegativity?

(a) Electronegativity increases from left to right in a period of the Periodic Table.
(b) Electronegativity increases from top to bottom in a column of the Periodic Table.
(c) Hydrogen, the element with the lowest atomic number, has the smallest electronegativity.
(d) The higher the atomic number of an element, the greater is its electronegativity.

1.36 Why does fluorine, the element in the upper right corner of the Periodic Table, have the largest electronegativity of any element?

1.37 Arrange the single covalent bonds within each set in order of increasing polarity:

(a) C—H, O—H, N—H
(b) C—H, C—Cl, C—I
(c) C—C, C—O, C—N
(d) C—Li, C—Hg, C—Mg

1.38 Using the values of electronegativity given in Table 1.4, predict which indicated bond in each set is more polar and, using the symbols $\delta+$ and $\delta-$, show the direction of its polarity: **(See Example 1.5)**

(a) CH_3—OH or CH_3O—H
(b) H—NH_2 or CH_3—NH_2

(c) CH_3—SH or CH_3S—H
(d) CH_3—F or H—F
(e) H_2C=NH or H_2C=O
(f) H_2B—H or F_2B—F
(g) H_2C=O or H_2C=S
(h) CH_3—MgBr or CH_3—Li

1.39 Identify the most polar bond in each molecule:

(a) $HSCH_2CH_2OH$
(b) $CHCl_2F$
(c) $HOCH_2CH_2NH_2$

1.40 Predict whether the carbon–metal bond in each of these organometallic compounds is nonpolar cova-

lent, polar covalent, or ionic. For each polar covalent bond, show its direction of polarity using the symbols $\delta+$ and $\delta-$. **(See Example 1.5)**

(a) CH_3CH_2—$\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_2CH_3}{\overset{|}{\underset{|}{Pb}}}}$—$CH_2CH_3$
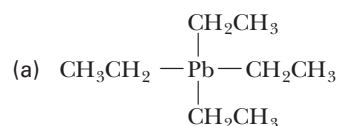
   Tetraethyllead

(b) CH_3—Mg—Cl
   Methylmagnesium chloride

(c) CH_3—Hg—CH_3
   Dimethylmercury

Section 1.3   Bond Angles and Shapes of Molecules

1.41 Using VSEPR, predict bond angles about each highlighted atom: **(See Example 1.8)**

(a) H—C—C—O—H (with H's above and below each C)

(b) H—C=C—Cl (with H's below)

(c) H—C—C≡C—H (with H's around first C)

(d) H—C—O—H (with O double-bonded above C)

(e) H—C—N—H (with H's around C and N)

(f) H—O—N=O
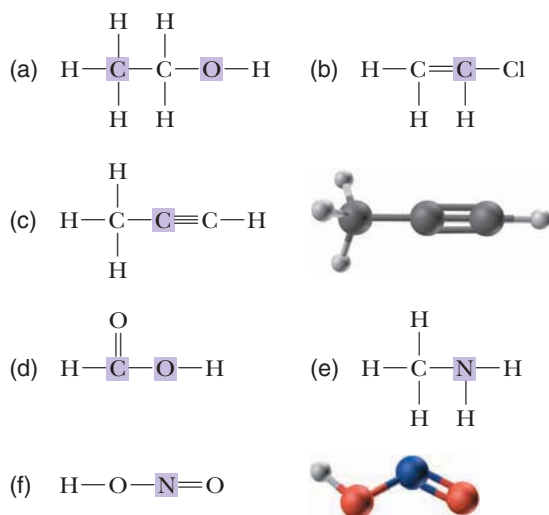
1.42 Using VSEPR, predict bond angles about each atom of carbon, nitrogen, and oxygen in these molecules. (*Hint*: First add unshared pairs of electrons as necessary to complete the valence shell of each atom, and then make your predictions of bond angles.) **(See Example 1.8)**

(a) CH_3—CH_2—CH_2—OH

(b) CH_3—CH_2—$\overset{\displaystyle O}{\overset{\|}{C}}$—H

(c) CH_3—CH=CH_2

(d) CH_3—C≡C—CH_3

(e) CH_3—$\overset{\displaystyle O}{\overset{\|}{C}}$—O—$CH_3$

(f) CH_3—$\overset{\displaystyle CH_3}{\overset{|}{N}}$—$CH_3$

1.43 Silicon is immediately below carbon in the Periodic Table. Predict the C—Si—C bond angle in tetramethylsilane, $(CH_3)_4Si$. **(See Example 1.8)**

Section 1.4   Polar and Nonpolar Molecules

1.44 Draw a three-dimensional representation for each molecule. Indicate which molecules are polar and the direction of their polarity: **(See Example 1.9)**

(a) CH_3F (b) CH_2Cl_2 (c) $CHCl_3$
(d) CCl_4 (e) CH_2=CCl_2 (f) CH_2=CHCl
(g) CH_3C≡N   (h) $(CH_3)_2C$=O   (i) $N(CH_3)_3$

*1.45 Tetrafluoroethylene, C_2F_4, is the starting material for the synthesis of the polymer poly(tetrafluoroethylene), commonly known as Teflon. Molecules of tetrafluoro-

ethylene are nonpolar. Propose a structural formula for this compound.

*1.46 Until several years ago, the two chlorofluorocarbons (CFCs) most widely used as heat-transfer media for refrigeration systems were Freon-11 (trichlorofluoromethane, CCl_3F) and Freon-12 (dichlorodifluoromethane, CCl_2F_2). Draw a three-dimensional representation of each molecule, and indicate the direction of its polarity. **(See Example 1.9)**
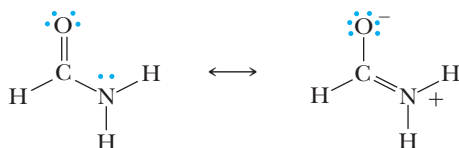
Section 1.5 Resonance Contributing Structures

**1.47** Which of these statements are true about resonance contributing structures? **(See Example 1.10)**

(a) All contributing structures must have the same number of valence electrons.

(b) All contributing structures must have the same arrangement of atoms.

(c) All atoms in a contributing structure must have complete valence shells.

(d) All bond angles in sets of contributing structures must be the same.

(e) The following pair represents acceptable resonance contributing structures:
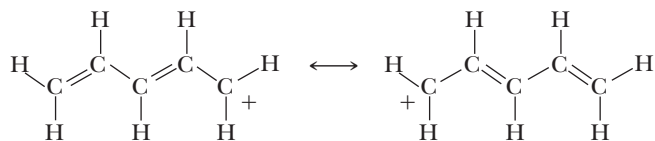
(f) The following pair represents acceptable resonance contributing structures:

(g) The following pair represents acceptable resonance contributing structures:
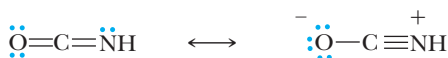
1.48 Draw the resonance contributing structure indicated by the curved arrow(s), and assign formal charges as appropriate: **(See Example 1.11)**

(a) ⟷ (b) ⟷

(c) ⟷
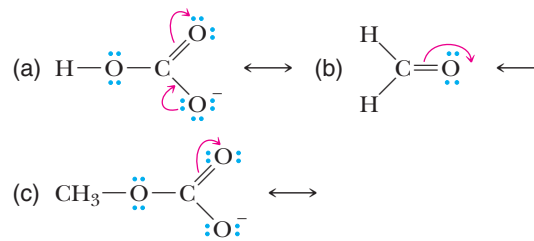
1.49 Using VSEPR, predict the bond angles about the carbon atom in each pair of contributing structures in Problem 1.48. In what way do the bond angles change from one contributing structure to the other?

1.50 Draw acceptable resonance contributing structure(s) for each of the compounds shown. **(See Example 1.11)**
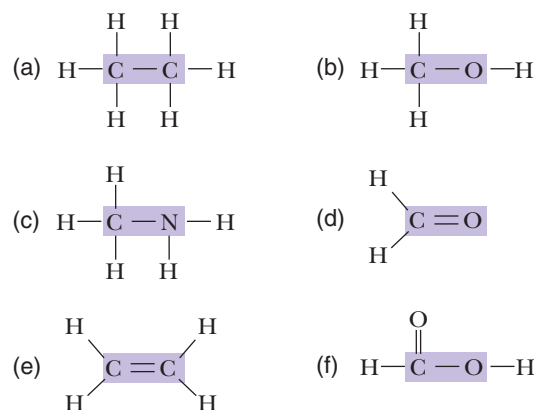
(a) (b) H—N≡C—N—H

(c) (d)

(e) (f)
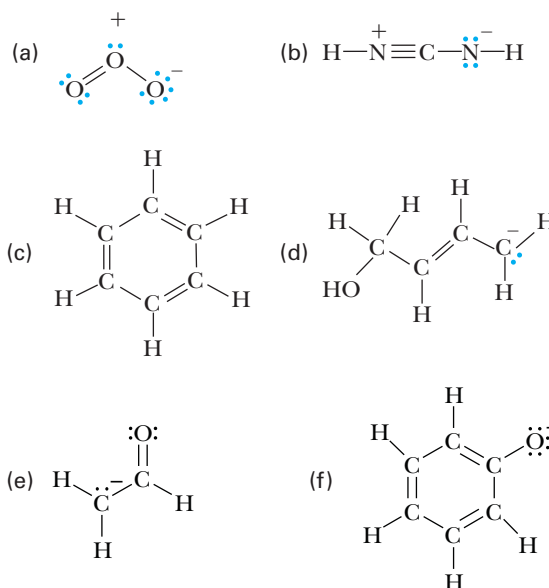
Section 1.6 Hybridization of Atomic Orbitals

1.51 State the hybridization of each highlighted atom:

(a) (b)

(c) H—C≡C—H (d)

(e) (f)
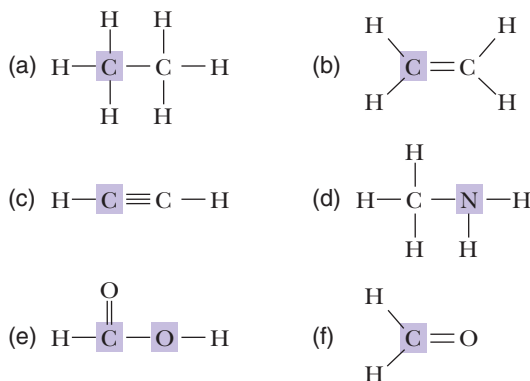
1.52 Describe each highlighted bond by indicating the type of bond(s) and the hybridization of the highlighted atoms: **(See Example 1.12)**

(a) (b)

(c) (d)

(e) (f)

Section 1.7 Functional Groups

1.53 Draw Lewis structures for these functional groups. Be certain to show all valence electrons on each: **(See Examples 1.13–1.16)**

(a) Carbonyl group (b) Carboxyl group
(c) Hydroxyl group (d) Primary amino group

1.54 Draw the structure for a compound with the molecular formula **(See Examples 1.13–1.16)**

(a) C_2H_6O that is an alcohol.
(b) C_3H_6O that is an aldehyde.
(c) C_3H_6O that is a ketone.
(d) $C_3H_6O_2$ that is a carboxylic acid.
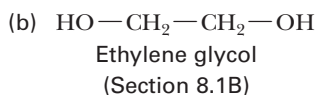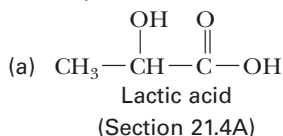(e) $C_4H_{11}N$ that is a tertiary amine.

1.55 Draw condensed structural formulas for all compounds with the molecular formula C_4H_8O that contain **(See Examples 1.13–1.16)**

(a) a carbonyl group. (There are two aldehydes and one ketone.)
(b) a carbon–carbon double bond and a hydroxyl group. (There are eight.)

1.56 Draw structural formulas for **(See Examples 1.13–1.16)**

(a) the eight alcohols with the molecular formula $C_5H_{12}O$.
(b) the eight aldehydes with the molecular formula $C_6H_{12}O$.
(c) the six ketones with the molecular formula $C_6H_{12}O$.
(d) the eight carboxylic acids with the molecular formula $C_6H_{12}O_2$.
(e) the three tertiary amines with the molecular formula $C_5H_{13}N$.

*1.57 Identify the functional groups in each compound (we study each compound in more detail in the indicated section):

$$\text{OH} \quad \text{O}$$
$$\qquad | \qquad \|$$
(a) $CH_3—CH—C—OH$
Lactic acid
(Section 21.4A)

(b) $HO—CH_2—CH_2—OH$
Ethylene glycol
(Section 8.1B)

$$\text{O}$$
$$\qquad \|$$
(c) $CH_3—CH—C—OH$
$$\qquad |$$
$$\qquad NH_2$$
Alanine
(Section 18.2B)

$$\text{OH} \quad \text{O}$$
$$\qquad | \qquad \|$$
(d) $HO—CH_2—CH—C—H$
Glyceraldehyde
(Section 17.2A)

$$\text{O} \qquad\qquad \text{O}$$
$$\quad \| \qquad\qquad \|$$
(e) $CH_3—C—CH_2—C—OH$
Acetoacetic acid
(Section 13.2B)

(f) $H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$
1,6-Hexanediamine
(Section 16.4A)
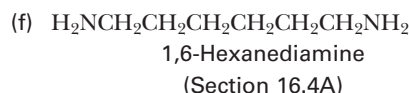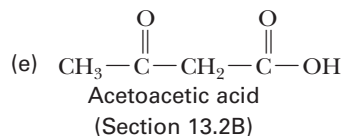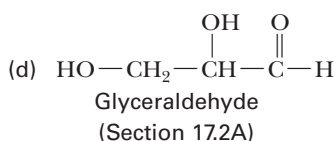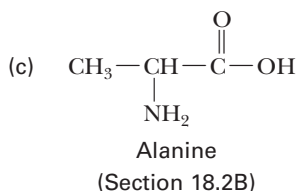
*1.58 Dihydroxyacetone, $C_3H_6O_3$, the active ingredient in many sunless tanning lotions, contains two 1° hydroxyl groups, each on a different carbon, and one ketone group. Draw a structural formula for dihydroxyacetone. **(See Examples 1.13–1.16)**

*1.59 Propylene glycol, $C_3H_8O_2$, commonly used in airplane deicers, contains a 1° alcohol and a 2° alcohol. Draw a structural formula for propylene glycol. **(See Examples 1.13–1.16)**

*1.60 Ephedrine is a molecule found in the dietary supplement ephedra, which has been linked to adverse health reactions such as heart attacks, strokes, and heart palpitations. The use of ephedra in dietary supplements is now banned by the FDA.

(a) Identify at least two functional groups in ephedrine.
(b) Would you predict ephedrine to be polar or nonpolar?

Ephedrine
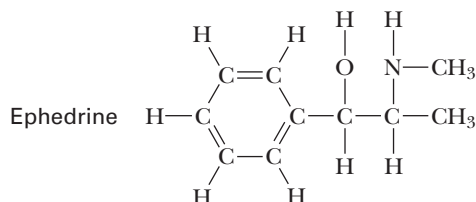
*1.61 Ozone (O_3) and carbon dioxide (CO_2) are both known as greenhouse gases. Compare and contrast their shapes, and indicate the hybridization of each atom in the two molecules.

*1.62 In the lower atmosphere that is also contaminated with unburned hydrocarbons, NO_2 participates in a series of reactions. One product of these reactions is peroxyacetyl nitrate (PAN). The connectivity of the atoms in PAN appears below.
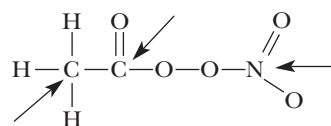
(a) Determine the number of valence electrons in this molecule, and then complete its Lewis structure.
(b) Give the approximate values of the bond angles around each atom indicated with an arrow.

LOOKING AHEAD

1.63   Allene, C_3H_4, has the structural formula $H_2C{=}C{=}CH_2$. Determine the hybridization of each carbon in allene and predict the shape of the molecule.

1.64   Dimethylsulfoxide, $(CH_3)_2SO$, is a common solvent used in organic chemistry.

   (a)   Write a Lewis structure for dimethylsulfoxide.
   (b)   Predict the hybridization of the sulfur atom in the molecule.
   (c)   Predict the geometry of dimethylsulfoxide.
   (d)   Is dimethylsulfoxide a polar or a nonpolar molecule?

1.65   In Chapter 5, we study a group of organic cations called carbocations. Following is the structure of one such carbocation, the *tert*-butyl cation:
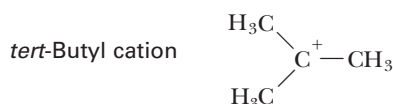
tert-Butyl cation

   (a)   How many electrons are in the valence shell of the carbon bearing the positive charge?
   (b)   Predict the bond angles about this carbon.
   (c)   Given the bond angles you predicted in (b), what hybridization do you predict for this carbon?

1.66   We also study the isopropyl cation, $(CH_3)_2CH^+$, in Chapter 5.

   (a)   Write a Lewis structure for this cation. Use a plus sign to show the location of the positive charge.
   (b)   How many electrons are in the valence shell of the carbon bearing the positive charge?

   (c)   Use VSEPR to predict all bond angles about the carbon bearing the positive charge.
   (d)   Describe the hybridization of each carbon in this cation.

1.67   In Chapter 9, we study benzene, C_6H_6, and its derivatives.
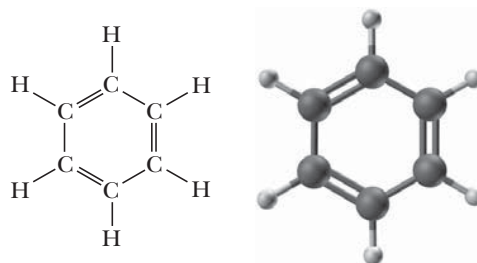
   (a)   Predict each H—C—C and each C—C—C bond angle on benzene.
   (b)   State the hybridization of each carbon in benzene.
   (c)   Predict the shape of a benzene molecule.

1.68   Explain why all the carbon–carbon bonds in benzene are equal in length.


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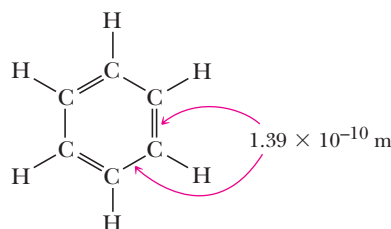
GROUP LEARNING ACTIVITIES

Studies have shown that working in groups enhances learning and fosters camaraderie. The following problems represent activities that you can do in groups of two or more.

1.69   Take turns by naming a functional group and challenging each other to draw an organic molecule with at least three carbon atoms that contains that functional group.

1.70   Draw all possible contributing structures for the molecules shown. Then discuss which of these contributing structures would not contribute significantly to the resonance hybrid. Provide good reasons for the structures you eliminate.

   (a)   (b)
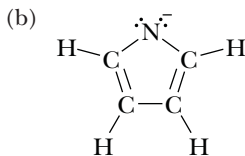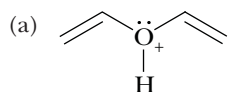
1.71   Refer to the list of functional groups on the inside front cover of this text. Take turns choosing one of the examples in the list and indicate the hybridization of each C, O, N, or S atom in the example.