1

The Basics

BONDING AND MOLECULAR STRUCTURE

Organic chemistry plays a role in all aspects of our lives, from the clothing we wear, to the pixels of our television and computer screens, to preservatives in food, to the inks that color the pages of this book. If you take the time to understand organic chemistry, to learn its overall logic, then you will truly have the power to change society. Indeed, organic chemistry provides the power to synthesize new drugs, to engineer molecules that can make computer processors run more quickly, to understand why grilled meat can cause cancer and how its effects can be combated, and to design ways to knock the calories out of sugar while still making food taste deliciously sweet. It can explain biochemical processes like aging, neural functioning, and cardiac arrest, and show how we can prolong and improve life. It can do almost anything.

IN THIS CHAPTER WE WILL CONSIDER:

- what kinds of atoms make up organic molecules
- the principles that determine how the atoms in organic molecules are bound together
- how best to depict organic molecules

[**WHY** DO THESE TOPICS MATTER?]   At the end of the chapter, we will see how some of the unique organic structures that nature has woven together possess amazing properties that we can harness to aid human health. See ▶ **WileyPLUS** for additional examples, videos, and practice.

1.1 LIFE AND THE CHEMISTRY OF CARBON COMPOUNDS—WE ARE STARDUST
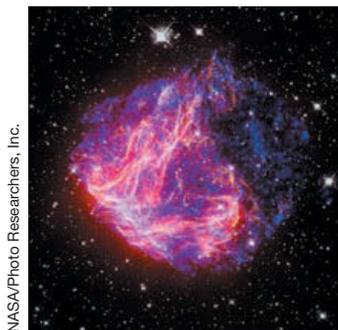
Supernovae were the crucibles in which the heavy elements were formed.

Organic chemistry is the chemistry of compounds that contain the element carbon. If a compound does not contain the element carbon, it is said to be *inorganic.*

Look for a moment at the periodic table inside the front cover of this book. More than a hundred elements are listed there. The question that comes to mind is this: why should an entire field of chemistry be based on the chemistry of compounds that contain this one element, carbon? There are several reasons, the primary one being this: **carbon compounds are central to the structure of living organisms and therefore to the existence of life on Earth. We exist because of carbon compounds.**

What is it about carbon that makes it the element that nature has chosen for living organisms? There are two important reasons: carbon atoms can form strong bonds to other carbon atoms to form rings and chains of carbon atoms, and carbon atoms can also form strong bonds to elements such as hydrogen, nitrogen, oxygen, and sulfur. Because of these bond-forming properties, carbon can be the basis for the huge diversity of compounds necessary for the emergence of living organisms.

From time to time, writers of science fiction have speculated about the possibility of life on other planets being based on the compounds of another element—for example, silicon, the element most like carbon. However, the bonds that silicon atoms form to each other are not nearly as strong as those formed by carbon, and therefore it is very unlikely that silicon could be the basis for anything equivalent to life as we know it.

### 1.1A What Is the Origin of the Element Carbon?

Through the efforts of physicists and cosmologists, we now understand much of how the elements came into being. The light elements hydrogen and helium were formed at the beginning, in the Big Bang. Lithium, beryllium, and boron, the next three elements, were formed shortly thereafter when the universe had cooled somewhat. All of the heavier elements were formed millions of years later in the interiors of stars through reactions in which the nuclei of lighter elements fuse to form heavier elements.

The energy of stars comes primarily from the fusion of hydrogen nuclei to produce helium nuclei. This nuclear reaction explains why stars shine. Eventually some stars begin to run out of hydrogen, collapse, and explode—they become supernovae. Supernovae explosions scatter heavy elements throughout space. Eventually, some of these heavy elements drawn by the force of gravity became part of the mass of planets like the Earth.

1.1B How Did Living Organisms Arise?

This question is one for which an adequate answer cannot be given now because there are many things about the emergence of life that we do not understand. However, we do know this. Organic compounds, some of considerable complexity, are detected in outer space, and meteorites containing organic compounds have rained down on Earth since it was formed. A meteorite that fell near Murchison, Victoria, Australia, in 1969 was found to contain over 90 different amino acids, 19 of which are found in living organisms on Earth. While this does not mean that life arose in outer space, it does suggest that events in outer space may have contributed to the emergence of life on Earth.

In 1924 Alexander Oparin, a biochemist at the Moscow State University, postulated that life on Earth may have developed through the gradual evolution of carbon-based molecules in a "primordial soup" of the compounds that were thought to exist on a prebiotic Earth: methane, hydrogen, water, and ammonia. This idea was tested by experiments carried out at the University of Chicago in 1952 by Stanley Miller and Harold Urey. They showed that amino acids and other complex organic compounds are synthesized when an electric spark (think of lightning) passes through a flask containing a mixture of these four compounds (think of the early atmosphere). Miller and Urey reported in their 1953 publication that five amino acids (essential constituents of proteins) were formed. In 2008, examination of archived solutions from Miller and Urey's original experiments revealed that 22 amino acids, rather than the 5 amino acids originally reported, were actually formed.
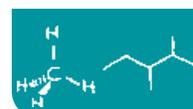
Similar experiments have shown that other precursors of biomolecules can also arise in this way—compounds such as ribose and adenine, two components of RNA. Some RNA molecules can not only store genetic information as DNA does, they can also act as catalysts, as enzymes do.

There is much to be discovered to explain exactly how the compounds in this soup became living organisms, but one thing seems certain. The carbon atoms that make up our bodies were formed in stars, so, in a sense, we are stardust.

An RNA molecule

### 1.1C Development of the Science of Organic Chemistry

The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were considered those compounds that came from nonliving sources. Friedrich Wöhler, however, discovered in 1828 that an organic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.

$$NH_4^+NCO^- \xrightarrow{\text{heat}} \underset{\text{Urea}}{H_2N-\overset{\overset{\text{O}}{\|}}{C}-NH_2}$$

Ammonium cyanate   **Urea**
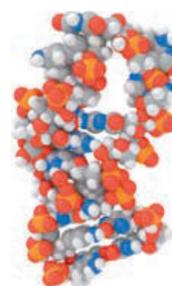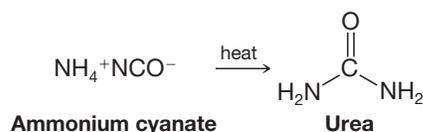
THE CHEMISTRY OF... Natural Products

Despite the demise of vitalism in science, the word "organic" is still used today by some people to mean "coming from living organisms" as in the terms "organic vitamins" and "organic fertilizers." The commonly used term "organic food" means that the food was grown without the use of synthetic fertilizers and pesticides. An "organic vitamin" means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while "natural" vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure "natural" vitamin C, for example, is healthier than pure "synthetic" vitamin C, since the two substances are identical in all respects. In science today, the study of compounds from living organisms is called natural products chemistry. In the closer to this chapter we will consider more about why natural products chemistry is important.
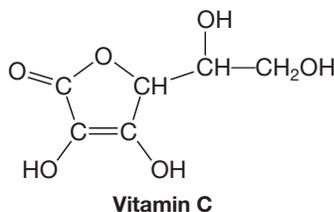
Vitamin C

Vitamin C is found in various citrus fruits.

1.2 ATOMIC STRUCTURE

Before we begin our study of the compounds of carbon we need to review some basic but familiar ideas about the chemical elements and their structure.

- The **compounds** we encounter in chemistry are made up of **elements** combined in different proportions.
- **Elements** are made up of **atoms**. An atom (Fig. 1.1) consists of a dense, positively charged *nucleus* containing **protons** and **neutrons** and a surrounding cloud of **electrons**.

Each proton of the nucleus bears one positive charge; electrons bear one negative charge. Neutrons are electrically neutral; they bear no charge. Protons and neutrons have

Electron cloud

Nucleus

FIGURE 1.1 An atom is composed of a tiny nucleus containing protons and neutrons and a large surrounding volume containing electrons. The diameter of a typical atom is about 10,000 times the diameter of its nucleus.
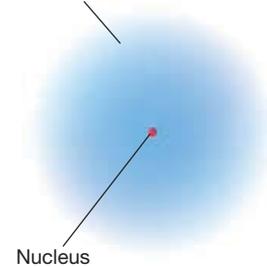
nearly equal masses (approximately 1 atomic mass unit each) and are about 1800 times as heavy as electrons. Most of the **mass** of an atom, therefore, comes from the mass of the nucleus; the atomic mass contributed by the electrons is negligible. Most of the **volume** of an atom, however, comes from the electrons; the volume of an atom occupied by the electrons is about 10,000 times larger than that of the nucleus.

The elements commonly found in organic molecules are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur, as well as the halogens (fluorine, chlorine, bromine, and iodine).

Each **element** is distinguished by its **atomic number** (Z), a **number equal to the number of protons in its nucleus**. Because an atom is electrically neutral, **the atomic number also equals the number of electrons surrounding the nucleus**.

1.2A Isotopes

Before we leave the subject of atomic structure and the periodic table, we need to examine one other observation: **the existence of atoms of the same element that have different masses**.

For example, the element carbon has six protons in its nucleus giving it an atomic number of 6. Most carbon atoms also have six neutrons in their nuclei, and because each proton and each neutron contributes one atomic mass unit (1 amu) to the mass of the atom, carbon atoms of this kind have a mass number of 12 and are written as ^{12}C.

- **Although all the nuclei of all atoms of the same element will have the same number of protons**, some atoms of the same element **may have different masses** because they have **different numbers of neutrons**. Such atoms are called **isotopes**.

For example, about 1% of the atoms of elemental carbon have nuclei containing 7 neutrons, and thus have a mass number of 13. Such atoms are written ^{13}C. A tiny fraction of carbon atoms have 8 neutrons in their nucleus and a mass number of 14. Unlike atoms of carbon-12 and carbon-13, atoms of carbon-14 are radioactive. The ^{14}C isotope is used in *carbon dating*. The three forms of carbon, ^{12}C, ^{13}C, and ^{14}C, are isotopes of one another.

Most atoms of the element hydrogen have one proton in their nucleus and have no neutron. They have a mass number of 1 and are written ^{1}H. A very small percentage (0.015%) of the hydrogen atoms that occur naturally, however, have one neutron in their nucleus. These atoms, called *deuterium* atoms, have a mass number of 2 and are written ^{2}H. An unstable (and radioactive) isotope of hydrogen, called *tritium* (^{3}H), has two neutrons in its nucleus.

● PRACTICE PROBLEM 1.1   There are two stable isotopes of nitrogen, ^{14}N and ^{15}N. How many protons and neutrons does each isotope have?

1.2B Valence Electrons

We discuss the electron configurations of atoms in more detail in Section 1.10. For the moment we need only to point out that the electrons that surround the nucleus exist in **shells** of increasing energy and at increasing distances from the nucleus. The most important shell, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.

- How do we know how many electrons an atom has in its valence shell? We look at the periodic table. The number of electrons in the valence shell (called **valence electrons**) is equal to the group number of the atom. For example, carbon is in group **IVA** and carbon has *four* valence electrons; oxygen is in group **VIA** and oxygen has *six* valence electrons. The halogens of group **VIIA** all have *seven* electrons.

● PRACTICE PROBLEM 1.2   How many valence electrons does each of the following atoms have?
(a) Na   **(b)** Cl   **(c)** Si   **(d)** B   **(e)** Ne   **(f)** N
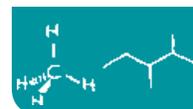
1.3 CHEMICAL BONDS: THE OCTET RULE

The first explanations of the nature of chemical bonds were advanced by G. N. Lewis (of the University of California, Berkeley) and W. Kössel (of the University of Munich) in 1916. Two major types of chemical bonds were proposed:

1. Ionic (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.

2. Covalent bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

- The **valence shell** is the outermost shell of electrons in an atom.
- The tendency for an atom to achieve a configuration where its valence shell contains eight electrons is called the **octet rule**.

The concepts and explanations that arise from the original propositions of Lewis and Kössel are satisfactory for explanations of many of the problems we deal with in organic chemistry today. For this reason we shall review these two types of bonds in more modern terms.

1.3A Ionic Bonds

Atoms may gain or lose electrons and form charged particles called **ions**.

- An **ionic bond** is an attractive force between oppositely charged ions.

One source of such ions is a reaction between atoms of widely differing electronegativities (Table 1.1).

- **Electronegativity** *is a measure of the ability of an atom to attract electrons.*
- Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column (Table 1.1).

An example of the formation of an ionic bond is the reaction of lithium and fluorine atoms:
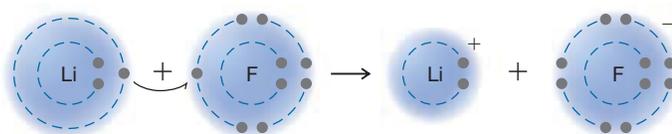
Lithium, a typical metal, has a very low electronegativity; fluorine, a nonmetal, is the most electronegative element of all. The loss of an electron (a negatively charged species)

TABLE 1.1 ELECTRONEGATIVITIES OF SOME OF THE ELEMENTS

Increasing electronegativity →

Increasing electronegativity ↑

			H 2.1			
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	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8						Br 2.8

by the lithium atom leaves a lithium cation (Li^+); the gain of an electron by the fluorine atom gives a fluoride anion (F^-).

- Ions form because atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons.

The lithium cation with two electrons in its valence shell is like an atom of the noble gas helium, and the fluoride anion with eight electrons in its valence shell is like an atom of the noble gas neon. Moreover, crystalline lithium fluoride forms from the individual lithium and fluoride ions. In this process, negative fluoride ions become surrounded by positive lithium ions, and positive lithium ions by negative fluoride ions. In this crystalline state, the ions have substantially lower energies than the atoms from which they have been formed. Lithium and fluorine are thus "stabilized" when they react to form crystalline lithium fluoride. We represent the formula for lithium fluoride as LiF, because that is the simplest formula for this ionic compound.

Ionic substances, because of their strong internal electrostatic forces, are usually very high melting solids, often having melting points above 1000 °C. In polar solvents, such as water, the ions are solvated (see Section 2.13D), and such solutions usually conduct an electric current.

- Ionic compounds, often called **salts**, form only when atoms of very different electronegativities transfer electrons to become ions.

● **PRACTICE PROBLEM 1.3**   Using the periodic table, which element in each pair is more electronegative?
(a) Si, O   **(b)** N, C   **(c)** Cl, Br   **(d)** S, P

1.3B Covalent Bonds and Lewis Structures

When two or more atoms of the same or similar electronegativities react, a complete transfer of electrons does not occur. In these instances the atoms achieve noble gas configurations by *sharing electrons*.

- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.

- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.

Molecules may be represented by electron-dot formulas or, more conveniently, by formulas where each pair of electrons shared by two atoms is represented by a line.
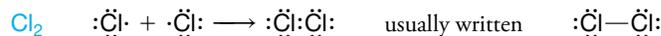
- A **dash structural formula** has lines that show bonding electron pairs and includes elemental symbols for the atoms in a molecule.
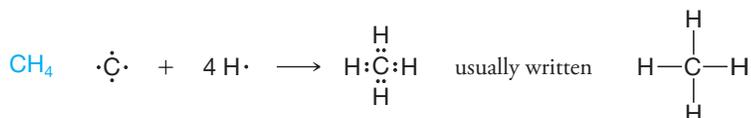
Some examples are shown here:

1. Hydrogen, being in group IA of the periodic table, has one valence electron. Two hydrogen atoms share electrons to form a hydrogen molecule, H_2.

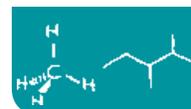$$H_2 \qquad H\cdot + \cdot H \longrightarrow H\!:\!H \qquad \text{usually written} \qquad H\!-\!H$$

2. Because chlorine is in group VIIA, its atoms have seven valence electrons. Two chlorine atoms can share electrons (one electron from each) to form a molecule of Cl_2.

$$Cl_2 \qquad :\ddot{C}l\cdot + \cdot\ddot{C}l: \longrightarrow :\ddot{C}l\!:\!\ddot{C}l: \qquad \text{usually written} \qquad :\ddot{C}l\!-\!\ddot{C}l:$$
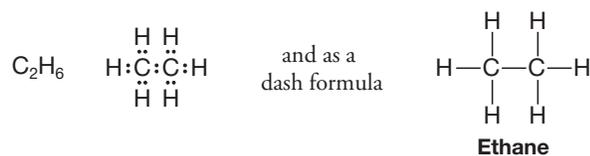
3. A carbon atom (group IVA) with four valence electrons can share each of these electrons with four hydrogen atoms to form a molecule of methane, CH_4.

$$CH_4 \qquad \cdot\dot{\underset{\cdot}{C}}\cdot \;+\; 4\,H\cdot \;\longrightarrow\; H\!:\!\overset{\overset{\displaystyle H}{\cdot\cdot}}{\underset{\underset{\displaystyle H}{\cdot\cdot}}{C}}\!:\!H \qquad \text{usually written} \qquad H\!-\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\!-\!H$$
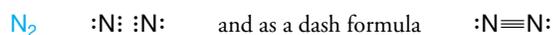
Two carbon atoms can use one electron pair between them to form a **carbon–carbon single bond** while also bonding hydrogen atoms or other groups to achieve an octet of valence electrons. Consider the example of ethane below.
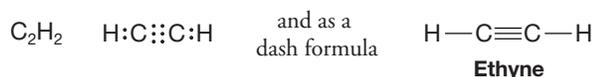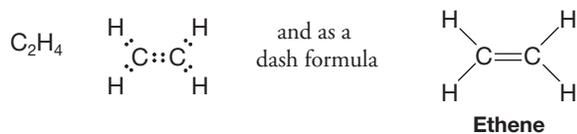
C_2H_6

H:C:C:H (with H above and below each C)

and as a dash formula

H—C—C—H (ethane dash structure with H atoms)

Ethane

These formulas are often called **Lewis structures**; in writing them we show all of the valence electrons. Unshared electron pairs are shown as dots, and in dash structural formulas, bonding electron pairs are shown as lines.

4. Atoms can share *two or more pairs of electrons* to form **multiple covalent bonds**. For example, two nitrogen atoms possessing five valence electrons each (because nitrogen is in group VA) can share electrons to form a **triple bond** between them.

N_2 :N: :N: and as a dash formula   :N≡N:

Carbon atoms can also share more than one electron pair with another atom to form a multiple covalent bond. Consider the examples of a **carbon–carbon double bond** in ethene (ethylene) and a **carbon–carbon triple bond** in ethyne (acetylene).

C_2H_4

C::C (with H atoms)

and as a dash formula

C=C (ethene dash structure with H atoms)

Ethene

C_2H_2 H:C::C:H

and as a dash formula

H—C≡C—H

Ethyne

5. Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion.

$\overset{+}{N}H_4$

H:N:H (with H above and below, + charge)

and as a dash formula

H—N—H (with H above and below, + charge)
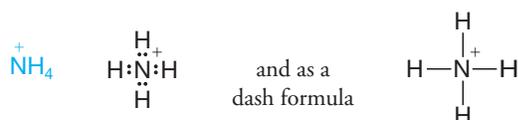
Consider the following compounds and decide whether the bond in them would be ionic or covalent.

(a) KCl   **(b)** F_2 **(c)** PH_3 **(d)** CBr_4

●● 1.4 **HOW TO** WRITE LEWIS STRUCTURES

Several simple rules allow us to draw proper Lewis structures:

1. Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved. Valence electrons are those of an atom's outermost shell.

2. For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table.

[HELPFUL HINT]

The ability to write proper **Lewis structures** is one of the most important tools for learning organic chemistry.

Carbon, for example, is in group IVA and has four valence electrons; the halogens (e.g., fluorine) are in group VIIA and each has seven valence electrons; hydrogen is in group IA and has one valence electron.

3. If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.

4. In drawing Lewis structures we try to give each atom the electron configuration of a noble gas. To do so, we draw structures where atoms share electrons to form covalent bonds or transfer electrons to form ions.

   a. Hydrogen forms one covalent bond by sharing its electron with an electron of another atom so that it can have two valence electrons, the same number as in the noble gas helium.

   b. Carbon forms four covalent bonds by sharing its four valence electrons with four valence electrons from other atoms, so that it can have eight electrons (the same as the electron configuration of neon, satisfying the octet rule).

   c. To achieve an octet of valence electrons, elements such as nitrogen, oxygen, and the halogens typically share only some of their valence electrons through covalent bonding, leaving others as unshared electron pairs. Nitrogen typically shares three electrons, oxygen two, and the halogens one.

The following problems illustrate the rules above.

●●● SOLVED PROBLEM 1.1

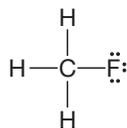Write the Lewis structure of CH_3F.

STRATEGY AND ANSWER:

   1. We find the total number of valence electrons of all the atoms:

$$4 + 3(1) + 7 = 14$$
$$\uparrow \qquad \uparrow \quad \uparrow$$
$$C \quad 3H \quad F$$
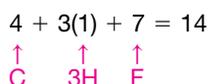
   2. We use pairs of electrons to form bonds between all atoms that are bonded to each other. We represent these bonding pairs with lines. In our example this requires four pairs of electrons (8 of the 14 valence electrons).
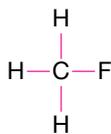
   3. We then add the remaining electrons in pairs so as to give each hydrogen 2 electrons (a duet) and every other atom 8 electrons (an octet). In our example, we assign the remaining 6 valence electrons to the fluorine atom in three non-bonding pairs.

● PRACTICE PROBLEM 1.5   Write the Lewis structure of **(a)** CH_2F_2 (difluoromethane) and **(b)** $CHCl_3$ (chloroform).
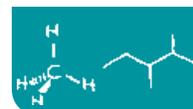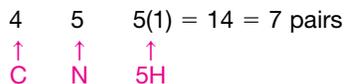
Write a Lewis structure for methylamine (CH_3NH_2).

STRATEGY AND ANSWER:

1. We find the total number of valence electrons for all the atoms.

$$4 \quad 5 \quad 5(1) = 14 = 7 \text{ pairs}$$
$$\uparrow \quad \uparrow \quad \uparrow$$
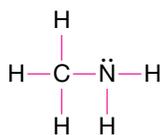$$C \quad N \quad 5H$$

2. We use one electron pair to join the carbon and nitrogen.

$$C—N$$

3. We use three pairs to form single bonds between the carbon and three hydrogen atoms.
4. We use two pairs to form single bonds between the nitrogen atom and two hydrogen atoms.
5. This leaves one electron pair, which we use as a lone pair on the nitrogen atom.

$$\begin{array}{c} H \\ | \\ H—C—\ddot{N}—H \\ | \quad | \\ H \quad H \end{array}$$

Write the Lewis structure of CH_3OH.

5. **If necessary, we use multiple bonds to satisfy the octet rule (i.e., give atoms the noble gas configuration).** The carbonate ion (CO_3^{2-}) illustrates this:

$$\left[\begin{array}{c} \ddot{O} \\ \| \\ C \\ \ddot{O} \quad \ddot{O} \end{array} \right]^{2-}$$
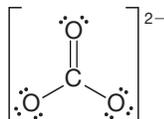
The organic molecules ethene (C_2H_4) and ethyne (C_2H_2), as mentioned earlier, have a double and triple bond, respectively:

$$\begin{array}{cc} H \qquad H \\ \diagdown \quad \diagup \\ C=C \\ \diagup \quad \diagdown \\ H \qquad H \end{array} \qquad \text{and} \qquad H—C\equiv C—H$$
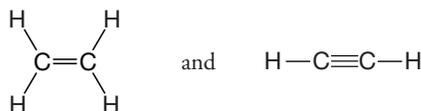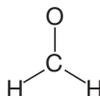
Write the Lewis structure of CH_2O (formaldehyde).

STRATEGY AND ANSWER:

1. Find the total number of valence electrons of all the atoms:

$$2(1) + 1(4) + 1(6) = 12$$
$$\uparrow \qquad \uparrow \qquad \uparrow$$
$$2H \qquad 1C \qquad 1O$$
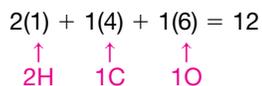
2. **(a)** Use pairs of electrons to form single bonds.

$$\begin{array}{c} O \\ | \\ C \\ \diagup \quad \diagdown \\ H \qquad H \end{array}$$

(continues on next page)

(b) Determine which atoms already have a full valence shell and which ones do not, and how many valence electrons we have used so far. In this case, we have used 6 valence electrons, and the valence shell is full for the hydrogen atoms but not for the carbon and oxygen atoms.

(c) We use the remaining electrons as bonds or unshared electron pairs, to fill the valence shell of any atoms whose valence shell is not yet full, taking care not to exceed the octet rule. In this case 6 of the initial 12 valence electrons are left to use. We use 2 electrons to fill the valence shell of the carbon by another bond to the oxygen, and the remaining 4 electrons as two unshared electron pairs with the oxygen, filling its valence shell.
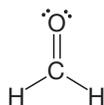
● PRACTICE PROBLEM 1.7   Write a dash structural formula showing all valence electrons for CH_3CHO (acetaldehyde).

---

6. Before we can write some Lewis structures, we must know how the atoms are connected to each other. Consider nitric acid, for example. Even though the formula for nitric acid is often written HNO_3, the hydrogen is actually connected to an oxygen, not to the nitrogen. The structure is $HONO_2$ and not HNO_3. Thus the correct Lewis structure is:

and not

[HELPFUL HINT]

Check your progress by doing each Practice Problem as you come to it in the text.

This knowledge comes ultimately from experiments. If you have forgotten the structures of some of the common inorganic molecules and ions (such as those listed in Practice Problem 1.8), this may be a good time for a review of the relevant portions of your general chemistry text.

●●● SOLVED PROBLEM 1.4

Assume that the atoms are connected in the same way they are written in the formula, and write a Lewis structure for the toxic gas hydrogen cyanide (HCN).

STRATEGY AND ANSWER:

1. We find the total number of valence electrons on all of the atoms:

$$1 + 4 + 5 = 10$$
$$\uparrow \quad \uparrow \quad \uparrow$$
$$H \quad C \quad N$$
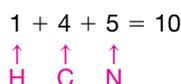
2. We use one pair of electrons to form a single bond between the hydrogen atom and the carbon atom (see below), and we use three pairs to form a triple bond between the carbon atom and the nitrogen atom. This leaves two electrons. We use these as an unshared pair on the nitrogen atom. Now each atom has the electronic structure of a noble gas. The hydrogen atom has two electrons (like helium) and the carbon and nitrogen atoms each have eight electrons (like neon).

$$H—C≡N:$$
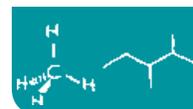
Write a Lewis structure for each of the following:

(a) HF **(c)** CH_3F **(e)** H_2SO_3 **(g)** H_3PO_4

(b) F_2 **(d)** HNO_2 **(f)** BH_4^- **(h)** H_2CO_3

1.4A Exceptions to the Octet Rule

Atoms share electrons, not just to obtain the configuration of an inert gas, but because sharing electrons produces increased electron density between the positive nuclei. The resulting attractive forces of nuclei for electrons is the "glue" that holds the atoms together (cf. Section 1.11).

- Elements of the second period of the periodic table can have a maximum of four bonds (i.e., have eight electrons around them) because these elements have only one $2s$ and three $2p$ orbitals available for bonding.

Each orbital can contain two electrons, and a total of eight electrons fills these orbitals (Section 1.10A). The **octet rule**, therefore, only applies to these elements, and even here, as we shall see in compounds of beryllium and boron, fewer than eight electrons are possible.

- Elements of the third period and beyond have d orbitals that can be used for bonding.

These elements can accommodate more than eight electrons in their valence shells and therefore can form more than four covalent bonds. Examples are compounds such as PCl_5 and SF_6. Bonds written as ⋰ (dashed wedges) project behind the plane of the paper. Bonds written as ✔ (solid wedges) project in front of the paper.
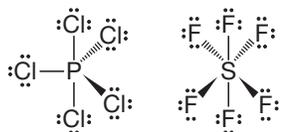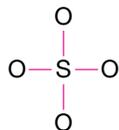
Write a Lewis structure for the sulfate ion (SO_4^{2-}). (*Note*: The sulfur atom is bonded to all four oxygen atoms.)

STRATEGY AND ANSWER:

1. We find the total number of valence electrons including the extra 2 electrons needed to give the ion the double negative charge:

$$6 + 4(6) + 2 = 32$$
$$\uparrow \qquad \uparrow \qquad \uparrow$$
$$S \qquad 4O \qquad 2e^-$$

**2.** We use four pairs of electrons to form bonds between the sulfur atom and the four oxygen atoms:

3. We add the remaining 24 electrons as unshared pairs on oxygen atoms and as **double bonds** between the sulfur atom and two oxygen atoms. This gives each oxygen 8 electrons and the sulfur atom 12:
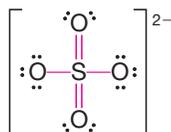
Write a Lewis structure for the phosphate ion (PO_4^{3-}).

Some highly reactive molecules or ions have atoms with fewer than eight electrons in their outer shell. An example is boron trifluoride (BF_3). In a BF_3 molecule the central boron atom has only six electrons around it:

$$:\ddot{F}:$$
$$|$$
$$B$$
$$:\ddot{F} \quad \ddot{F}:$$
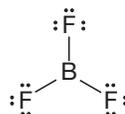
•• 1.5 FORMAL CHARGES AND **HOW TO** CALCULATE THEM

Many **Lewis structures** are incomplete until we decide whether any of their atoms have a **formal charge**. Calculating the formal charge on an atom in a Lewis structure is simply a bookkeeping method for its valence electrons.

- First, we examine each atom and, using the periodic table, we determine how many **valence electrons** it would have if it were an isolated atom. **This is equal to the group number of the atom in the periodic table**. For hydrogen this number equals 1, for carbon it equals 4, for nitrogen it equals 5, and for oxygen it equals 6.

Next, we examine the atom in the Lewis structure and we assign the valence electrons in the following way:

- **We assign to each atom half of the electrons it is sharing with another atom and all of its unshared (lone) electron pairs.**

Then we do the following calculation for the atom:

Formal charge = number of valence electrons − 1/2 number of shared electrons
    − number of unshared electrons

or

$$F = Z - (1/2)S - U$$

where F is the formal charge, Z is the group number of the element, S equals the number of shared electrons, and U is the number of unshared electrons.

- It is important to note, too, that **the arithmetic sum of all the formal charges in a molecule or ion will equal the overall charge on the molecule or ion**.

Let us consider several examples showing how this is done.

The Ammonium Ion (NH_4^+) As we see below, the ammonium ion has no unshared electron pairs. We divide all of the electrons in bonds equally between the atoms that share them. Thus, each hydrogen is assigned one electron. We subtract this from one (the number of valence electrons in a hydrogen atom) to give each hydrogen atom a formal charge of zero. The nitrogen atom is assigned four electrons (one from each shared pair in a bond). We subtract four from five (the number of valence electrons in an isolated nitrogen atom) to give the nitrogen a formal charge of +1.
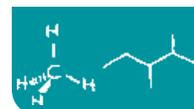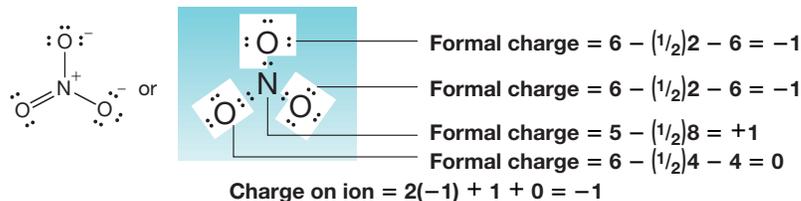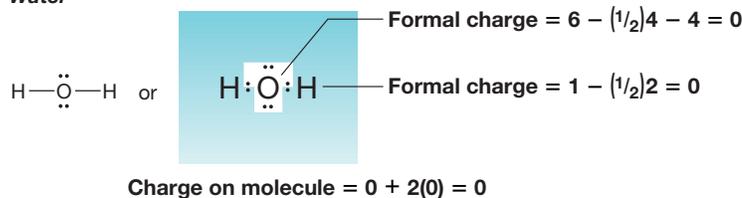
Ammonium Ion

H
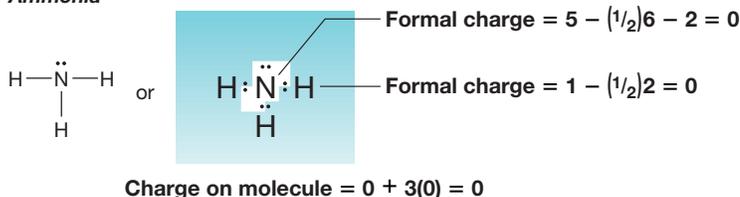|
H—N⁺—H   or   H:N:H
|
H
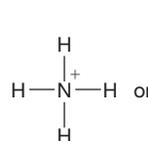
For hydrogen:	valence electrons of free atom	=	1
	subtract assigned electrons	=	−1
	Formal charge on each hydrogen	=	0
For nitrogen:	valence electrons of free atom	=	5
	subtract assigned electrons	=	$-(1/2)8$
	Formal charge on nitrogen	=	+1

Overall charge on ion = 4(0) + 1 = +1

The Nitrate Ion (NO_3^-) Let us next consider the nitrate ion (NO_3^-), an ion that has oxygen atoms with unshared electron pairs. Here we find that the nitrogen atom has a formal charge of +1, that two oxygen atoms have formal charges of −1, and that one oxygen has a formal charge equal to 0.

Nitrate Ion

Formal charge = $6 - (1/2)2 - 6 = -1$
Formal charge = $6 - (1/2)2 - 6 = -1$
Formal charge = $5 - (1/2)8 = +1$
Formal charge = $6 - (1/2)4 - 4 = 0$

Charge on ion = $2(-1) + 1 + 0 = -1$

Water and Ammonia The sum of the formal charges on each atom making up a molecule must be zero. Consider the following examples:

Water

Formal charge = $6 - (1/2)4 - 4 = 0$
Formal charge = $1 - (1/2)2 = 0$

Charge on molecule = $0 + 2(0) = 0$

Ammonia

Formal charge = $5 - (1/2)6 - 2 = 0$
Formal charge = $1 - (1/2)2 = 0$

Charge on molecule = $0 + 3(0) = 0$

• **PRACTICE PROBLEM 1.10**

Write a Lewis structure for each of the following negative ions, and assign the formal negative charge to the correct atom:

(a) H_3CO^- **(b)** NH_2^- **(c)** CN^- **(d)** HCO_2^- **(e)** HCO_3^- **(f)** HC_2^-

1.5A A Summary of Formal Charges

With this background, it should now be clear that each time an oxygen atom of the type $-\ddot{O}:$ appears in a molecule or ion, it will have a formal charge of -1, and that each time an oxygen atom of the type $=\dot{O}:$ or $-\ddot{O}-$ appears, it will have a formal charge of 0. Similarly, $-\overset{|}{\underset{|}{N}}-$ will be $+1$, and $-\overset{|}{\ddot{N}}-$ will be zero. These and other common structures are summarized in Table 1.2.

[HELPFUL HINT]

In later chapters, when you are evaluating how reactions proceed and what products form, you will find it essential to keep track of formal charges.

TABLE 1.2 A SUMMARY OF FORMAL CHARGES

Group	Formal Charge of +1			Formal Charge of 0			Formal Charge of −1		
IIIA				`\B/` `|`			`-B-` `|`		
IVA	`\C/` `+`	`=C-` `+`	`≡C` `+`	`-C-` `|`	`=C\`	`≡C-`	`\ddot{C}-`	`=\dot{C}\`	`≡C:`
VA	`-N+` `|`	`=N/` `+`	`=N-` `+`	`-\ddot{N}-`	`\ddot{N}\`	`≡N:`	`-\ddot{N}-`	`=\dot{N}`	
VIA	`-\ddot{O}-` `+`	`\ddot{O}+/`		`-\ddot{O}-`	`=\ddot{O}:`		`-\ddot{O}:`		
VIIA	`-\ddot{X}+-`			`-\ddot{X}:` (X = F, Cl, Br, or I)			`:\ddot{X}:-`		

● **PRACTICE PROBLEM 1.11**   Assign the proper formal charge to the colored atom in each of the following structures:

(a)
$$\text{H}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\text{C}}}-\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{\text{C}}}$$

(b)
$$\text{H}-\ddot{\text{O}}-\text{H}$$
$$\underset{|}{\text{H}}$$

(c)
$$\overset{\cdot\ddot{\text{O}}\cdot}{\overset{\|}{\underset{\text{H}}{\text{C}}}}-\overset{}{\underset{\ddot{\text{O}}:}{}}$$

(d)
$$\overset{:\ddot{\text{O}}:}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{\text{H}-\text{C}-\text{H}}}}$$

(e)
$$\text{H}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\text{C}}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\text{N}}}-\text{H}$$

(f)
$$\overset{\text{H}-\ddot{\text{O}}-\text{H}}{\underset{\underset{\displaystyle H}{|}}{\text{H}-\text{C}-\text{H}}}$$

(g) $\text{CH}_3-\text{C}\equiv\text{N}:$

(h) $\text{CH}_3-\text{N}\equiv\text{N}:$
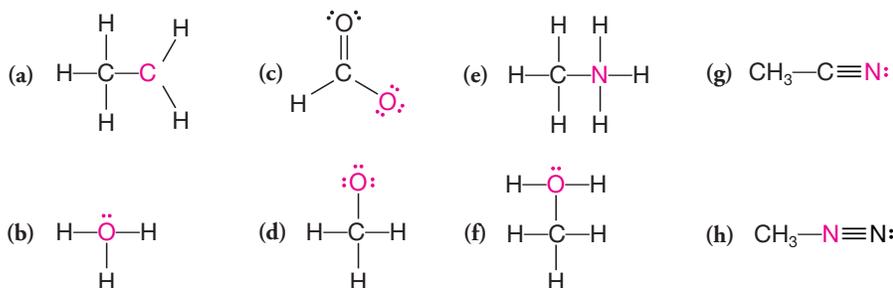
1.6 ISOMERS: DIFFERENT COMPOUNDS THAT HAVE THE SAME MOLECULAR FORMULA

Now that we have had an introduction to Lewis structures, it is time to discuss isomers.

● **Isomers** are compounds that have the same **molecular formula** but different structures.

We will learn about several kinds of isomers during the course of our study. For now, let us consider a type called constitutional isomers.

● **Constitutional isomers** are different compounds that have the same molecular formula but differ in the sequence in which their atoms are bonded—that is, their **connectivity**.

Acetone, used in nail polish remover and as a paint solvent, and propylene oxide, used with seaweed extracts to make food-grade thickeners and foam stabilizers for beer (among other applications), are isomers. Both of these compounds have the molecular formula C_3H_6O and therefore the same molecular weight. Yet acetone and propylene oxide have distinctly different boiling points and chemical reactivity that, as a result, lend themselves to distinctly different practical applications. Their shared molecular formula simply gives us no basis for understanding the differences between them. We must, therefore, move to a consideration of their structural formulas.

On examining the structures of acetone and propylene oxide several key aspects are clearly different (Fig. 1.2). Acetone contains a double bond between the oxygen atom and the central carbon atom. Propylene oxide does not contain a double bond, but has three atoms joined in a ring. The connectivity of the atoms is clearly different in acetone
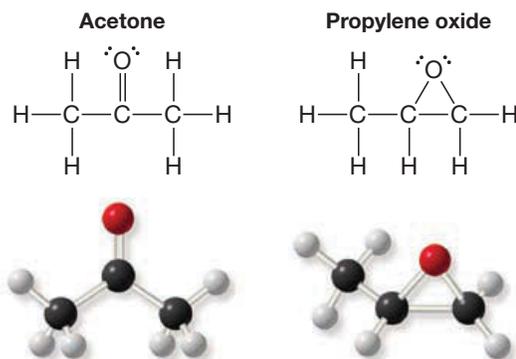
Acetone is used in some nail polish removers.

Propylene oxide alginates, made from propylene oxide and seaweed extracts, are used as food thickeners.

Acetone   **Propylene oxide**

FIGURE 1.2 Ball-and-stick models and chemical formulas show the different structures of acetone and propylene oxide.

[**HELPFUL HINT**]

Build hand-held models of these compounds and compare their structures.
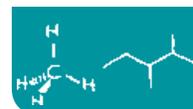
and propylene oxide. Their structures have the same molecular formula but a different constitution. They are constitutional isomers.*

- Constitutional isomers usually have different physical properties (e.g., melting point, boiling point, and density) and different chemical properties (reactivity).

● ● ● **SOLVED PROBLEM 1.6**

There are two constitutional isomers with the formula C_2H_6O. Write structural formulas for these isomers.

STRATEGY AND ANSWER: If we recall that carbon can form four covalent bonds, oxygen can form two, and hydrogen only one, we can arrive at the following constitutional isomers.

Dimethyl ether   **Ethanol**
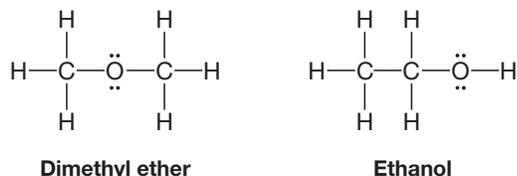
It should be noted that these two isomers are clearly different in their physical properties. At room temperature and 1 atm pressure, dimethyl ether is a gas. Ethanol is a liquid.

● ● ● **SOLVED PROBLEM 1.7**

Which of the following compounds are constitutional isomers of one another?

A   **B**   **C**   **D**   **E**
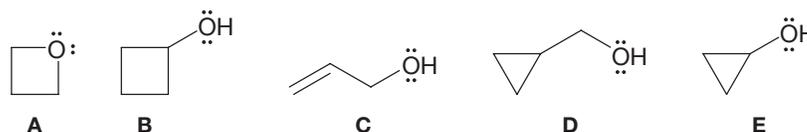
ANSWER: First determine the molecular formula for each compound. You will then see that **B** and **D** have the same molecular formula (C_4H_8O) but have different connectivities. They are, therefore, constitutional isomers of each other. **A**, **C**, and **E** also have the same molecular formula (C_3H_6O) and are constitutional isomers of one another.

● ● 1.7 HOW TO WRITE AND INTERPRET STRUCTURAL FORMULAS

Organic chemists use a variety of formats to write **structural formulas**. We have already used electron-dot formulas and dash formulas in previous sections. Two other important types of formulas are **condensed formulas** and **bond-line formulas** or **skeletal formulas**. Examples of these four types of structural formulas are shown in Fig. 1.3 using propyl alcohol as an example.

Ball-and-stick model   Electron-dot formula   Dash formula   Condensed formula   Bond-line formula
(a)   (b)   (c)   (d)   (e)
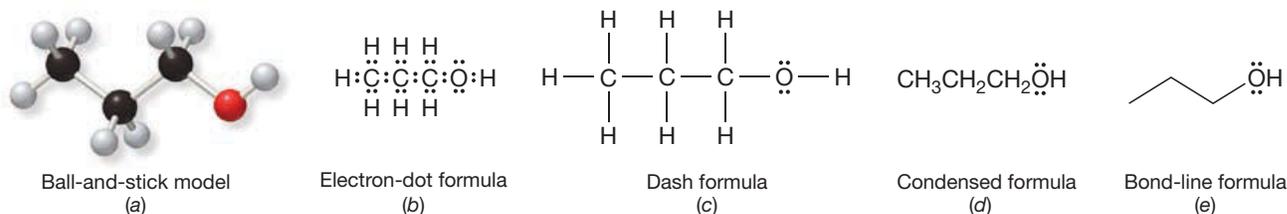
FIGURE 1.3 Structural formulas for propyl alcohol.

*An older term for isomers of this type was **structural isomers**. The International Union of Pure and Applied Chemistry (IUPAC) now recommends that use of the term "structural" when applied to constitutional isomers be abandoned.

Although electron-dot formulas account explicitly for all of the valence electrons in a molecule, they are tedious and time-consuming to write. Dash, condensed, and bond-line formulas are therefore used more often.

Generally it is best to draw unshared electron pairs in chemical formulas, though sometimes they are omitted if we are not considering the chemical properties or reactivity of a compound. When we write chemical reactions, however, we shall see that it is necessary to include the unshared electron pairs when they participate in a reaction. It is a good idea, therefore, to be in the habit of writing unshared electron pairs.

1.7A More About Dash Structural Formulas

- **Dash structural formulas** have lines that show bonding electron pairs, and include elemental symbols for all of the atoms in a molecule.

If we look at the ball-and-stick model for propyl alcohol given in Fig. 1.3*a* and compare it with the electron-dot, dash, and condensed formulas in Figs. 1.3*b–d* we find that the chain of atoms is straight in those formulas. In the ball-and-stick model, which corresponds more accurately to the actual shape of the molecule, the chain of atoms is not at all straight. Also of importance is this: ***Atoms joined by single bonds can rotate relatively freely with respect to one another***. (We shall discuss the reason for this in Section 1.12B.) This relatively free rotation means that the chain of atoms in propyl alcohol can assume a variety of arrangements like these and an infinite number of others that all have the same sequence of connections of their atoms.
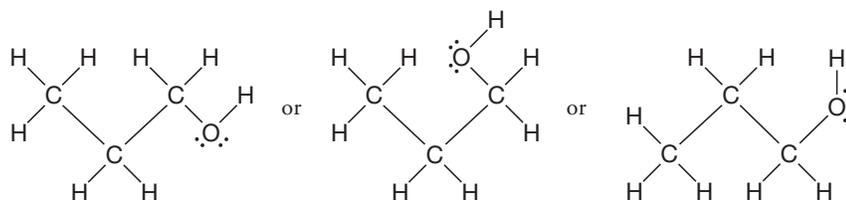
Equivalent dash formulas for propyl alcohol

All of the structural formulas above are *equivalent* and all represent propyl alcohol. Dash structural formulas such as these indicate the way in which the atoms are attached to each other and *are not* representations of the actual shapes of the molecule. Propyl alcohol does not have 90° **bond angles**. It has tetrahedral bond angles. Dash structural formulas show what is called the **connectivity** of the atoms. *Constitutional isomers (Section 1.6A) have different connectivities and, therefore, must have different structural formulas*.

Consider the compound called isopropyl alcohol, whose formula we might write in a variety of ways:
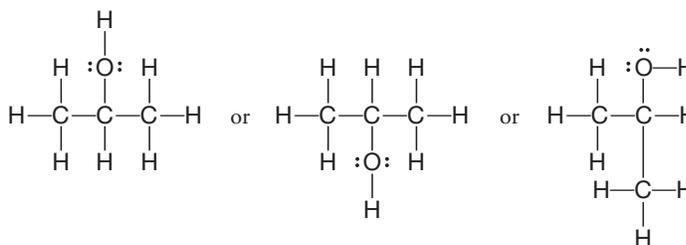
Equivalent dash formulas for isopropyl alcohol

Isopropyl alcohol is a constitutional isomer (Section 1.6A) of propyl alcohol because its atoms are connected in a different order and both compounds have the same molecular formula, C_3H_8O In isopropyl alcohol the OH group is attached to the central carbon; in propyl alcohol it is attached to an end carbon.

We suggest that you build two hand-held molecular models of propyl alcohol. Rotate the position of groups at the ends of bonds in each model to make them appear different, then adjust the models to see if you can make them appear identical. Do the same with two models of isopropyl alcohol. Next, compare a model of propyl alcohol with a model of isopropyl alcohol.
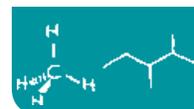
- In problems you will often be asked to write structural formulas for all the isomers that have a given molecular formula. Do not make the error of writing several equivalent formulas, like those that we have just shown, mistaking them for different constitutional isomers.

There are actually three constitutional isomers with the molecular formula C_3H_8O. We have seen two of them in propyl alcohol and isopropyl alcohol. Write a dash formula for the third isomer.
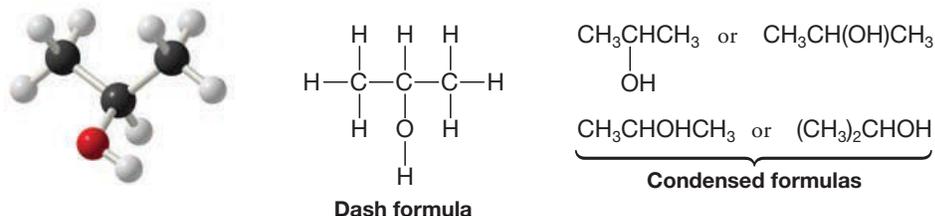
● **PRACTICE PROBLEM 1.12**

1.7B Condensed Structural Formulas

Condensed structural formulas are somewhat faster to write than dash formulas and, when we become familiar with them, they will impart all the information that is contained in the dash structure. In condensed formulas all of the hydrogen atoms that are attached to a particular carbon are usually written immediately after the carbon. In fully condensed formulas, all of the atoms that are attached to the carbon are usually written immediately after that carbon, listing hydrogens first. For example,

$$CH_3CHCH_2CH_3 \quad \text{or} \quad CH_3CHClCH_2CH_3$$
$$\underset{\displaystyle Cl}{|}$$

Dash formula   **Condensed formulas**
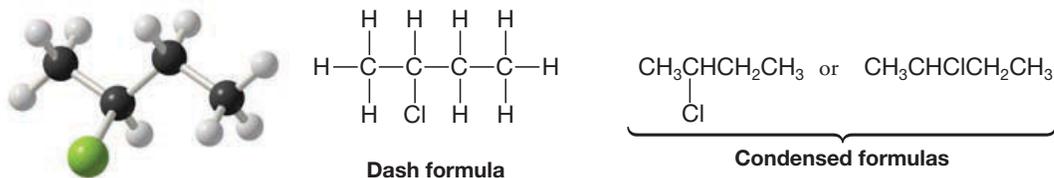
The condensed formula for isopropyl alcohol can be written in four different ways:

$$CH_3CHCH_3 \quad \text{or} \quad CH_3CH(OH)CH_3$$
$$\underset{\displaystyle OH}{|}$$

$$CH_3CHOHCH_3 \quad \text{or} \quad (CH_3)_2CHOH$$

Dash formula   **Condensed formulas**

●●● **SOLVED PROBLEM 1.8**

Write a condensed structural formula for the compound that follows:

ANSWER:

$$CH_3CHCH_2CH_3 \quad \text{or} \quad CH_3CH(CH)_3CH_2CH_3 \quad \text{or} \quad (CH_3)_2CHCH_2CH_3$$
$$\underset{\displaystyle CH_3}{|}$$

$$\text{or} \quad CH_3CH_2CH(CH_3)_2 \quad \text{or} \quad CH_3CH_2CHCH_3$$
$$\underset{\displaystyle CH_3}{|}$$
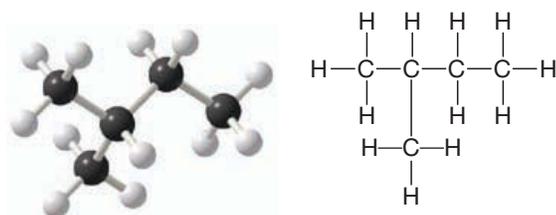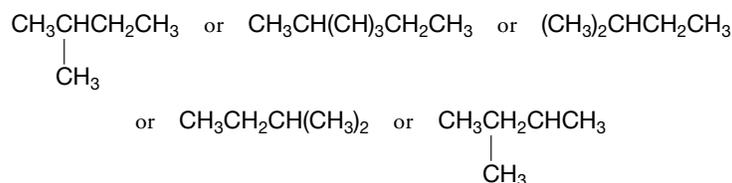
● **PRACTICE PROBLEM 1.13** Write a condensed structural formula for the following compound.
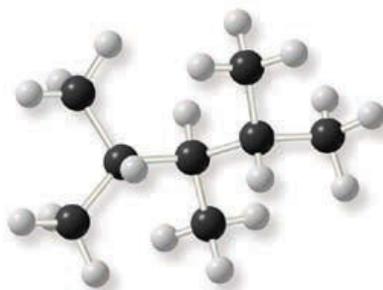
1.7C Bond-Line Formulas

The most common type of structural formula used by organic chemists, and the fastest to draw, is the **bond-line formula**. (Some chemists call these **skeletal formulas**.) The formula in Fig. 1.3*e* is a bond-line formula for propyl alcohol. The sooner you master the use of bond-line formulas, the more quickly you will be able to draw molecules when you take notes and work problems. And, lacking all of the symbols that are explicitly shown in dash and condensed structural formulas, bond-line formulas allow you to more quickly interpret molecular connectivity and compare one molecular formula with another.

● ● **HOW TO** Draw Bond-Line Formulas

We apply the following rules when we draw bond-line formulas:

- Each line represents a bond.
- Each **bend** in a line or **terminus** of a line represents a carbon atom, unless another group is shown explicitly.
- No Cs are written for carbon atoms, except optionally for CH_3 groups at the end of a chain or branch.
- No Hs are shown for hydrogen atoms, unless they are needed to give a three-dimensional perspective, in which case we use dashed or solid wedges (as explained in the next section).
- The number of hydrogen atoms bonded to each carbon is inferred by assuming that as many hydrogen atoms are present as needed to fill the valence shell of the carbon, unless a charge is indicated.
- When an atom other than carbon or hydrogen is present, the symbol for that element is written at the appropriate location (i.e., in place of a bend or at the terminus of the line leading to the atom).
- Hydrogen atoms bonded to atoms other than carbon (e.g., oxygen or nitrogen) are written explicitly.

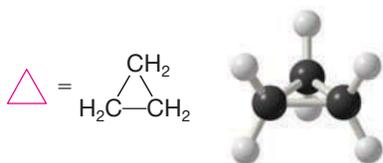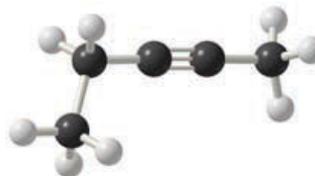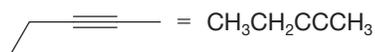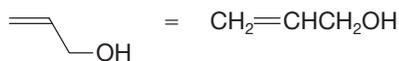Consider the following examples of molecules depicted by bond-line formulas.
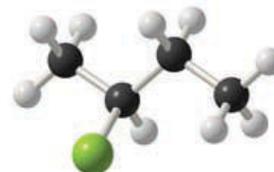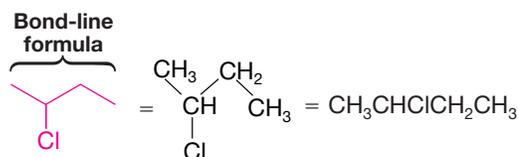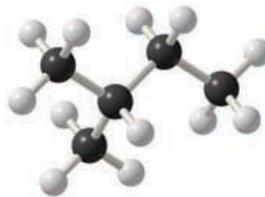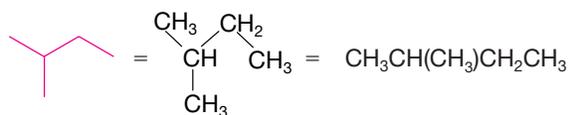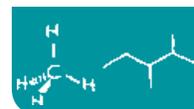
Bond-line formula

$$
\begin{array}{ccc}
& CH_3 & CH_2 \\
= & CH & CH_3 \\
& | & \\
Cl & Cl &
\end{array}
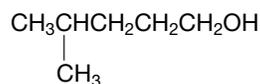= CH_3CHClCH_2CH_3
$$

$$CH_3CH(CH_3)CH_2CH_3$$

$$(CH_3)_2NCH_2CH_3$$
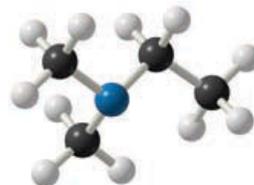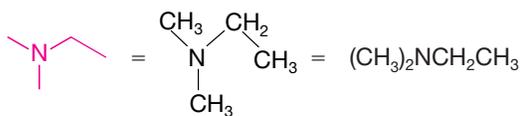
Bond-line formulas are easy to draw for molecules with multiple bonds and for cyclic molecules, as well. The following are some examples.
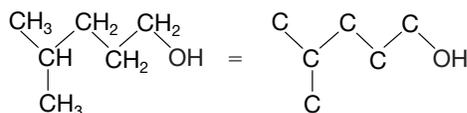
and

$$CH_2=CHCH_2OH$$

$$CH_3CH_2CCCH_3$$
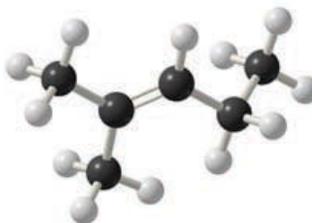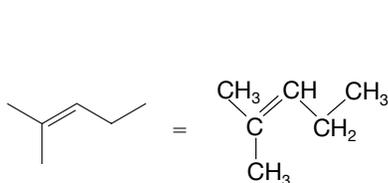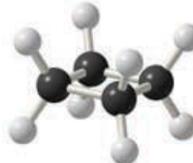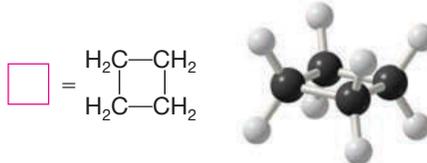
●●● SOLVED PROBLEM 1.9

Write the bond-line formula for

$$CH_3CHCH_2CH_2CH_2OH$$
$$CH_3$$

STRATEGY AND ANSWER: First, for the sake of practice, we outline the carbon skeleton, including the OH group, as follows:

Then we write the bond-line formula as ⟍∕⟍∕⟍OH. As you gain experience you will likely skip the intermediate steps shown above and proceed directly to writing bond-line formulas.

● PRACTICE PROBLEM 1.14 | Write each of the following condensed structural formulas as a bond-line formula:

(a) $(CH_3)_2CHCH_2CH_3$ (f) $CH_2{=}C(CH_2CH_3)_2$

(b) $(CH_3)_2CHCH_2CH_2OH$

(c) $(CH_3)_2C{=}CHCH_2CH_3$ (g) $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$

(d) $CH_3CH_2CH_2CH_2CH_3$ (h) $CH_3CHClCH_2CH(CH_3)_2$

(e) $CH_3CH_2CH(OH)CH_2CH_3$

● PRACTICE PROBLEM 1.15 | Which molecules in Practice Problem 1.14 form sets of constitutional isomers?

● PRACTICE PROBLEM 1.16 | Write a dash formula for each of the following bond-line formulas:
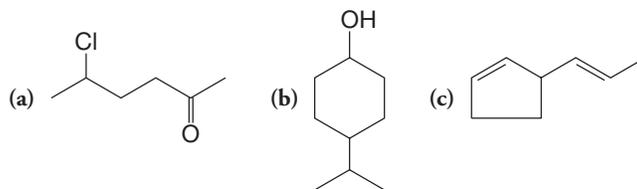

1.7D Three-Dimensional Formulas

None of the formulas that we have described so far convey any information about how the atoms of a molecule are arranged in space. Molecules exist in three dimensions. We can depict three-dimensional geometry in molecules using bonds represented by dashed wedges, solid wedges, and lines.

- A dashed wedge (⸗) represents a bond that projects behind the plane of the paper.
- A solid wedge (◀) represents a bond that projects out of the plane of the paper.
- An ordinary line (—) represents a bond that lies in the plane of the paper.

For example, the four C—H bonds of methane (CH_4) are oriented toward the corners of a regular tetrahedron, with the carbon in the center and an approximately 109° angle between each C—H bond, as was originally postulated by J. H. van't Hoff and L. A. Le Bel in 1874. Figure l.4 shows the tetrahedral structure of methane.

We will discuss the physical basis for the geometries of carbon when it has only single bonds, a double bond, or a triple bond in Sections 1.12–14. For now, let us consider some guidelines for representing these bonding patterns in three dimensions using dashed and solid wedge bonds.
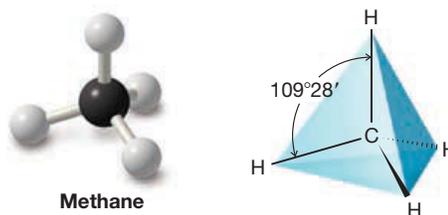
Methane

FIGURE 1.4 The tetrahedral structure of methane.
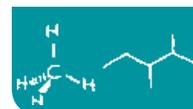
In general for carbon atoms that have only single bonds:

- A carbon atom with **four single bonds** has tetrahedral geometry (Section 1.12) and can be drawn with two bonds in the plane of the paper separated by approximately 109°, one bond behind the plane using a dashed wedge, and one bond in front of the plane using a solid wedge.
- The dashed wedge and solid wedge bonds in tetrahedral geometry nearly eclipse each other when drawn in proper three-dimensional perspective.

For carbon atoms with a double or a triple bond:

- A carbon atom with a **double bond** has trigonal planar geometry (Section 1.13) and can be depicted with bonds that are all in the plane of the paper and separated by 120°.
- A carbon atom with a **triple bond** has linear geometry (Section 1.14) and can be depicted with its bonds in the plane of the paper and separated by a 180° angle.
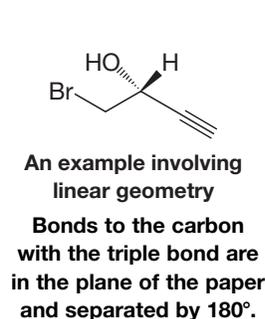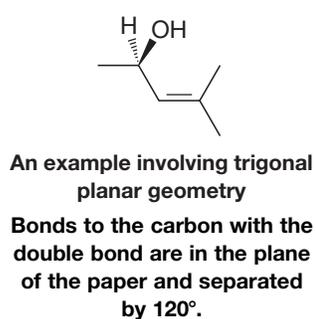
Last, when drawing three-dimensional formulas for molecules:

- Draw as many carbon atoms in the plane of the paper as possible using ordinary lines, then use dashed or solid wedge bonds for substituent groups or hydrogen atoms that are needed to show three dimensions.

Some examples of three-dimensional formulas are shown below.

Ethane   **Bromomethane**

Examples of bond-line formulas that include three-dimensional representations
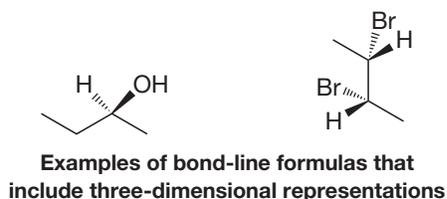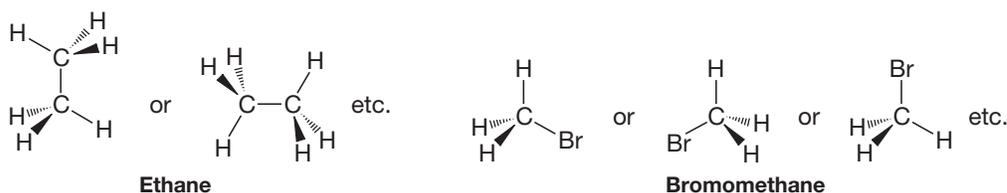
The carbon chains are shown in the plane of the paper. The dashed and solid wedge bonds nearly eclipse each other.

An example involving trigonal planar geometry

Bonds to the carbon with the double bond are in the plane of the paper and separated by 120°.

An example involving linear geometry

Bonds to the carbon with the triple bond are in the plane of the paper and separated by 180°.

● ● ●SOLVED PROBLEM 1.10

Write a bond-line formula for the following compound showing three dimensions at the carbon bearing the chlorine atom.

$$CH_3CH_2CHCH_2CH_3$$
$$|$$
$$Cl$$
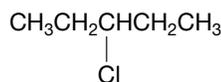
STRATEGY AND ANSWER: First draw the carbon skeleton, placing as many carbon atoms in the plane of the paper as possible (which is all of them, in this case).

Then add the chlorine atom at the appropriate carbon using a three-dimensional representation.
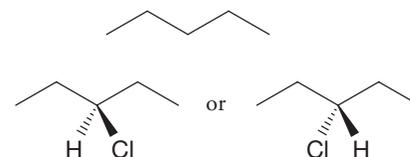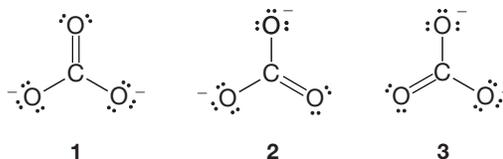

Write three-dimensional (wedge–dashed wedge–line) representations for each of the following:

● PRACTICE PROBLEM 1.17

(a) CH_3Cl **(b)** CH_2Cl_2 **(c)** CH_2BrCl **(d)** CH_3CH_2Cl

1.8 RESONANCE THEORY

Often more than one *equivalent* Lewis structure can be written for a molecule or ion. Consider, for example, the carbonate ion ($CO_3{}^{2-}$). We can write three *different* but *equivalent* structures, **1–3**:

Notice two important features of these structures. First, each atom has the noble gas configuration. Second, *and this is especially important*, we can convert one structure into any other by *changing only the positions of the electrons*. We do not need to change the relative positions of the atomic nuclei. For example, if we move the electron pairs in the manner indicated by the **curved arrows** in structure **1**, we change structure **1** into structure **2**:

In a similar way we can change structure **2** into structure **3**:
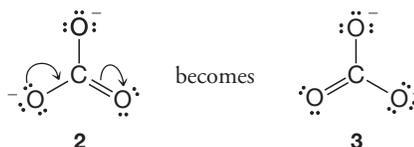
Structures **1–3**, although not identical on paper, *are equivalent*. None of them alone, however, fits important data about the carbonate ion.

X-ray studies have shown that carbon–oxygen double bonds are shorter than single bonds. The same kind of study of the carbonate ion shows, however, that all of its carbon–oxygen bonds *are of equal length*. One is not shorter than the others as would be expected from representations **1**, **2**, and **3**. Clearly none of the three structures agrees with this evidence. In each structure, **1–3**, one carbon–oxygen bond is a double bond and the other two are single bonds. None of the structures, therefore, is correct. How, then, should we represent the carbonate ion?

One way is through a theory called **resonance theory**. This theory states that whenever a molecule or ion can be represented by two or more Lewis structures *that differ only in the positions of the electrons*, two things will be true:

1. None of these structures, which we call **resonance structures** or **resonance contributors**, will be a realistic representation for the molecule or ion. None will be in complete accord with the physical or chemical properties of the substance.

2. The actual molecule or ion will be better represented by a *hybrid (average) of these structures*.

- *Resonance structures, then, are not real structures for the actual molecule or ion; they exist only on paper*. As such, they can never be isolated. No single contributor adequately represents the molecule or ion. In resonance theory we view the carbonate ion, which is, of course, a real entity, as having a structure that is a **hybrid** of the three **hypothetical** resonance structures.

What would a hybrid of structures **1–3** be like? Look at the structures and look especially at a particular carbon–oxygen bond, say, the one at the top. This carbon–oxygen bond
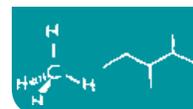
is a double bond in one structure (**1**) and a single bond in the other two (**2** and **3**). The actual carbon–oxygen bond, since it is a hybrid, must be something in between a double bond and a single bond. Because the carbon–oxygen bond is a single bond in two of the structures and a double bond in only one, it must be more like a single bond than a double bond. It must be like a one and one-third bond. We could call it a partial double bond. And, of course, what we have just said about any one carbon–oxygen bond will be equally true of the other two. Thus all of the carbon–oxygen bonds of the carbonate ion are partial double bonds, and *all are equivalent*. All of them *should be* the same length, and this is exactly what experiments tell us. The bonds are all 1.28 Å long, a distance which is intermediate between that of a carbon–oxygen single bond (1.43 Å) and that of a carbon–oxygen double bond (1.20 Å). One angstrom equals 1×10^{-10} meter.

- One other important point: by convention, when we draw resonance structures, we connect them by double-headed arrows ($\longleftrightarrow$) to indicate clearly that they are hypothetical, not real. For the carbonate ion we write them this way:
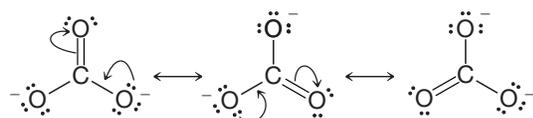

We should not let these arrows, or the word "resonance," mislead us into thinking that the carbonate ion fluctuates between one structure and another. These structures individually do not represent reality and exist only on paper; therefore, the carbonate ion cannot fluctuate among them because it is a hybrid of them.

- Resonance structures do not represent an equilibrium.

In an equilibrium between two or more species, it is quite correct to think of different structures with atoms in different positions, *but not in the case of resonance* (as in the carbonate ion). Here the atoms do not move, and the "structures" exist only on paper. **An equilibrium is indicated by $\rightleftharpoons$ and resonance by $\longleftrightarrow$.**

How can we write the structure of the carbonate ion in a way that will indicate its actual structure? We may do two things: we may write all of the resonance structures as we have just done and let you, the reader, mentally fashion the hybrid, or we may write a non-Lewis structure that attempts to represent the hybrid. For the carbonate ion we might do the following:

**Hybrid**   **Contributing resonance structures**
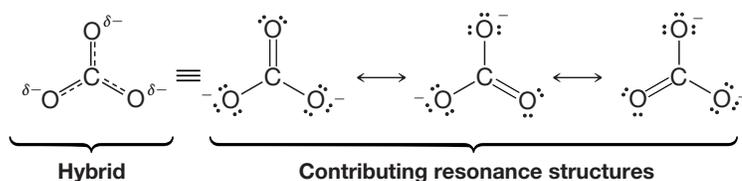
The bonds in the structure on the left are indicated by a combination of a solid line and a dashed line. This depiction is to indicate that the bonds are something in between a single bond and a double bond. As a rule, we use a solid line whenever a bond appears in all structures, and a dashed line when a bond exists in one or more but not all. We also place a $\delta-$ (read partial minus) beside each oxygen to indicate that something less than a full negative charge resides on each oxygen atom. In this instance, each oxygen atom has two-thirds of a full negative charge.

Calculations from theory show the equal charge density at each oxygen in the carbonate anion. Figure 1.5 shows a calculated **electrostatic potential map** of the electron density in the carbonate ion. In an electrostatic potential map, regions of relatively more negative charge are red, while more positive regions (i.e., less negative regions) are indicated by colors trending toward blue. Equality of the bond lengths in the carbonate anion (partial double bonds as shown in the resonance hybrid above) is also evident in this model.
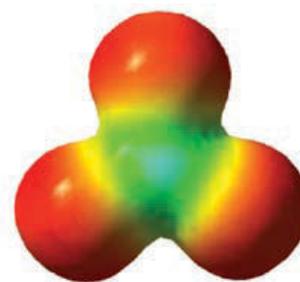
FIGURE 1.5 A calculated electrostatic potential map for the carbonate anion, showing the equal charge distribution at the three oxygen atoms. In electrostatic potential maps like this one, colors trending toward red mean increasing concentration of negative charge, while those trending toward blue mean less negative (or more positive) charge.

## • • 1.8A The Use of Curved Arrows: HOW TO Write Resonance Structures

As we have mentioned earlier, curved arrows are often used in writing **resonance structures**, and as we shall see in Section 3.2 they are essential in writing reaction mechanisms. Let us now point out several important things to remember about their use.

- Curved arrows are used to show the movement of both **bonding** and **unshared** electrons.
- A double-barbed curved arrow (⌒) shows the movement of **two** electrons (an electron pair). [Later, we will see that a single-barbed arrow (⌒) can be used to show the movement of a single electron.]
- A curved arrow should originate precisely at the location of the relevant electrons in the initial formula and point precisely to where those electrons will be drawn in the new formula.
- A new formula should be drawn to show the result of the electron shift(s). All formulas should be proper Lewis structures and should include formal charges as appropriate. The maximum number of valence electrons should not be exceeded for any atom in a formula.

1.8B Rules for Writing Resonance Structures

1. Resonance structures exist only on paper. Although they have no real existence of their own, **resonance structures** are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows (⟷), and we say that the real molecule or ion is a hybrid of all of them.

2. We are only allowed to move electrons in writing resonance structures. The positions of the nuclei of the atoms must remain the same in all of the structures. Structure **3** is not a resonance structure of **1** or **2**, for example, because in order to form it we would have to move a hydrogen atom and this is not permitted:

These are resonance structures.

This is not a resonance structure of 1 or 2. It is an isomer because a hydrogen atom has been moved.
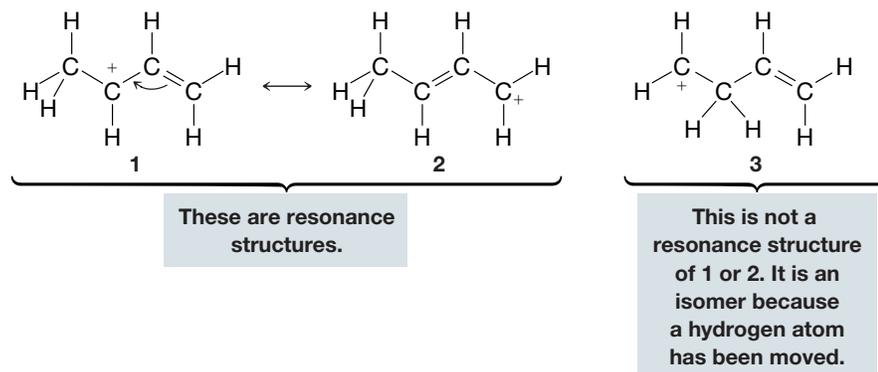
Generally speaking, when we move electrons, we move only those of **multiple bonds** (as in the example above) and those of **nonbonding electron pairs**.

3. All of the structures must be proper Lewis structures. We should not write structures in which carbon has five bonds, for example:
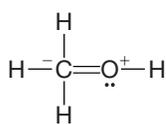
This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the first major row of the periodic table cannot have more than eight electrons in their valence shell.

4. The energy of the resonance hybrid is lower than the energy of any contributing structure. Resonance stabilizes a molecule or ion. This is especially true when the
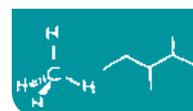
resonance structures are equivalent. Chemists call this stabilization *resonance stabilization*. **If the resonance structures are equivalent, then the resonance stabilization is large.**

In Chapter 14 we shall find that benzene is highly resonance stabilized because it is a hybrid of the two equivalent forms that follow:

**Resonance structures
for benzene**   **Representation
of hybrid**
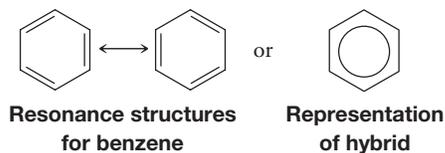
5. The more stable a structure is (when taken by itself), the greater is its contribution to the hybrid.

•• 1.8C **HOW TO** Decide When One Resonance Structure Contributes More to the Hybrid Than Another

The following rules will help us:

1. The more covalent bonds a structure has, the more stable it is. Consider the resonance structures for formaldehyde below. (Formaldehyde is a chemical used to preserve biological specimens.) Structure **A** has more covalent bonds, and therefore makes a larger contribution to the hybrid. In other words, the hybrid is more like structure **A** than structure **B**.

**Four
covalent
bonds**   **Three
covalent
bonds**

A   **B**

More stable   **Less stable**

Resonance structures for formaldehyde
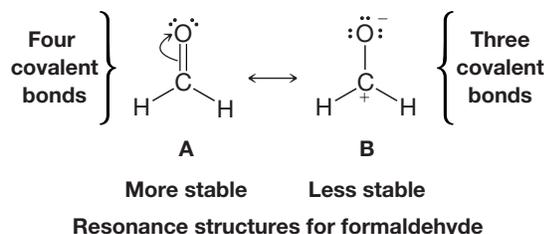
These structures also illustrate two other considerations:

2. Charge separation decreases stability. It takes energy to separate opposite charges, and therefore a structure with separated charges is less stable. Structure **B** for formaldehyde has separated plus and minus charges; therefore, on this basis, too, it is the less stable contributor and makes a smaller contribution to the hybrid.

3. Structures in which all the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are more stable. Look again at structure **B**. The carbon atom has only six electrons around it, whereas in **A** it has eight. On this basis we can conclude that **A** is more stable and makes a larger contribution.

●●●SOLVED PROBLEM 1.11

The following is one way of writing the structure of the nitrate ion:
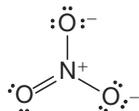
However, considerable physical evidence indicates that all three nitrogen–oxygen bonds are equivalent and that they have the same length, a bond distance between that expected for a nitrogen–oxygen single bond and a nitrogen–oxygen double bond. Explain this in terms of resonance theory.

STRATEGY AND ANSWER: We recognize that if we move the electron pairs in the following way, we can write three *different* but *equivalent* structures for the nitrate ion:
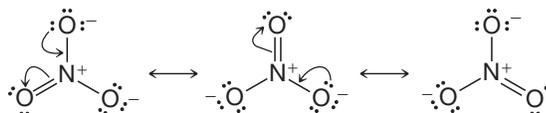
Since these structures differ from one another *only in the positions of their electrons*, they are *resonance structures* or *resonance contributors*. As such, no single structure taken alone will adequately represent the nitrate ion. The actual molecule will be best represented by a *hybrid of these three structures*. We might write this hybrid in the following way to indicate that all of the bonds are equivalent and that they are more than single bonds and less than double bonds. We also indicate that each oxygen atom bears an equal partial negative charge. This charge distribution corresponds to what we find experimentally.


Hybrid structure for the nitrate ion

● **PRACTICE PROBLEM 1.18**   (a) Write two resonance structures for the formate ion HCO_2^-. (*Note*: The hydrogen and oxygen atoms are bonded to the carbon.) (b) Explain what these structures predict for the carbon–oxygen bond lengths of the formate ion, and (c), for the electrical charge on the oxygen atoms.

● **PRACTICE PROBLEM 1.19**   Write the resonance structure that would result from moving the electrons as the curved arrows indicate. Be sure to include formal charges if needed.
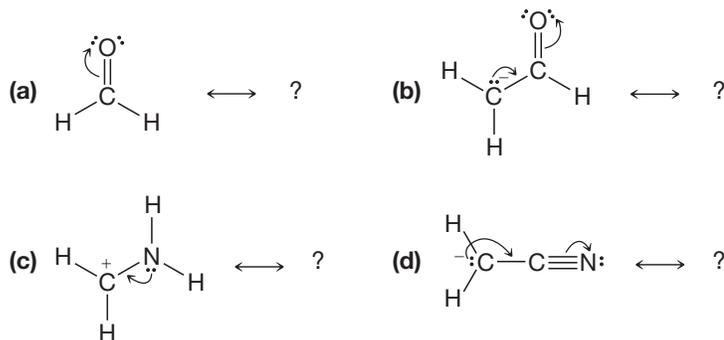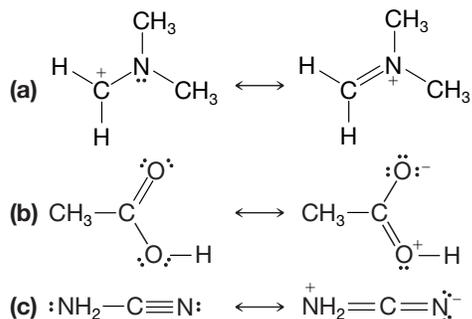

● **PRACTICE PROBLEM 1.20**   Add any missing unshared electron pairs (if any), then, using curved arrows to show the shifts in electrons, write the contributing resonance structures and resonance hybrid for each of the following:

(g) $CH_3\overset{+}{S}CH_2$

(h) CH_3NO_2
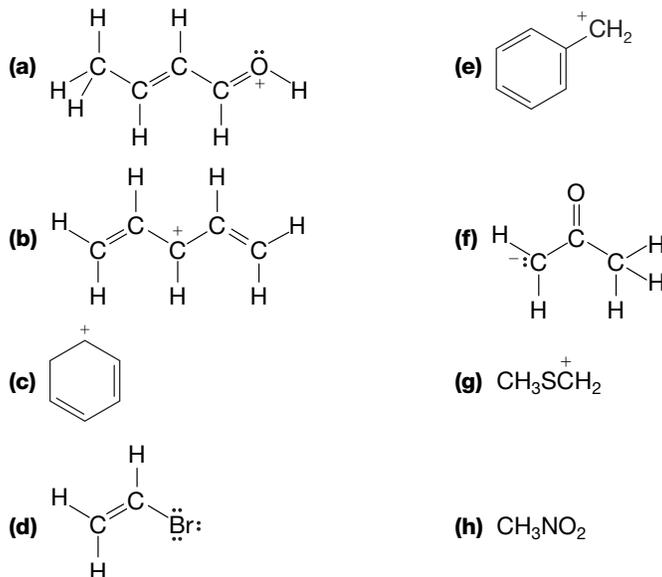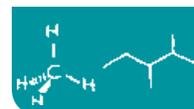
For each set of resonance structures that follow, add a curved arrow that shows how electrons in the left formula shift to become the right formula, and designate the formula that would contribute most to the hybrid. Explain your choice:

(a) [structures with CH₃, N, C, H groups]

(b) CH_3-C [structure with O groups] $\longleftrightarrow$ CH_3-C [structure with O groups]

(c) $:NH_2-C\equiv N:$ $\longleftrightarrow$ $\overset{+}{N}H_2=C=\overset{..}{\underset{..}{N}}{}^{-}$

1.9 QUANTUM MECHANICS AND ATOMIC STRUCTURE

A theory of atomic and molecular structure was advanced independently and almost simultaneously by three people in 1926: Erwin Schrödinger, Werner Heisenberg, and Paul Dirac. This theory, called **wave mechanics** by Schrödinger and **quantum mechanics** by Heisenberg, has become the basis from which we derive our modern understanding of bonding in molecules. At the heart of quantum mechanics are equations called wave functions (denoted by the Greek letter **psi**, ψ).
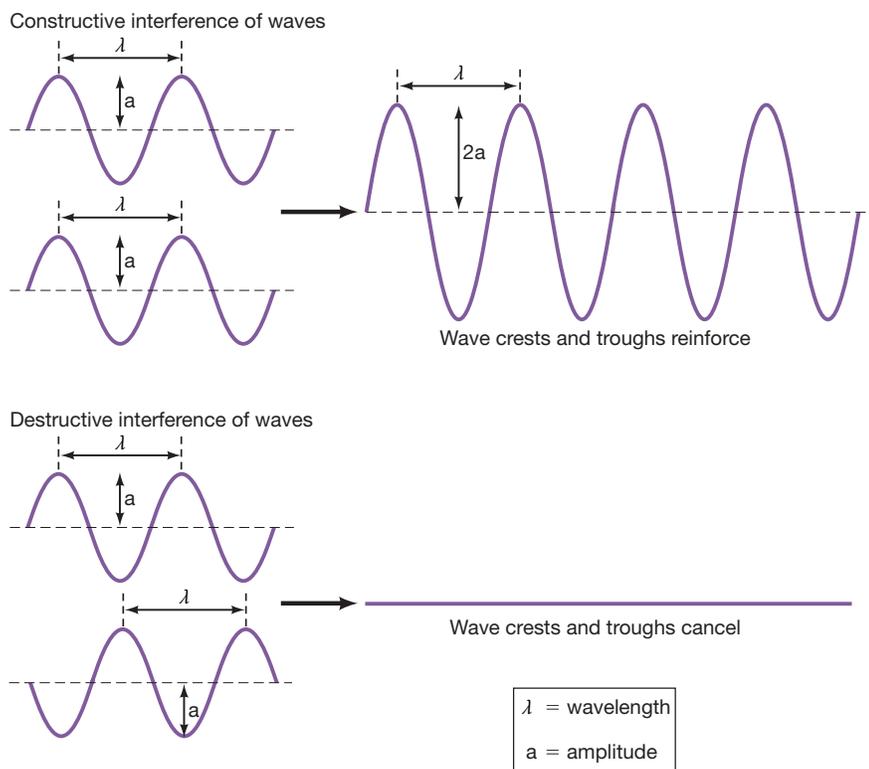
- Each **wave function** (ψ) corresponds to a different *energy state* for an electron.

- Each *energy state* is a sublevel where one or two electrons can reside.

- The **energy** associated with the state of an electron can be calculated from the wave function.

- The **relative probability** of finding an electron in a given region of space can be calculated from the wave function (Section 1.10).

- The solution to a wave function can be positive, negative, or zero (Fig. 1.6).

- The **phase sign** of a wave equation indicates whether the solution is positive or negative when calculated for a given point in space relative to the nucleus.

Wave functions, whether they are for sound waves, lake waves, or the energy of an electron, have the possibility of constructive interference and destructive interference.

- **Constructive interference** occurs when wave functions with the same phase sign interact. There is a *reinforcing effect* and the amplitude of the wave function increases.

- **Destructive interference** occurs when wave functions with opposite phase signs interact. There is a *subtractive effect* and the amplitude of the wave function goes to zero or changes sign.
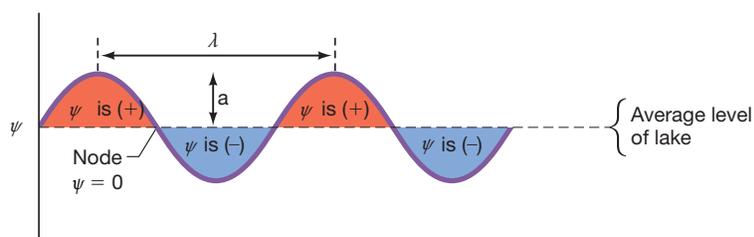
FIGURE 1.6 A wave moving across a lake is viewed along a slice through the lake. For this wave the wave function, ψ, is plus (+) in crests and minus (−) in troughs. At the average level of the lake it is zero; these places are called nodes. The magnitude of the crests and troughs is the amplitude (a) of the wave. The distance from the crest of one wave to the crest of the next is the wavelength (λ, or lambda).

Constructive interference of waves

Wave crests and troughs reinforce

Destructive interference of waves

Wave crests and troughs cancel

λ	= wavelength
a	= amplitude

Experiments have shown that electrons have properties of waves and particles, which was an idea first put forth by Louis de Broglie in 1923. Our discussion will focus on the wavelike properties of electrons.

1.10 ATOMIC ORBITALS AND ELECTRON CONFIGURATION

A physical interpretation related to the electron wave function was put forth by Max Born in 1926:

- The square of a wave function (ψ^2) for a particular x, y, z location expresses the probability of finding an electron at that location in space.

If the value of ψ^2 is large in a unit volume of space, the probability of finding an electron in that volume is high—we say that the **electron probability density** is large. Conversely, if ψ^2 for some other volume of space is small, the probability of finding an electron there is low.* This leads to the general definition of an orbital and, by extension, to the familiar shapes of atomic orbitals.

- An **orbital** is a region of space where the probability of finding an electron is high.
- **Atomic orbitals** are plots of ψ^2 in three dimensions. These plots generate the familiar s, p, and d orbital shapes.

The volumes that we show are those that would contain the electron 90–95% of the time. There is a finite, but very small, probability of finding an electron at a greater distance from the nucleus than shown in the plots.

The shapes of s and p orbitals are shown in Fig. 1.7.

All **s orbitals** are spheres. A 1s orbital is a simple sphere. A 2s orbital is a sphere with an inner nodal surface ($\psi^2 = 0$). The inner portion of the 2s orbital, ψ_2, has a negative phase sign.

*Integration of ψ^2 over all space must equal 1; that is, the probability of finding an electron somewhere in all of space is 100%.
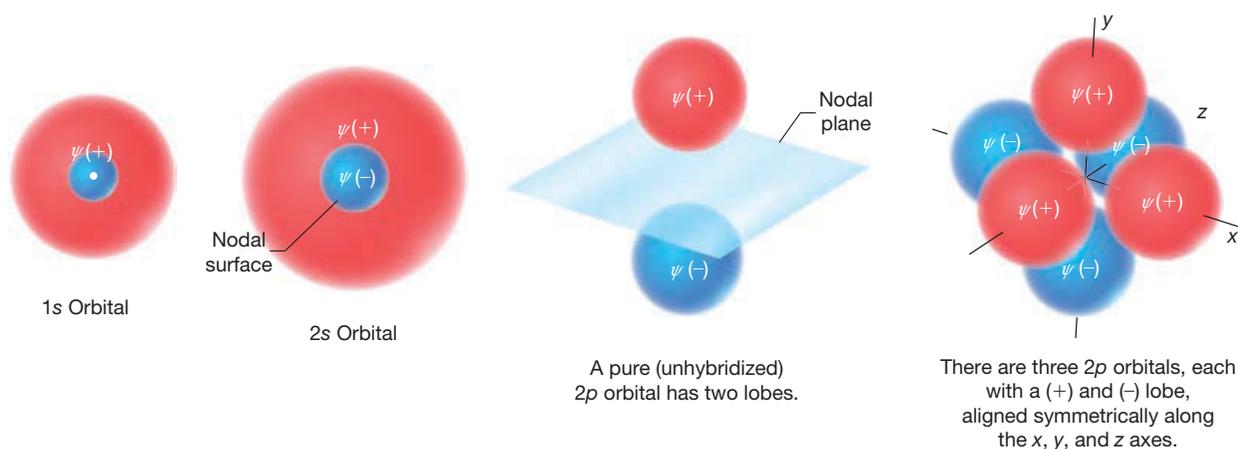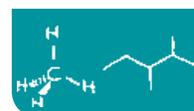
FIGURE 1.7 The shapes of some *s* and *p* orbitals. Pure, unhybridized *p* orbitals are almost-touching spheres. The *p* orbitals in hybridized atoms are lobe-shaped (Section 1.13).

The shape of a **p orbital** is like that of almost-touching spheres or lobes. The phase sign of a $2p$ wave function, ψ_{2p} is positive in one lobe and negative in the other. A nodal plane separates the two lobes of a p orbital, and the three p orbitals of a given energy level are arranged in space along the x, y, and z axes in a Cartesian coordinate system.

- The $+$ and $-$ signs of wave functions do not imply positive or negative charge or greater or lesser probability of finding an electron.
- ψ^2 (the probability of finding an electron) is always positive, because squaring either a positive or negative solution to ψ leads to a positive value.

Thus, the probability of finding an electron in either lobe of a p orbital is the same. We shall see the significance of the $+$ and $-$ signs later when we see how atomic orbitals combine to form molecular orbitals.
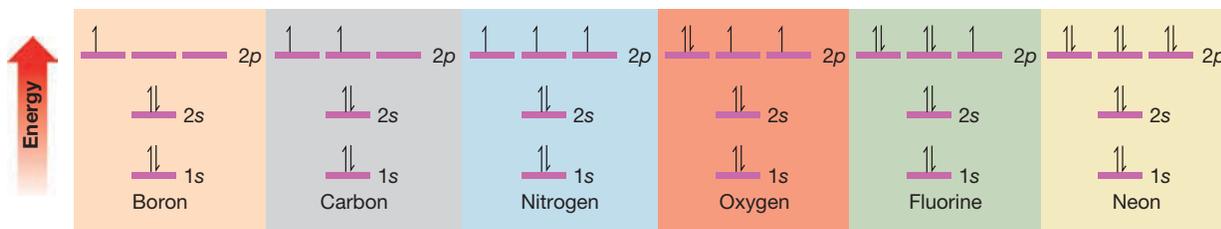
1.10A Electron Configurations

The relative energies of atomic orbitals in the first and second principal shells are as follows:

- Electrons in $1s$ orbitals have the lowest energy because they are closest to the positive nucleus.
- Electrons in $2s$ orbitals are next lowest in energy.
- Electrons of the three $2p$ orbitals have equal but higher energy than the $2s$ orbital.
- Orbitals of equal energy (such as the three $2p$ orbitals) are called **degenerate orbitals**.

We can use these relative energies to arrive at the electron configuration of any atom in the first two rows of the periodic table. We need follow only a few simple rules.

1. Aufbau principle: Orbitals are filled so that those of lowest energy are filled first. (*Aufbau* is German for "building up.")

2. Pauli exclusion principle: A maximum of two electrons may be placed in each orbital *but only when the spins of the electrons are paired*. An electron spins about its own axis. For reasons that we cannot develop here, an electron is permitted only one or the other of just two possible spin orientations. We usually show these orientations by arrows, either ↑ or ↓. Thus two spin-paired electrons would be designated ↓↑. Unpaired electrons, which are not permitted in the same orbital, are designated ↑↑ (or ↓↓).

3. Hund's rule: When we come to orbitals of equal energy (degenerate orbitals) such as the three p orbitals, we add one electron to each *with their spins unpaired* until each of the degenerate orbitals contains one electron. (This allows the electrons, which repel each other, to be farther apart.) Then we begin adding a second electron to each degenerate orbital so that the spins are paired.

FIGURE 1.8 The ground state electron configurations of some second-row elements.

If we apply these rules to some of the second-row elements of the periodic table, we get the results shown in Fig. 1.8.

1.11 MOLECULAR ORBITALS

Atomic orbitals provide a means for understanding how atoms form covalent bonds. Let us consider a very simple case—formation of a bond between two hydrogen atoms to form a hydrogen molecule (Fig. 1.9).

When two hydrogen atoms are relatively far apart their total energy is simply that of two isolated hydrogen atoms (**I**). Formation of a covalent bond reduces the overall energy of the system, however. As the two hydrogen atoms move closer together (**II**), each nucleus increasingly attracts the other's electron. This attraction more than compensates for the repulsive force between the two nuclei (or the two electrons). The result is a covalent bond (**III**), such that the internuclear distance is an ideal balance that allows the two electrons to be shared between both atoms while at the same time avoiding repulsive interactions between their nuclei. This ideal internuclear distance between hydrogen atoms is 0.74 Å, and we call this the **bond length** in a hydrogen molecule. If the nuclei are moved closer together (**IV**) the repulsion of the two positively charged nuclei predominates, and the energy of the system rises.

Notice that each H· has a shaded area around it, indicating that its precise position is uncertain. Electrons are constantly moving.

- According to the **Heisenberg uncertainty principle**, we cannot simultaneously know the position and momentum of an electron.

These shaded areas in our diagram represent orbitals, and they result from applying the principles of quantum mechanics. Plotting the square of the wave function (ψ^2) gives us a three-dimensional region called an orbital where finding an electron is highly probable.

- An **atomic orbital** represents the region of space where one or two electrons of an isolated atom are likely to be found.
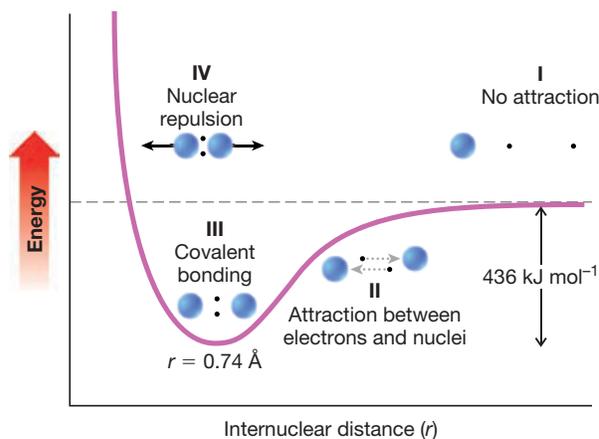
FIGURE 1.9 The potential energy of the hydrogen molecule as a function of internuclear distance.
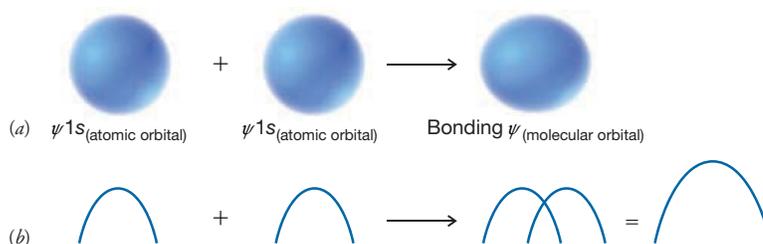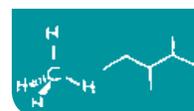
FIGURE 1.10 (*a*) The overlapping of two hydrogen 1*s* atomic orbitals with the same phase sign (indicated by their identical color) to form a bonding molecular orbital. (*b*) The analogous overlapping of two waves with the same phase, resulting in constructive interference and enhanced amplitude.

In the case of our hydrogen model above, the shaded spheres represent the 1*s* orbital of each hydrogen atom. As the two hydrogen atoms approach each other their 1*s* orbitals begin to overlap until their atomic orbitals combine to form molecular orbitals.

- A **molecular orbital (MO)** represents the region of space where one or two electrons of a molecule are likely to be found.

- An orbital (atomic or molecular) can contain a maximum of two spin-paired electrons (Pauli exclusion principle).

- When atomic orbitals combine to form molecular orbitals, **the number of molecular orbitals that result always equals the number of atomic orbitals that combine**.

Thus, in the formation of a hydrogen molecule the two ψ_{1s} atomic orbitals combine to produce two molecular orbitals. Two orbitals result because the mathematical properties of wave functions permit them to be combined by either addition or subtraction. That is, they can combine either in or out of phase.

- A **bonding molecular orbital** (ψ_{molec}) results when two orbitals of the same phase overlap (Fig. 1.10).
- An **antibonding molecular orbital** (ψ^*_{molec}) results when two orbitals of opposite phase overlap (Fig. 1.11).

The bonding molecular orbital of a hydrogen molecule in its lowest energy (ground) state contains both electrons from the individual hydrogen atoms. The value of ψ (and therefore also ψ^2) is large between the nuclei, precisely as expected since the electrons are shared by both nuclei to form the covalent bond.

The antibonding molecular orbital contains no electrons in the ground state of a hydrogen molecule. Furthermore, the value of ψ (and therefore also ψ^2) goes to zero between the nuclei, creating a node ($\psi = 0$). The antibonding orbital does not provide for electron density between the atoms, and thus it is not involved in bonding.

What we have just described has its counterpart in a mathematical treatment called the **LCAO (linear combination of atomic orbitals)** method. In the LCAO treatment, wave functions for the atomic orbitals are combined in a linear fashion (by addition or subtraction) in order to obtain new wave functions for the molecular orbitals.
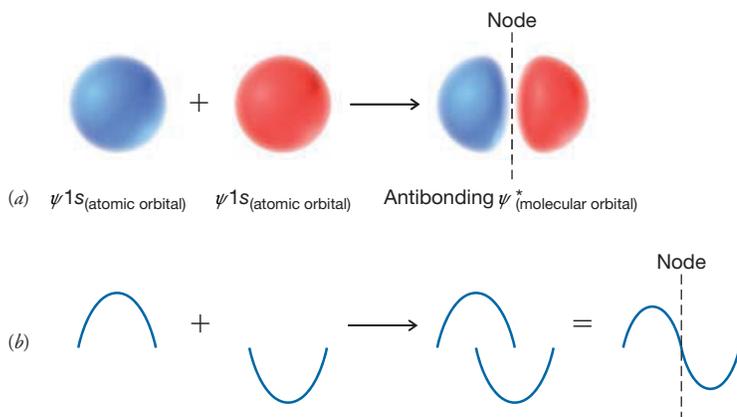
FIGURE 1.11 (*a*) The overlapping of two hydrogen 1*s* atomic orbitals with opposite phase signs (indicated by their different colors) to form an antibonding molecular orbital. (*b*) The analogous overlapping of two waves with the opposite sign, resulting in destructive interference and decreased amplitude. A node exists where complete cancellation by opposite phases makes the value of the combined wave function zero.

FIGURE 1.12 Energy diagram for the hydrogen molecule. Combination of two atomic orbitals, ψ_{1s}, gives two molecular orbitals, ψ_{molec} and ψ^*_{molec}. The energy of ψ_{molec} is lower than that of the separate atomic orbitals, and in the lowest electronic energy state of molecular hydrogen the bonding MO contains both electrons.
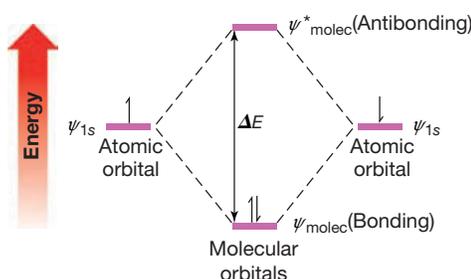

Molecular orbitals, like atomic orbitals, correspond to particular energy states for an electron. Calculations show that the relative energy of an electron in the bonding molecular orbital of the hydrogen molecule is substantially less than its energy in a ψ_{1s} atomic orbital. These calculations also show that the energy of an electron in the antibonding molecular orbital is substantially greater than its energy in a ψ_{1s} atomic orbital.

An energy diagram for the molecular orbitals of the hydrogen molecule is shown in Fig. 1.12. Notice that electrons are placed in molecular orbitals in the same way that they are in atomic orbitals. Two electrons (with their spins opposed) occupy the bonding molecular orbital, where their total energy is less than in the separate atomic orbitals. This is, as we have said, the *lowest electronic state* or *ground state* of the hydrogen molecule. An electron may occupy the antibonding molecular orbital in what is called an *excited state* for the molecule. This state forms when the molecule in the ground state (Fig. 1.12) absorbs a photon of light having the proper energy (ΔE).

1.12 THE STRUCTURE OF METHANE AND ETHANE: sp^3 HYBRIDIZATION

The *s* and *p* orbitals used in the quantum mechanical description of the carbon atom, given in Section 1.10, were based on calculations for hydrogen atoms. These simple *s* and *p* orbitals do not, when taken alone, provide a satisfactory model for the *tetravalent–tetrahedral* carbon of methane (CH_4). However, a satisfactory model of methane's structure that is based on quantum mechanics *can* be obtained through an approach called **orbital hybridization**. Orbital hybridization, in its simplest terms, is nothing more than a mathematical approach that involves the combining of individual wave functions for *s* and *p* orbitals to obtain wave functions for new orbitals. The new orbitals have, *in varying proportions*, the properties of the original orbitals taken separately. These new orbitals are called **hybrid atomic orbitals**.

According to quantum mechanics, the electronic configuration of a carbon atom in its lowest energy state—called the **ground state**—is that given here:

$$\text{C} \quad \frac{\uparrow\downarrow}{1s} \quad \frac{\uparrow\downarrow}{2s} \quad \frac{\uparrow}{2p_x} \quad \frac{\uparrow}{2p_y} \quad \frac{}{2p_z}$$
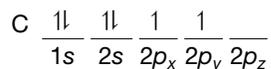
Ground state of a carbon atom

The valence electrons of a carbon atom (those used in bonding) are those of the *outer level*, that is, the 2*s* and 2*p* electrons.

1.12A The Structure of Methane

Hybrid atomic orbitals that account for the structure of methane can be derived from carbon's second-shell *s* and *p* orbitals as follows (Fig. 1.13):

- Wave functions for the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals of ground state carbon are mixed to form four new and equivalent $2sp^3$ hybrid orbitals.
- The designation **sp^3** signifies that the hybrid orbital has one part *s* orbital character and three parts *p* orbital character.
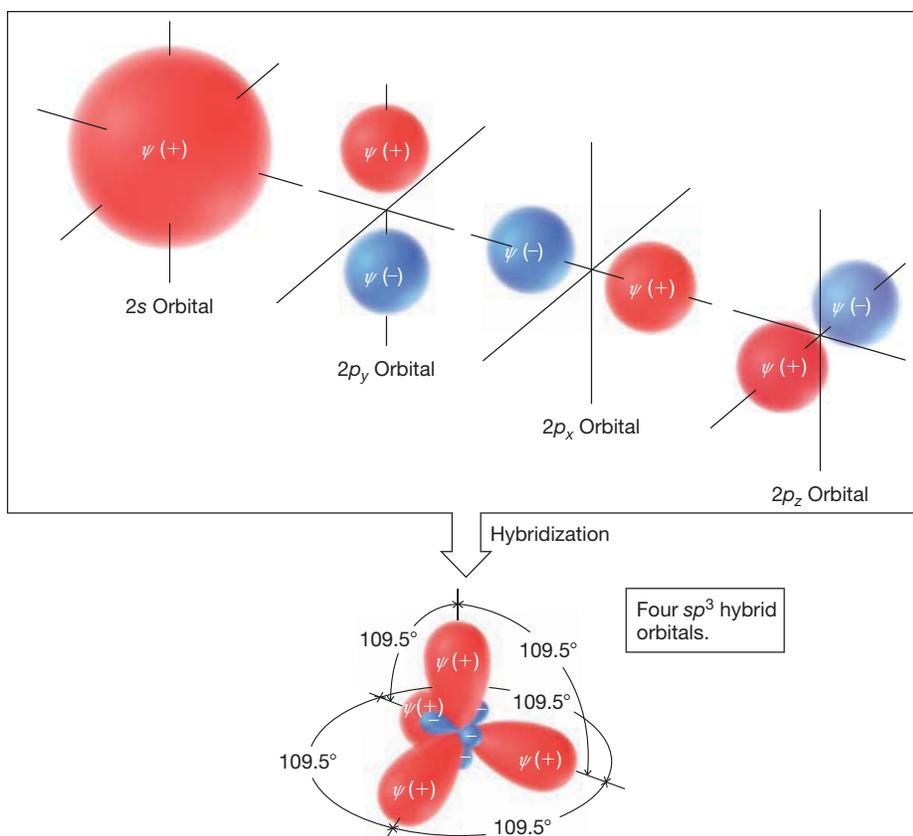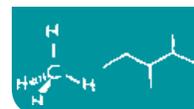
FIGURE 1.13 Hybridization of pure atomic orbitals of a carbon atom to produce sp^3 hybrid orbitals.

- The mathematical result is that the four $2sp^3$ orbitals are oriented at angles of 109.5° with respect to each other. This is precisely the orientation of the four hydrogen atoms of methane. Each H—C—H bond angle is 109.5°.

If, in our imagination, we visualize the hypothetical formation of methane from an sp^3-hybridized carbon atom and four hydrogen atoms, the process might be like that shown in Fig. 1.14. For simplicity we show only the formation of the **bonding molecular orbital** for each carbon–hydrogen bond. We see that an sp^3-hybridized carbon gives a *tetrahedral structure for methane, and one with four equivalent C—H bonds.*

In addition to accounting properly for the shape of methane, the orbital hybridization model also explains the very strong bonds that are formed between carbon and hydrogen.
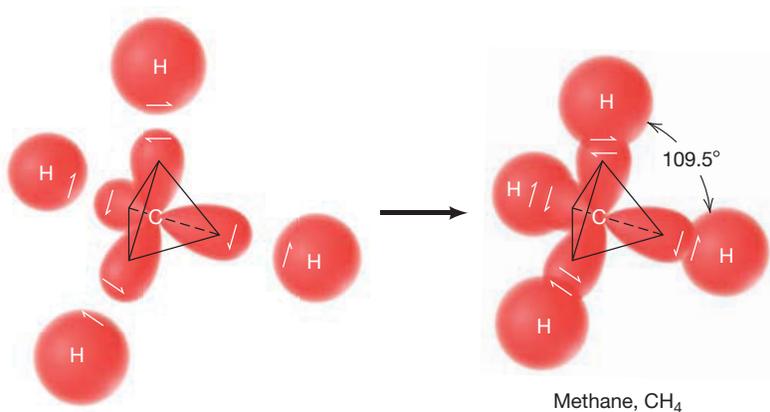

FIGURE 1.14 The hypothetical formation of methane from an sp^3-hybridized carbon atom and four hydrogen atoms. In orbital hybridization we combine orbitals, *not* electrons. The electrons can then be placed in the hybrid orbitals as necessary for bond formation, but always in accordance with the Pauli principle of no more than two electrons (with opposite spin) in each orbital. In this illustration we have placed one electron in each of the hybrid carbon orbitals. In addition, we have shown only the bonding molecular orbital of each C—H bond because these are the orbitals that contain the electrons in the lowest energy state of the molecule.

Methane, CH_4
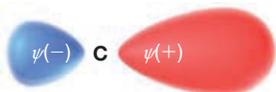
FIGURE 1.15 The shape of an sp^3 orbital.

To see how this is so, consider the shape of an individual sp^3 orbital shown in Fig. 1.15. Because an sp^3 orbital has the character of a p orbital, the positive lobe of an sp^3 orbital is large and extends relatively far from the carbon nucleus.

It is the positive lobe of an sp^3 orbital that overlaps with the positive $1s$ orbital of hydrogen to form the bonding molecular orbital of a carbon–hydrogen bond (Fig. 1.16).

sp^3 Orbital $1s$ Orbital   Carbon–hydrogen bond (bonding MO)
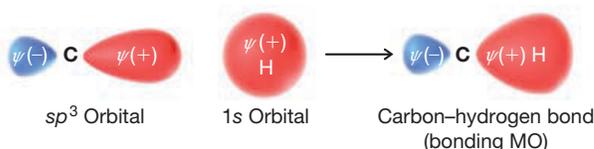
FIGURE 1.16 Formation of a C—H bond.

Because the positive lobe of the sp^3 orbital is large and is extended into space, the overlap between it and the $1s$ orbital of hydrogen is also large, and the resulting carbon–hydrogen bond is quite strong.

The bond formed from the overlap of an sp^3 orbital and a $1s$ orbital is an example of a **sigma (σ) bond** (Fig. 1.17).
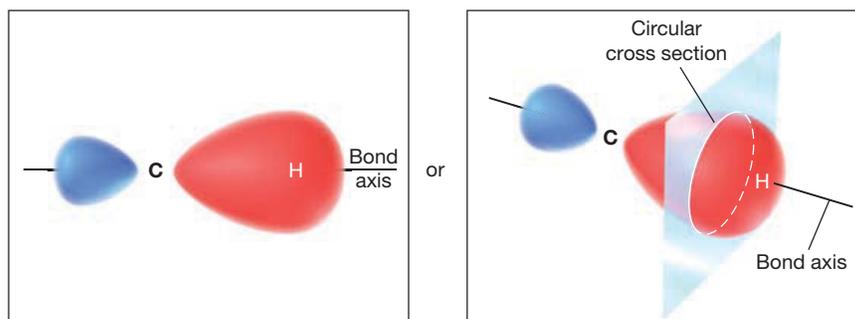

FIGURE 1.17 A σ (sigma) bond.

- A **sigma (σ) bond** has a circularly symmetrical orbital cross section when viewed along the bond between two atoms.
- All **single bonds** are sigma bonds.

From this point on we shall often show only the bonding molecular orbitals because they are the ones that contain the electrons when the molecule is in its lowest energy state. Consideration of antibonding orbitals is important when a molecule absorbs light and in explaining certain reactions. We shall point out these instances later.

In Fig. 1.18 we show a calculated structure for methane where the tetrahedral geometry derived from orbital hybridization is clearly apparent.

FIGURE 1.18 (a) In this structure of methane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (b) This ball-and-stick model of methane is like the kind you might build with a molecular model kit. (c) This structure is how you would draw methane. Ordinary lines are used to show the two bonds that are in the plane of the paper, a solid wedge is used to show the bond that is in front of the paper, and a dashed wedge is used to show the bond that is behind the plane of the paper.

(a)   (b)   (c)
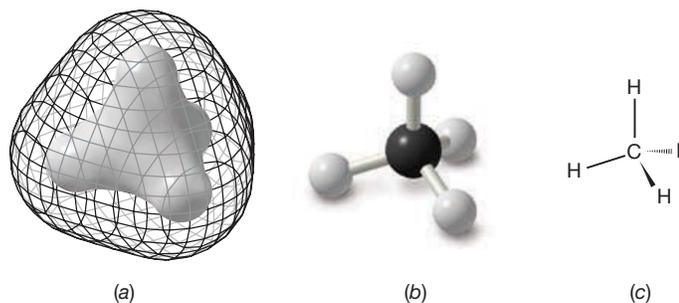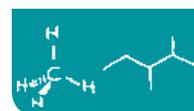
1.12B The Structure of Ethane

The bond angles at the carbon atoms of ethane, and of all alkanes, are also tetrahedral like those in methane. A satisfactory model for ethane can be provided by sp^3-hybridized carbon atoms. Figure 1.19 shows how we might imagine the bonding molecular orbitals of an ethane molecule being constructed from two sp^3-hybridized carbon atoms and six hydrogen atoms.
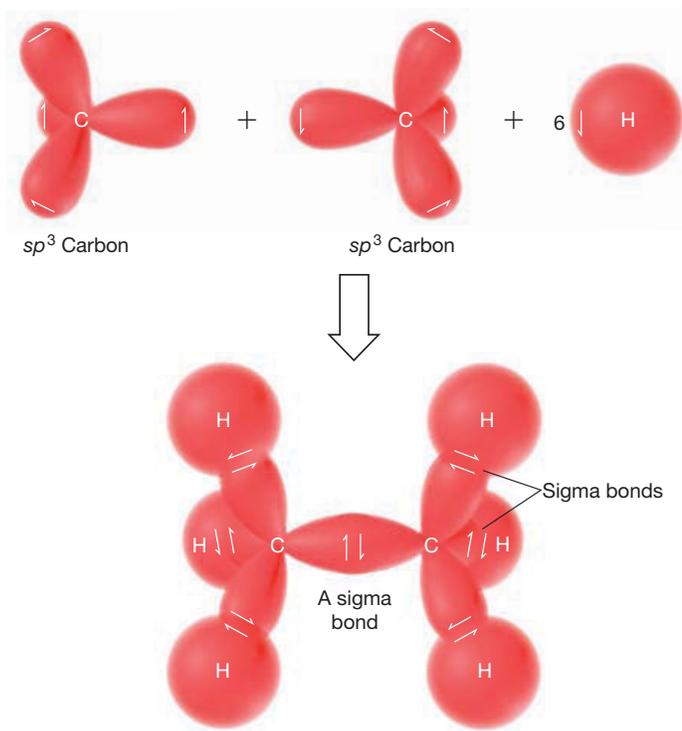

FIGURE 1.19 The hypothetical formation of the bonding molecular orbitals of ethane from two sp^3-hybridized carbon atoms and six hydrogen atoms. All of the bonds are sigma bonds. (Antibonding sigma molecular orbitals—called σ^* orbitals—are formed in each instance as well, but for simplicity these are not shown.)

The carbon–carbon bond of ethane is a *sigma bond* with cylindrical symmetry, formed by two overlapping sp^3 orbitals. (The carbon–hydrogen bonds are also sigma bonds. They are formed from overlapping carbon sp^3 orbitals and hydrogen s orbitals.)

- Rotation of groups joined by a single bond does not usually require a large amount of energy.
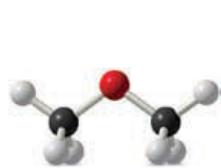
Consequently, groups joined by single bonds rotate relatively freely with respect to one another. (We discuss this point further in Section 4.8.) In Fig. 1.20 we show a calculated structure for ethane in which the tetrahedral geometry derived from orbital hybridization is clearly apparent.
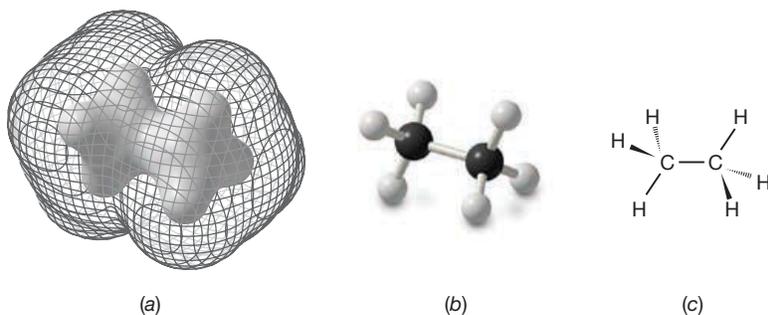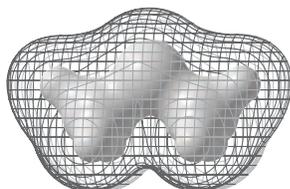

FIGURE 1.20 (*a*) In this structure of ethane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (*b*) A ball-and-stick model of ethane, like the kind you might build with a molecular model kit. (*c*) A structural formula for ethane as you would draw it using lines, wedges, and dashed wedges to show in three dimensions its tetrahedral geometry at each carbon.

THE CHEMISTRY OF... Calculated Molecular Models: Electron Density Surfaces

In this book we make frequent use of molecular models derived from quantum mechanical calculations. These models will help us visualize the shapes of molecules as well as understand their properties and reactivity. A useful type of model is one that shows a calculated three-dimensional surface at which a chosen value of electron density is the same all around a molecule, called an **electron density surface**. If we make a plot where the value chosen is for low electron density, the result is a van der Waals surface, the surface that represents approximately the overall shape of a molecule as determined by the furthest extent of its electron cloud. On the other hand, if we make a plot where the value of electron density is relatively high, the resulting surface is one that approximately represents the region of covalent bonding in a molecule. Surfaces of low and high electron density are shown in this box for dimethyl ether. Similar models are shown for methane and ethane in Figs. 1.18 and 1.20.

Dimethyl ether

1.13 THE STRUCTURE OF ETHENE (ETHYLENE): sp^2 HYBRIDIZATION

The carbon atoms of many of the molecules that we have considered so far have used their four valence electrons to form four single covalent (sigma) bonds to four other atoms. We find, however, that many important organic compounds exist in which carbon atoms share more than two electrons with another atom. In molecules of these compounds some bonds that are formed are multiple covalent bonds. When two carbon atoms share two pairs of electrons, for example, the result is a carbon–carbon double bond:
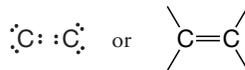
Hydrocarbons whose molecules contain a carbon–carbon double bond are called **alkenes**. Ethene (C_2H_4) and propene (C_3H_6) are both alkenes. Ethene is also called ethylene, and propene is sometimes called propylene.
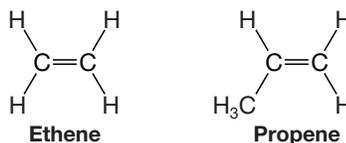
**Ethene**   **Propene**

In ethene the only carbon–carbon bond is a double bond. Propene has one carbon–carbon single bond and one carbon–carbon double bond.

The spatial arrangement of the atoms of alkenes is different from that of alkanes. The six atoms of ethene are coplanar, and the arrangement of atoms around each carbon atom is triangular (Fig. 1.21).

- Carbon–carbon double bonds are comprised of sp^2-hybridized carbon atoms.

The mathematical mixing of orbitals that furnish the **sp^2 orbitals** for our model can be visualized in the way shown in Fig. 1.22. The $2s$ orbital is mathematically mixed (or hybridized) with two of the $2p$ orbitals. (The hybridization procedure applies only to the orbitals, not to the electrons.) One $2p$ orbital is left unhybridized. One electron is then placed in each of the sp^2 hybrid orbitals and one electron remains in the $2p$ orbital.

FIGURE 1.21 The structure and bond angles of ethene. The plane of the atoms is perpendicular to the paper. The dashed wedge bonds project behind the plane of the paper, and the solid wedge bonds project in front of the paper.
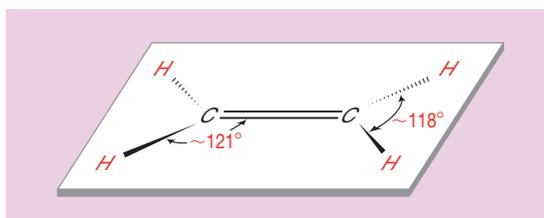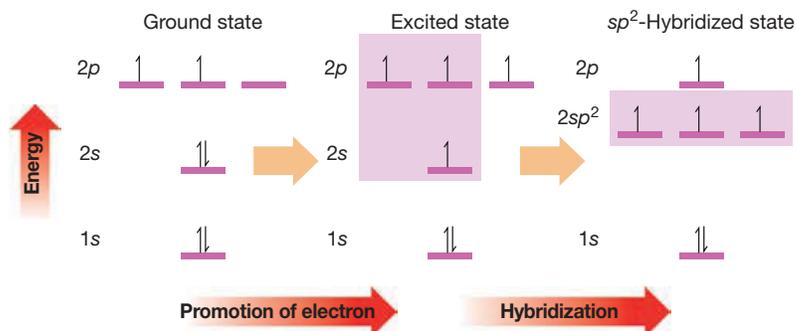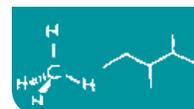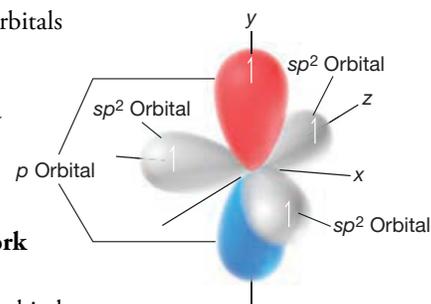
FIGURE 1.22 A process for deriving sp^2-hybridized carbon atoms.

The three sp^2 orbitals that result from hybridization are directed toward the corners of a regular triangle (with angles of 120° between them). The carbon p orbital that is not hybridized is perpendicular to the plane of the triangle formed by the hybrid sp^2 orbitals (Fig. 1.23).

In our model for ethene (Fig. 1.24) we see the following:

FIGURE 1.23 An sp^2-hybridized carbon atom.

- Two sp^2-hybridized carbon atoms form a sigma (σ) bond between them by overlap of one sp^2 orbital from each carbon. The remaining carbon sp^2 orbitals form σ bonds to four hydrogens through overlap with the hydrogen $1s$ orbitals. These five σ bonds account for 10 of the 12 valence electrons contributed by the two carbons and four hydrogens, and comprise the **σ-bond framework** of the molecule.

- The remaining two bonding electrons are each located in an unhybridized p orbital of each carbon. Sideways overlap of these p orbitals and sharing of the two electrons between the carbons leads to a **pi (π) bond**. The overlap of these orbitals is shown schematically in Fig. 1.25.

The bond angles that we would predict on the basis of sp^2-hybridized carbon atoms (120° all around) are quite close to the bond angles that are actually found (Fig. 1.21).

We can better visualize how these p orbitals interact with each other if we view a structure showing calculated molecular orbitals for ethene (Fig. 1.25). We see that the parallel p orbitals *overlap above and below the plane of the σ framework*.

Note the difference in shape of the bonding molecular orbital of a π bond as contrasted to that of a σ bond. A σ bond has cylindrical symmetry about a line connecting the two bonded nuclei. A π bond has a nodal plane passing through the two bonded nuclei and between the π molecular orbital lobes.

- When two p atomic orbitals combine to form a π bond, two **pi (π) molecular orbital** molecular orbitals form: one is a bonding molecular orbital and the other is an **antibonding molecular orbital**.
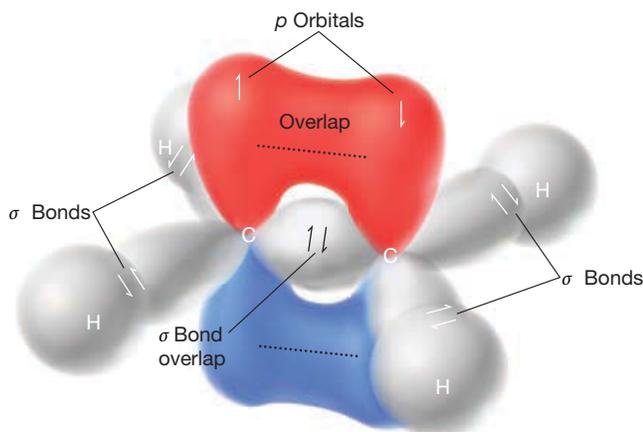
FIGURE 1.24 A model for the bonding molecular orbitals of ethene formed from two sp^2-hybridized carbon atoms and four hydrogen atoms.

FIGURE 1.25 (*a*) A wedge–dashed wedge formula for the sigma bonds in ethene and a schematic depiction of the overlapping of adjacent *p* orbitals that form the π bond. (*b*) A calculated structure for ethene. The blue and red colors indicate opposite phase signs in each lobe of the π molecular orbital. A ball-and-stick model for the σ bonds in ethene can be seen through the mesh that indicates the π bond.

π Bond
(*a*)   (*b*)
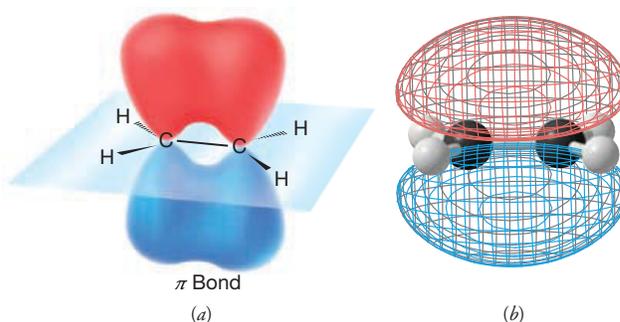
The bonding π molecular orbital results when *p*-orbital lobes of like signs overlap; the antibonding π molecular orbital results when opposite signs overlap (Fig. 1.26).

The bonding π orbital is the lower energy orbital and contains both π electrons (with opposite spins) in the ground state of the molecule. The region of greatest probability of finding the electrons in the bonding π orbital is a region generally situated above and below the plane of the σ-bond framework between the two carbon atoms. The antibonding π* orbital is of higher energy, and it is not occupied by electrons when the molecule is in the ground state. It can become occupied, however, if the molecule absorbs light of the right frequency and an electron is promoted from the lower energy level to the higher one. The antibonding π* orbital has a nodal plane between the two carbon atoms.

- To summarize, a carbon–carbon double bond consists of one σ bond and one π bond.

The σ bond results from two sp^2 orbitals overlapping end to end and is symmetrical about an axis linking the two carbon atoms. The π bond results from a sideways overlap of two *p* orbitals; it has a nodal plane like a *p* orbital. In the ground state the electrons of the π bond are located between the two carbon atoms but generally above and below the plane of the σ-bond framework.

Electrons of the π bond have greater energy than electrons of the σ bond. The relative energies of the σ and π molecular orbitals (with the electrons in the ground state) are shown in the margin diagram. The σ* orbital is the antibonding **sigma orbital**.
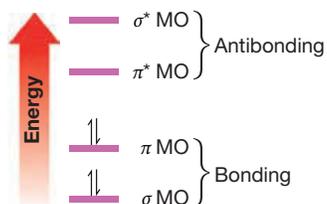
The relative energies of electrons involved in σ and π bonds
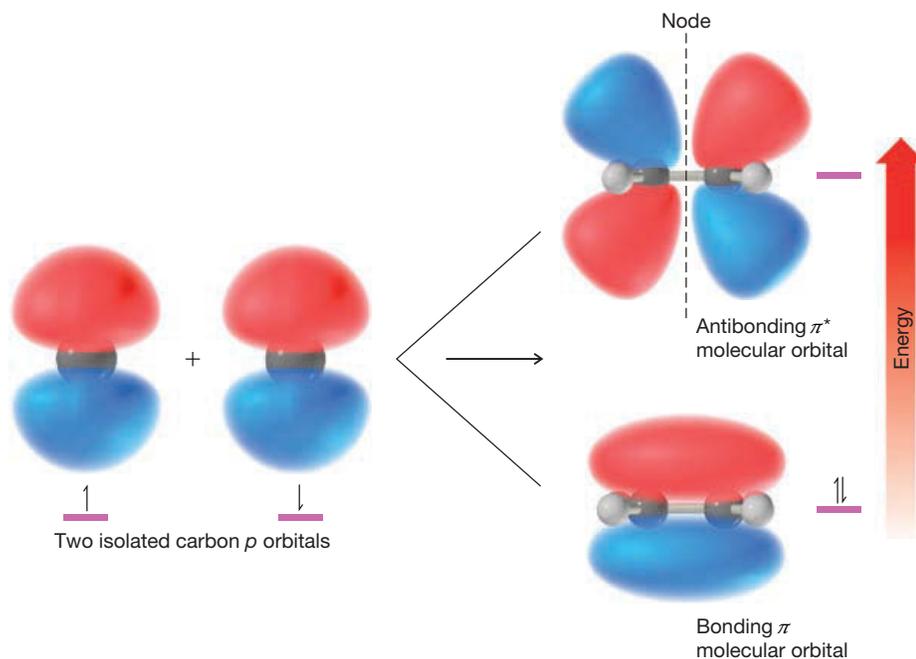
FIGURE 1.26 How two isolated carbon *p* orbitals combine to form two π (pi) molecular orbitals. The bonding MO is of lower energy. The higher energy antibonding MO contains an additional node. Both orbitals have a node in the plane containing the C and H atoms.
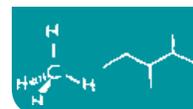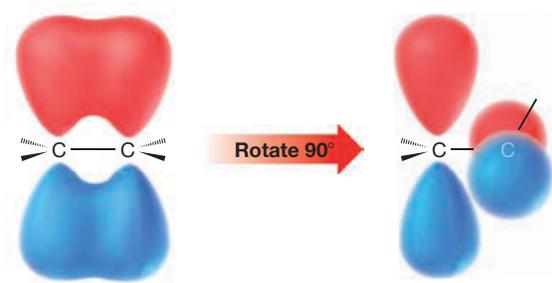
1.13A Restricted Rotation and the Double Bond

The σ–π model for the carbon–carbon double bond also accounts for an important property of the **double bond**:

- There is a large energy barrier to rotation associated with groups joined by a double bond.

Maximum overlap between the p orbitals of a π bond occurs when the axes of the p orbitals are exactly parallel. Rotating one carbon of the double bond 90° (Fig. 1.27) breaks the π bond, for then the axes of the p orbitals are perpendicular and there is no net overlap between them. Estimates based on thermochemical calculations indicate that the strength of the π bond is 264 kJ mol^{-1}. This, then, is the barrier to rotation of the double bond. It is markedly higher than the rotational barrier of groups joined by carbon–carbon single bonds (13–26 kJ mol^{-1}). While groups joined by single bonds rotate relatively freely at room temperature, those joined by double bonds do not.

FIGURE 1.27 A stylized depiction of how rotation of a carbon atom of a double bond through an angle of 90° results in breaking of the π bond.

1.13B Cis–Trans Isomerism

Restricted rotation of groups joined by a double bond causes a new type of isomerism that we illustrate with the two dichloroethenes written as the following structures:

cis-1,2-Dichloroethene   trans-1,2-Dichloroethene
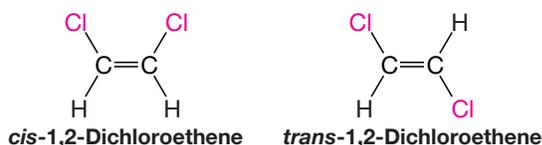
- These two compounds are isomers; they are different compounds that have the same molecular formula.

We can tell that they are different compounds by trying to place a model of one compound on a model of the other so that all parts coincide, that is, to try to **superpose** one on the other. We find that it cannot be done. Had one been **superposable** on the other, all parts of one model would correspond in three dimensions exactly with the other model. (*The notion of superposition is different from simply superimposing one thing on another*. The latter means only to lay one on the other without the necessary condition that all parts coincide.)

- We indicate that they are different isomers by attaching the prefix cis or trans to their names (*cis*, Latin: on this side; *trans*, Latin: across).

cis-1,2-Dichloroethene and *trans*-1,2-dichloroethene are not constitutional isomers because the connectivity of the atoms is the same in each. The two compounds ***differ only in the arrangement of their atoms in space***. Isomers of this kind are classified formally as **stereoisomers**, but often they are called simply cis–trans isomers. (We shall study stereoisomerism in detail in Chapters 4 and 5.)

The structural requirements for **cis–trans isomerism** will become clear if we consider a few additional examples. 1,1-Dichloroethene and 1,1,2-trichloroethene do not show this type of isomerism.

1,1-Dichloroethene
(no cis-trans isomerism)

1,1,2-Trichloroethene
(no cis-trans isomerism)

1,2-Difluoroethene and 1,2-dichloro-1,2-difluoroethene do exist as cis–trans isomers. Notice that we designate the isomer with two identical groups on the same side as being cis:


cis-**1,2-Difluoroethene**

trans-**1,2-Difluoroethene**

cis-**1,2-Dichloro-1,2-difluoroethene**

trans-**1,2-Dichloro-1,2-difluoroethene**
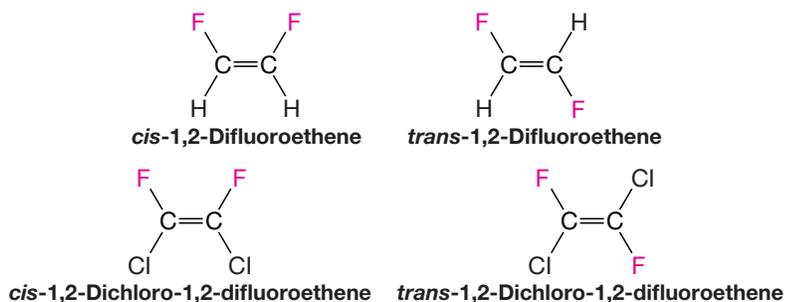
Clearly, then, *cis–trans isomerism of this type is not possible if one carbon atom of the double bond bears two identical groups*.

●●● SOLVED PROBLEM 1.12

Write structures of all the isomers of C_3H_5F.

ANSWER: Taking into account cis–trans isomerism and the possibility of a ring we have the following four possibilities.
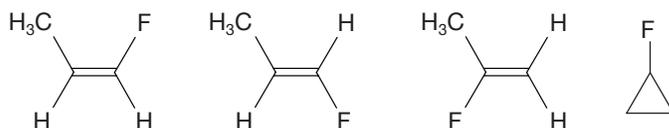



● PRACTICE PROBLEM 1.22 Which of the following alkenes can exist as cis–trans isomers? Write their structures. Build hand-held models to prove that one isomer is not superposable on the other.
(a) CH_2=$CHCH_2CH_3$ **(c)** CH_2=$C(CH_3)_2$
**(b)** CH_3CH=$CHCH_3$ **(d)** CH_3CH_2CH=$CHCl$

1.14 THE STRUCTURE OF ETHYNE (ACETYLENE): *sp* HYBRIDIZATION

Hydrocarbons in which two carbon atoms share three pairs of electrons between them, and are thus bonded by a triple bond, are called **alkynes**. The two simplest alkynes are ethyne and propyne.

$$H—C\equiv C—H \qquad CH_3—C\equiv C—H$$

Ethyne
(acetylene)
(C_2H_2)

Propyne
(C_3H_4)
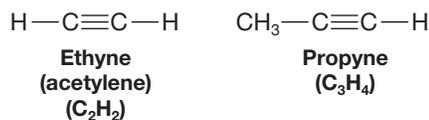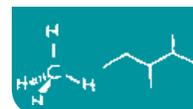
Ethyne, a compound that is also called **acetylene**, consists of a linear arrangement of atoms. The H—C≡C bond angles of ethyne molecules are 180°:

$$H—C≡C—H$$
$$180° \quad 180°$$
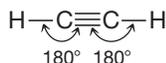
We can account for the structure of ethyne on the basis of orbital hybridization as we did for ethane and ethene. In our model for ethane (Section 1.12B) we saw that the carbon orbitals are sp^3 hybridized, and in our model for ethene (Section 1.13) we saw that they are sp^2 hybridized. In our model for ethyne we shall see that the carbon atoms are *sp hybridized*.

The mathematical process for obtaining the *sp* hybrid orbitals of ethyne can be visualized in the following way (Fig. 1.28).
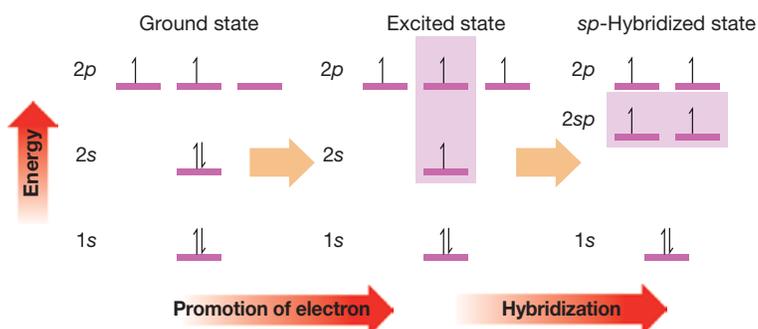

FIGURE 1.28 A process for deriving *sp*-hybridized carbon atoms.

- The 2*s* orbital and one 2*p* orbital of carbon are hybridized to form two *sp* **orbitals**.
- The remaining two 2*p* orbitals are not hybridized.

Calculations show that the *sp* hybrid orbitals have their large positive lobes oriented at an angle of 180° with respect to each other. The two 2*p* orbitals that were not hybridized are each perpendicular to the axis that passes through the center of the two *sp* orbitals (Fig. 1.29). We place one electron in each orbital.

We envision the bonding molecular orbitals of ethyne being formed in the following way (Fig. 1.30).

- Two carbon atoms overlap *sp* orbitals to form a sigma bond between them (this is one bond of the triple bond). The remaining two *sp* orbitals at each carbon atom overlap with *s* orbitals from hydrogen atoms to produce two sigma C—H bonds.
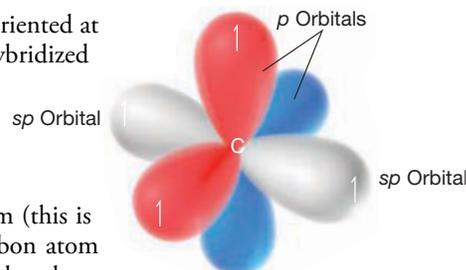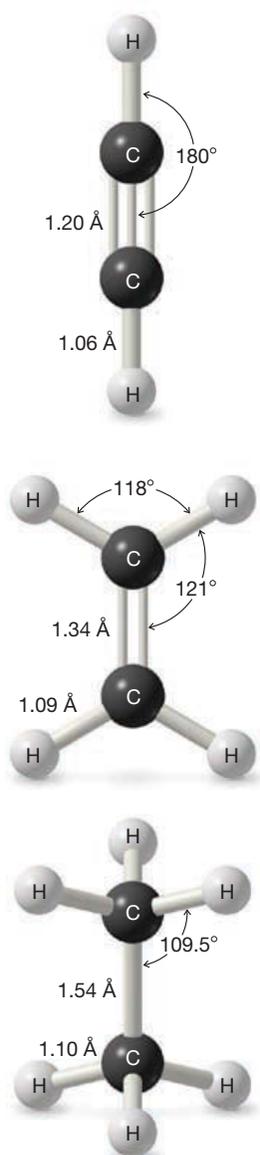

FIGURE 1.29 An *sp*-hybridized carbon atom.
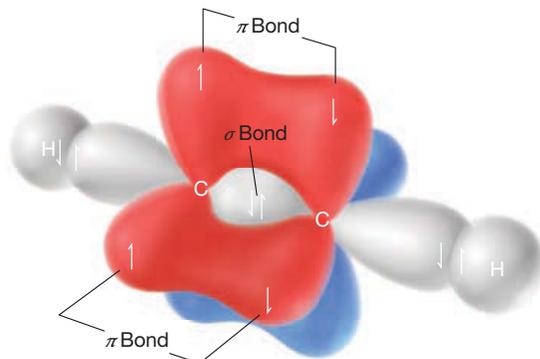
FIGURE 1.30 Formation of the bonding molecular orbitals of ethyne from two *sp*-hybridized carbon atoms and two hydrogen atoms. (Antibonding orbitals are formed as well, but these have been omitted for simplicity.)

(a)   (b)   (c)
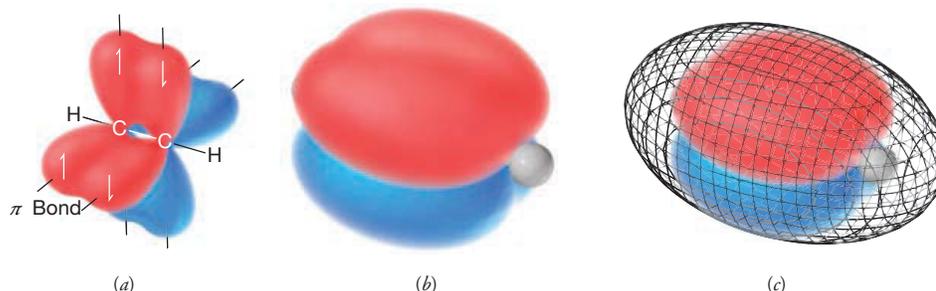
FIGURE 1.31 (a) The structure of ethyne (acetylene) showing the sigma-bond framework and a schematic depiction of the two pairs of p orbitals that overlap to form the two π bonds in ethyne. (b) A structure of ethyne showing calculated π molecular orbitals. Two pairs of π molecular orbital lobes are present, one pair for each π bond. The red and blue lobes in each π bond represent opposite phase signs. The hydrogen atoms of ethyne (white spheres) can be seen at each end of the structure (the carbon atoms are hidden by the molecular orbitals). (c) The mesh surface in this structure represents approximately the furthest extent of overall electron density in ethyne. Note that the overall electron density (but not the π-bonding electrons) extends over both hydrogen atoms.

- The two p orbitals on each carbon atom also overlap side to side to form two π bonds. These are the other two bonds of the triple bond.

- The carbon–carbon triple bond consists of two π bonds and one σ bond.

Structures for ethyne based on calculated molecular orbitals and electron density are shown in Fig. 1.31. Circular symmetry exists along the length of a triple bond (Fig.1.31b). As a result, there is no restriction of rotation for groups joined by a triple bond (as compared with alkenes), and if rotation would occur, no new compound would form.

## 1.14A Bond Lengths of Ethyne, Ethene, and Ethane

The carbon–carbon triple bond of ethyne is shorter than the carbon–carbon double bond of ethene, which in turn is shorter than the carbon–carbon single bond of ethane. The reason is that **bond lengths** are affected by the hybridization states of the carbon atoms involved.

- The greater the s orbital character in one or both atoms, the shorter is the bond. This is because s orbitals are spherical and have more electron density closer to the nucleus than do p orbitals.

- The greater the p orbital character in one or both atoms, the longer is the bond. This is because p orbitals are lobe-shaped with electron density extending away from the nucleus.

In terms of hybrid orbitals, an sp hybrid orbital has 50% s character and 50% p character. An sp^2 hybrid orbital has 33% s character and 67% p character. An sp^3 hybrid orbital has 25% s character and 75% p character. The overall trend, therefore, is as follows:

- Bonds involving sp hybrids are shorter than those involving sp^2 hybrids, which are shorter than those involving sp^3 hybrids. This trend holds true for both C—C and C—H bonds.

FIGURE 1.32 Bond angles and bond lengths of ethyne, ethene, and ethane.

The bond lengths and bond angles of ethyne, ethene, and ethane are summarized in Fig. 1.32.
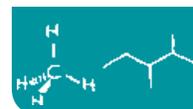
1.15 A SUMMARY OF IMPORTANT CONCEPTS THAT COME FROM QUANTUM MECHANICS

1. An **atomic orbital (AO)** corresponds to a region of space about the nucleus of a single atom where there is a high probability of finding an electron. Atomic orbitals called *s* orbitals are spherical; those called *p* orbitals are like two almost-tangent spheres. Orbitals can hold a maximum of two electrons when their spins are paired. Orbitals are described by the square of a wave function, ψ^2, and each orbital has a characteristic energy. The phase signs associated with an orbital may be $+$ or $-$.

2. When atomic orbitals overlap, they combine to form **molecular orbitals (MOs)**. Molecular orbitals correspond to regions of space encompassing two (or more) nuclei where electrons are to be found. Like atomic orbitals, molecular orbitals can hold up to two electrons if their spins are paired.

3. When atomic orbitals with the same phase sign interact, they combine to form a **bonding molecular orbital**:

Bonding molecular orbital
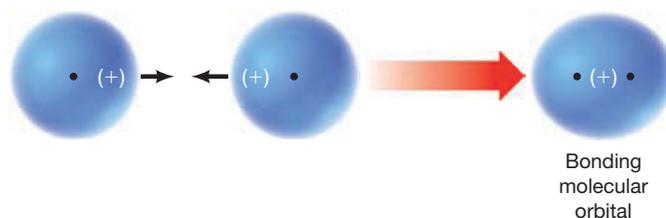
The electron probability density of a bonding molecular orbital is large in the region of space between the two nuclei where the negative electrons hold the positive nuclei together.

4. An **antibonding molecular orbital** forms when orbitals of opposite phase sign overlap:
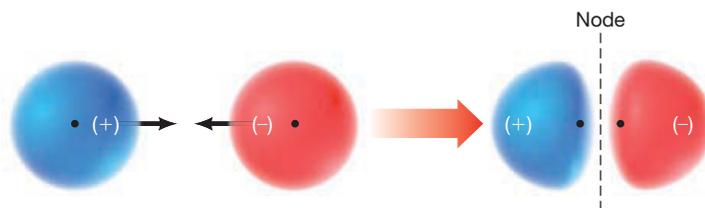
Node

An antibonding orbital has higher energy than a bonding orbital. The electron probability density of the region between the nuclei is small and it contains a **node**—a region where $\psi = 0$. Thus, having electrons in an antibonding orbital does not help hold the nuclei together. The internuclear repulsions tend to make them fly apart.

5. The **energy of electrons** in a bonding *molecular* orbital is less than the energy of the electrons in their separate *atomic* orbitals. The energy of electrons in an antibonding orbital is greater than that of electrons in their separate atomic orbitals.

6. The **number of molecular orbitals** always equals the number of atomic orbitals from which they are formed. Combining two atomic orbitals will always yield two molecular orbitals—one bonding and one antibonding.

7. **Hybrid atomic orbitals** are obtained by mixing (hybridizing) the wave functions for orbitals of different types (i.e., *s* and *p* orbitals) but from the same atom.

8. Hybridizing three *p* orbitals with one *s* orbital yields four sp^3 **orbitals**. Atoms that are sp^3 hybridized direct the axes of their four sp^3 orbitals toward the corners of a tetrahedron. The carbon of methane is sp^3 hybridized and **tetrahedral**.

9. Hybridizing two *p* orbitals with one *s* orbital yields three sp^2 **orbitals**. Atoms that are sp^2 hybridized point the axes of their three sp^2 orbitals toward the corners of an equilateral triangle. The carbon atoms of ethene are sp^2 hybridized and **trigonal planar**.

[**HELPFUL HINT**]

A summary of sp^3, sp^2, and sp hybrid orbital geometries.

10. Hybridizing one *p* orbital with one *s* orbital yields two *sp* **orbitals**. Atoms that are *sp* hybridized orient the axes of their two *sp* orbitals in opposite directions (at an angle of 180°). The carbon atoms of ethyne are *sp* hybridized and ethyne is a **linear** molecule.

11. A **sigma (σ) bond** (a type of single bond) is one in which the electron density has circular symmetry when viewed along the bond axis. In general, the skeletons of organic molecules are constructed of atoms linked by sigma bonds.

12. A **pi (π) bond**, part of double and triple carbon–carbon bonds, is one in which the electron densities of two adjacent parallel *p* orbitals overlap sideways to form a bonding pi molecular orbital.

●● 1.16 **HOW TO** PREDICT MOLECULAR GEOMETRY: THE VALENCE SHELL ELECTRON PAIR REPULSION MODEL

We can predict the arrangement of atoms in molecules and ions on the basis of a relatively simple idea called the **valence shell electron pair repulsion (VSEPR) model**. We apply the **VSEPR** model in the following way:

1. We consider molecules (or ions) in which the central atom is covalently bonded to two or more atoms or groups.

2. We consider all of the valence electron pairs of the central atom—both those that are shared in covalent bonds, called **bonding pairs**, and those that are unshared, called **nonbonding pairs** or **unshared pairs** or **lone pairs**.

3. Because electron pairs repel each other, the electron pairs of the valence shell tend to stay as far apart as possible. The repulsion between nonbonding pairs is generally greater than that between bonding pairs.

4. We arrive at the *geometry* of the molecule by considering all of the electron pairs, bonding and nonbonding, but we describe the *shape* of the molecule or ion by referring to the positions of the nuclei (or atoms) and not by the positions of the electron pairs.

In the following sections we consider several examples.

1.16A Methane

The valence shell of methane contains four pairs of bonding electrons. Only a tetrahedral orientation will allow four pairs of electrons to have equal and maximum possible separation from each other (Fig. 1.33). Any other orientation, for example, a square planar arrangement, places some electron pairs closer together than others. Thus, methane has a tetrahedral shape.
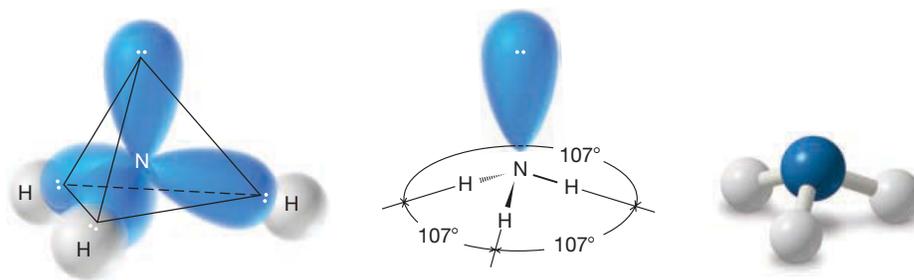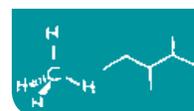
The bond angles for any atom that has a regular tetrahedral structure are 109.5°. A representation of these angles in methane is shown in Fig. 1.34.
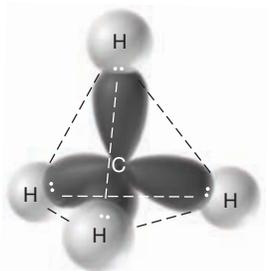
FIGURE 1.33 A tetrahedral shape for methane allows the maximum separation of the four bonding electron pairs.
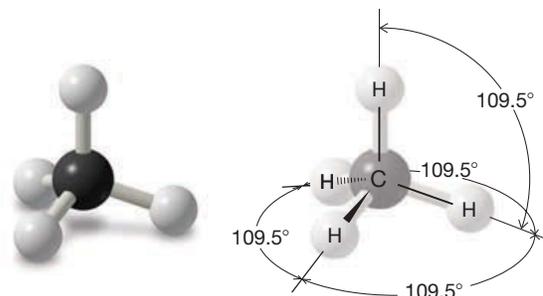
FIGURE 1.34 The bond angles of methane are 109.5°.

FIGURE 1.35 The tetrahedral arrangement of the electron pairs of an ammonia molecule that results when the nonbonding electron pair is considered to occupy one corner. This arrangement of electron pairs explains the trigonal pyramidal shape of the NH_3 molecule. Ball-and-stick models do not show unshared electrons.

1.16B Ammonia

The shape of a molecule of ammonia (NH_3) is a **trigonal pyramid**. There are three bonding pairs of electrons and one nonbonding pair. The bond angles in a molecule of ammonia are 107°, a value very close to the tetrahedral angle (109.5°). We can write a general tetrahedral structure for the electron pairs of ammonia by placing the nonbonding pair at one corner (Fig. 1.35). A *tetrahedral arrangement* of the electron pairs explains the *trigonal pyramidal* arrangement of the four atoms. The bond angles are 107° (not 109.5°) because the nonbonding pair occupies more space than the bonding pairs.

What do the bond angles of ammonia suggest about the hybridization state of the nitrogen atom of ammonia?

1.16C Water

A molecule of water has an **angular** or **bent** shape. The H—O—H bond angle in a molecule of water is 104.5°, an angle that is also quite close to the 109.5° bond angles of methane.

We can write a general tetrahedral structure for the electron pairs of a molecule of water *if we place the two bonding pairs of electrons and the two nonbonding electron pairs at the corners of the tetrahedron.* Such a structure is shown in Fig. 1.36. A *tetrahedral arrangement* of the electron pairs accounts for the *angular arrangement* of the three atoms. The bond angle is less than 109.5° because the nonbonding pairs are effectively "larger" than the bonding pairs and, therefore, the structure is not perfectly tetrahedral.
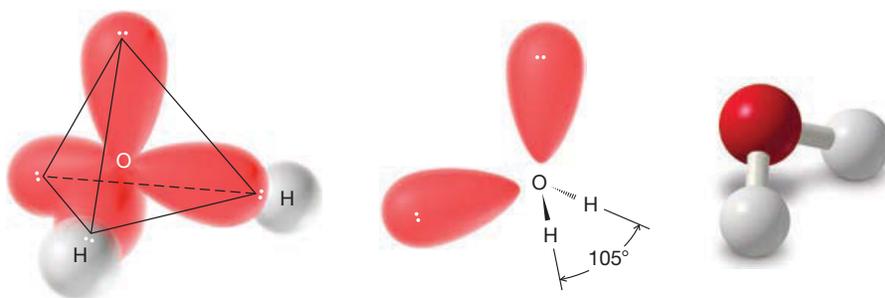
FIGURE 1.36 An approximately tetrahedral arrangement of the electron pairs of a molecule of water that results when the pairs of nonbonding electrons are considered to occupy corners. This arrangement accounts for the angular shape of the H_2O molecule.

What do the bond angles of water suggest about the hybridization state of the oxygen atom of water?

1.16D Boron Trifluoride

Boron, a group IIIA element, has only three valence electrons. In the compound boron trifluoride (BF_3) these three electrons are shared with three fluorine atoms. As a result, the boron atom in BF_3 has only six electrons (three bonding pairs) around it. Maximum separation of three bonding pairs occurs when they occupy the corners of an equilateral

FIGURE 1.37 The triangular (trigonal planar) shape of boron trifluoride maximally separates the three bonding pairs.
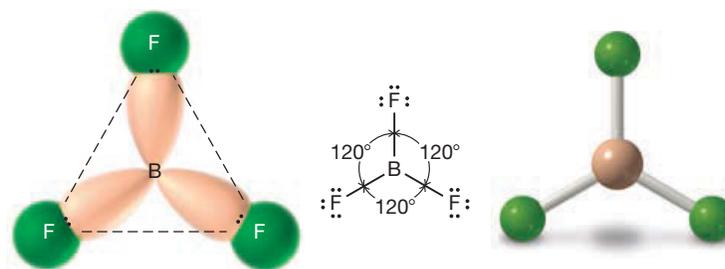
triangle. Consequently, in the boron trifluoride molecule the three fluorine atoms lie in a plane at the corners of an equilateral triangle (Fig. 1.37). Boron trifluoride is said to have a *trigonal planar structure*. The bond angles are 120°.

● **PRACTICE PROBLEM 1.25**   What do the bond angles of boron trifluoride suggest about the hybridization state of the boron atom?

1.16E Beryllium Hydride

The central beryllium atom of BeH_2 has only two electron pairs around it; both electron pairs are bonding pairs. These two pairs are maximally separated when they are on opposite sides of the central atom, as shown in the following structures. This arrangement of the electron pairs accounts for the *linear geometry* of the BeH_2 molecule and its bond angle of 180°.

H : Be : H   or   H ——180°—— Be ——H

Linear geometry of BeH₂
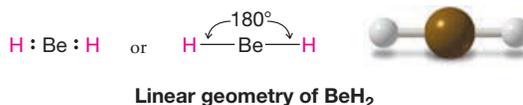
● **PRACTICE PROBLEM 1.26**   What do the bond angles of beryllium hydride suggest about the hybridization state of the beryllium atom?

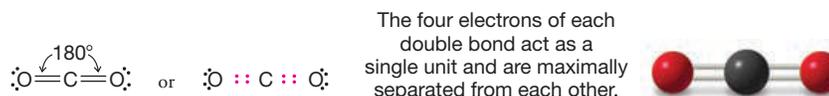● **PRACTICE PROBLEM 1.27**   Use VSEPR theory to predict the geometry of each of the following molecules and ions:

(a) $\bar{B}H_4$ (c) $\overset{+}{N}H_4$ (e) BH_3 (g) SiF_4

(b) BeF_2 (d) H_2S (f) CF_4 (h) $^-CCl_3$

1.16F Carbon Dioxide

The VSEPR method can also be used to predict the shapes of molecules containing multiple bonds if we assume that *all of the electrons of a multiple bond act as though they were a single unit* and, therefore, are located in the region of space between the two atoms joined by a multiple bond.

This principle can be illustrated with the structure of a molecule of carbon dioxide (CO_2). The central carbon atom of carbon dioxide is bonded to each oxygen atom by a double bond. Carbon dioxide is known to have a linear shape; the bond angle is 180°.

:O̤ ══ C ══ O̤:   or   :O̤ :: C :: O̤:

The four electrons of each double bond act as a single unit and are maximally separated from each other.

Such a structure is consistent with a maximum separation of the two groups of four bonding electrons. The nonbonding pairs associated with the oxygen atoms have no effect on the shape.
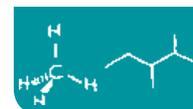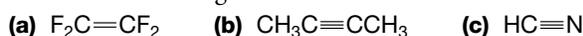
TABLE 1.3 SHAPES OF MOLECULES AND IONS FROM VSEPR THEORY

Number of Electron Pairs at Central Atom			Hybridization State of Central Atom	Shape of Molecule or Ion[a]	Examples
Bonding	Nonbonding	Total			
2 or 4	0	2 or 4	sp	Linear	BeH_2, CO_2
3	0	3	sp^2	Trigonal planar	BF_3, $\overset{+}{C}H_3$
4	0	4	sp^3	Tetrahedral	CH_4, $\overset{+}{N}H_4$
3	1	4	$\sim sp^3$	Trigonal pyramidal	NH_3, $\overset{-}{C}H_3$
2	2	4	$\sim sp^3$	Angular	H_2O

[a]Referring to positions of atoms and excluding nonbonding pairs.

Predict the bond angles of

(a) $F_2C{=}CF_2$ **(b)** $CH_3C{\equiv}CCH_3$ **(c)** $HC{\equiv}N$

● PRACTICE PROBLEM 1.28

The shapes of several simple molecules and ions as predicted by VSEPR theory are shown in Table 1.3. In this table we have also included the hybridization state of the central atom.

1.17 APPLICATIONS OF BASIC PRINCIPLES

Throughout the early chapters of this book we review certain basic principles that underlie and explain much of the chemistry we shall be studying. Consider the following principles and how they apply in this chapter.

Opposite Charges Attract We see this principle operating in our explanations for covalent and ionic bonds (Section 1.3A). It is the attraction of the *positively* charged nuclei for the *negatively* charged electrons that underlies our explanation for the covalent bond. It is the attraction of the oppositely charged ions in crystals that explains the ionic bond.

Like Charges Repel It is the repulsion of the electrons in covalent bonds of the valence shell of a molecule that is central to the valence shell electron pair repulsion model for explaining molecular geometry. And, although it is not so obvious, this same factor underlies the explanations of molecular geometry that come from orbital hybridization because these repulsions are taken into account in calculating the orientations of the hybrid orbitals.

Nature Tends toward States of Lower Potential Energy This principle explains so much of the world around us. It explains why water flows downhill: the potential energy of the water at the bottom of the hill is lower than that at the top. (We say that water is in a more stable state at the bottom.) This principle underlies the Aufbau principle (Section 1.10A): in its lowest energy state, the electrons of an atom occupy the lowest energy orbitals available [but Hund's rule still applies, as well as the Pauli exclusion principle (Section 1.10A), allowing only two electrons per orbital]. Similarly in molecular orbital theory (Section 1.11), electrons fill lower energy bonding molecular orbitals first because this gives the molecule lower potential energy (or greater stability). Energy has to be provided to move an electron to a higher orbital and provide an excited (less stable) state.

Orbital Overlap Stabilizes Molecules This principle is part of our explanation for covalent bonds. When orbitals of the same phase from different nuclei overlap, the electrons in these orbitals can be shared by both nuclei, resulting in stabilization. The result is a covalent bond.

[WHY Do These Topics Matter?]

NATURAL PRODUCTS THAT CAN TREAT DISEASE

Everywhere on Earth, organisms make organic molecules comprised almost exclusively of carbon, hydrogen, nitrogen, and oxygen. Sometimes a few slightly more exotic atoms, such as halogens and sulfur, are present. Globally, these compounds aid in day-to-day functioning of these organisms and/or their survival against predators. Organic molecules include many different compounds with diverse properties. For example, chlorophyll in green plants harnesses the energy of sunlight while vitamin C in citrus trees protects them against oxidative stress. Other molecules include capsaicin, a compound synthesized by pepper plants that wards off insects and birds that might try to eat them and is responsible for the "hotness" that we taste when we bite into a pepper. They also include salicylic acid, a signaling hormone made by willow trees, and lovastatin, a material found in oyster mushrooms that protects the mushroom against bacterial attacks.

Capsaicin

Chlorophyll core

Vitamin C

Salicylic acid

Lovastatin

Aspirin

Lipitor
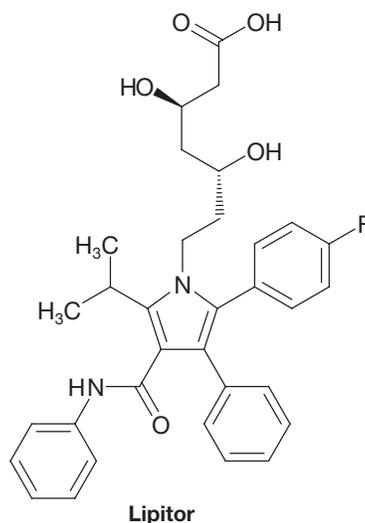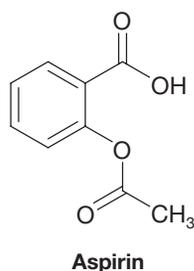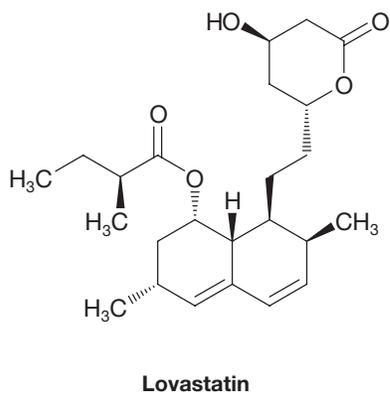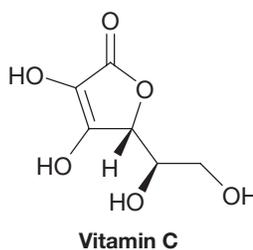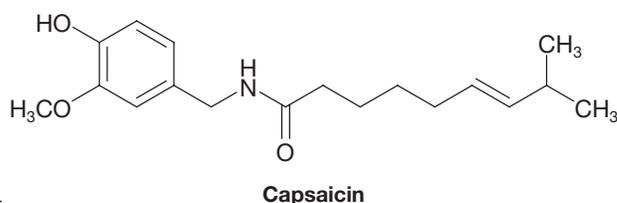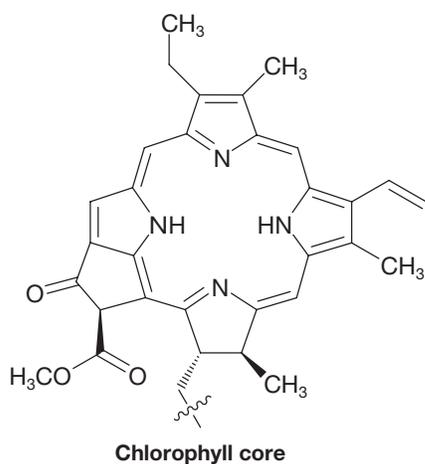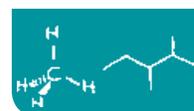
These compounds are all natural products, and many advances in modern society are the result of their study and use. Capsaicin, it turns out, is an effective analgesic. It can modulate pain when applied to the skin and is currently sold under the trade-name Capzacin. Salicylic acid is a painkiller as well as an anti-acne medication, while lovastatin is used as a drug to decrease levels of cholesterol in human blood. The power of modern organic chemistry lies in the ability to take such molecules, sometimes found in trace quantities in nature, and make them from readily available and inexpensive starting materials on a large scale so that all members of society can benefit from them. For instance, although we can obtain vitamin C from eating certain fruits, chemists can make large quantities in the laboratory for use in daily supplements; while some may think that "natural" vitamin C is healthier, the "synthetic" compound is equally effective since they are exactly the same chemically.

Perhaps more important, organic chemistry also provides the opportunity to change the structures of these and other natural products to make molecules with different, and potentially even more impressive, properties. For example, the addition of a few atoms to salicylic acid through a chemical reaction is what led to the discovery of aspirin (see Chapter 17), a molecule with far greater potency as a painkiller and fewer side effects than nature's compound. Similarly, scientists at Parke–Davis Warner–Lambert (now Pfizer) used the structure and activity of lovastatin as inspiration to develop Lipitor, a molecule that has saved countless lives by lowering levels of cholesterol in human serum. In fact, of the top 20 drugs based on gross sales, slightly over half are either natural products or their derivatives.

To learn more about these topics, see:

1. Nicolaou, K. C.; Montagnon, T. *Molecules that Changed the World*. Wiley-VCH: Weinheim, **2008**, p. 366.
2. Nicolaou, K. C.; Sorensen, E. J.; Winssinger, N, "The Art and Science of Organic and Natural Products Synthesis" in *J. Chem. Educ*. **1998**, *75*, 1225–1258.

SUMMARY AND REVIEW TOOLS

In Chapter 1 you have studied concepts and skills that are absolutely essential to your success in organic chemistry. You should now be able to use the periodic table to determine the number of valence electrons an atom has in its neutral state or as an ion. You should be able to use the periodic table to compare the relative electronegativity of one element with another, and determine the formal charge of an atom or ion. Electronegativity and formal charge are key concepts in organic chemistry.

You should be able to draw chemical formulas that show all of the valence electrons in a molecule (Lewis structures), using lines for bonds and dots to show unshared electrons. You should be proficient in representing structures as dash structural formulas, condensed structural formulas, and bond-line structural formulas. In particular, the more quickly you become skilled at using and interpreting bond-line formulas, the faster you will be able to process structural information in organic chemistry. You have also learned about resonance structures, the use of which will help us in understanding a variety of concepts in later chapters.

Last, you have learned to predict the three-dimensional structure of molecules using the valence shell electron pair repulsion (VSEPR) model and molecular orbital (MO) theory. An ability to predict three-dimensional structure is critical to understanding the properties and reactivity of molecules.

We encourage you to do all of the problems that your instructor has assigned. We also recommend that you use the summary and review tools in each chapter, such as the concept map that follows. Concept maps can help you see the flow of concepts in a chapter and also help remind you of key points. In fact, we encourage you to build your own concept maps for review when the opportunity arises.

Work especially hard to solidify your knowledge from this and other early chapters in the book. These chapters have everything to do with helping you learn basic tools you need for success throughout organic chemistry.

The study aids for this chapter include key terms and concepts (which are hyperlinked to the glossary from the bold, blue terms in the *WileyPLUS* version of the book at wileyplus.com) and a Concept Map after the end-of-chapter problems.

KEY TERMS AND CONCEPTS

WileyPLUS The key terms and concepts that are highlighted in bold, blue text within the chapter are defined in the glossary (at the back of the book) and have hyperlinked definitions in the accompanying *WileyPLUS* course (www.wileyplus.com).

PROBLEMS

WileyPLUS *Note to Instructors:* Many of the homework problems are available for assignment via *WileyPlus*, an online teaching and learning solution.

ELECTRON CONFIGURATION

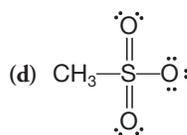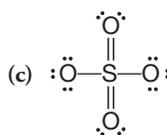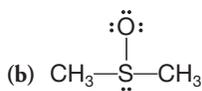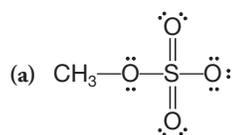**1.29** Which of the following ions possess the electron configuration of a noble gas?

(a) Na^+	**(c)** F^+	**(e)** Ca^{2+}	**(g)** O^{2-}
(b) Cl^-	**(d)** H^-	**(f)** S^{2-}	**(h)** Br^+

LEWIS STRUCTURES

**1.30** Write a Lewis structure for each of the following:

(a) $SOCl_2$ (b) $POCl_3$ (c) PCl_5 (d) $HONO_2$ (HNO_3)

1.31 Give the formal charge (if one exists) on each atom of the following:

1.32 Add any unshared electrons to give each element an octet in its valence shell in the formulas below and indicate any formal charges. Note that all of the hydrogen atoms that are attached to heteroatoms have been drawn if they are present.

(a)   (b)   (c)   (d)   (e)
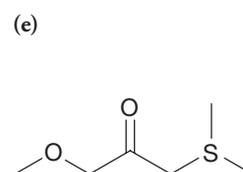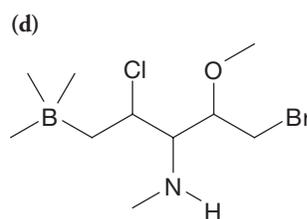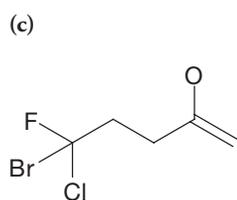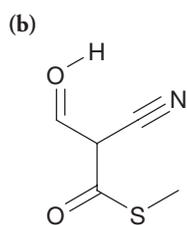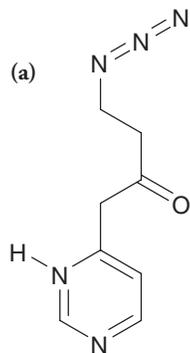
STRUCTURAL FORMULAS AND ISOMERISM

1.33 Write a condensed structural formula for each compound given here.
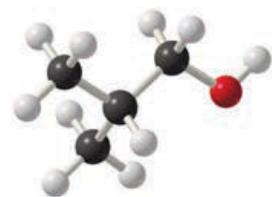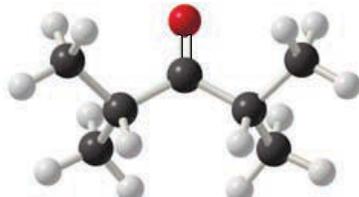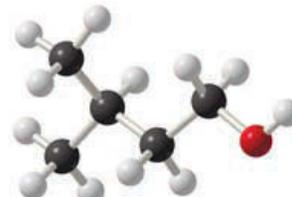
(a)   (b)   (c)   (d)

1.34 What is the molecular formula for each of the compounds given in Exercise 1.33?

1.35 Consider each pair of structural formulas that follow and state whether the two formulas represent the same compound, whether they represent different compounds that are constitutional isomers of each other, or whether they represent different compounds that are not isomeric.

(a) and

(e) $CH_3-C(CH_3)_2-CH_2Cl$ and

(b) and $ClCH_2CH(CH_3)_2$

(f) $CH_2=CHCH_2CH_3$ and

(c) and

(g) and

(d) and

(h) CH_3CH_2 and

(i) $CH_3OCH_2CH_3$ and

(m) H—C(CH₃)(H)—Br and CH_3—C(H)(H)—Br

(j) $CH_2ClCHClCH_3$ and $CH_3CHClCH_2Cl$

(n) CH_3—C(CH₃)(H)—H and CH_3—C(H)(H)—CH₃

(k) $CH_3CH_2CHClCH_2Cl$ and CH_3CHCH_2Cl with CH_2Cl

(o)

(l)

 and

(p)

1.36 Rewrite each of the following using bond-line formulas:

(a) $CH_3CH_2CH_2CCH_3$ (with =O)

(c) $(CH_3)_3CCH_2CH_2CH_2OH$

(e) $CH_2{=}CHCH_2CH_2CH{=}CHCH_3$

(b) $CH_3CHCH_2CH_2CHCH_2CH_3$ with CH_3 and CH_3 substituents

(d) $CH_3CH_2CHCH_2COH$ with CH_3 and =O

(f)

1.37 Write bond-line formulas for all of the constitutional isomers with the molecular formula C_4H_8.

1.38 Write structural formulas for at least three constitutional isomers with the molecular formula CH_3NO_2. (In answering this problem you should assign a formal charge to any atom that bears one.)

RESONANCE STRUCTURES

1.39 Write the resonance structure that would result from moving the electrons in the way indicated by the curved arrows.

1.40 Show the curved arrows that would convert **A** into **B**.

1.41 For the following write all possible resonance structures. Be sure to include formal charges where appropriate.

1.42 (a) Cyanic acid (H—O—C≡N) and isocyanic acid (H—N=C=O) differ in the positions of their electrons but their structures do not represent resonance structures. Explain. (b) Loss of a proton from cyanic acid yields the same anion as that obtained by loss of a proton from isocyanic acid. Explain.

1.43 Consider a chemical species (either a molecule or an ion) in which a carbon atom forms three single bonds to three hydrogen atoms and in which the carbon atom possesses no other valence electrons. (a) What formal charge would the carbon atom have? (b) What total charge would the species have? (c) What shape would you expect this species to have? (d) What would you expect the hybridization state of the carbon atom to be?

1.44 Consider a chemical species like the one in the previous problem in which a carbon atom forms three single bonds to three hydrogen atoms, but in which the carbon atom possesses an unshared electron pair. (a) What formal charge would the carbon atom have? (b) What total charge would the species have? (c) What shape would you expect this species to have? (d) What would you expect the hybridization state of the carbon atom to be?

1.45 Consider another chemical species like the ones in the previous problems in which a carbon atom forms three single bonds to three hydrogen atoms but in which the carbon atom possesses a single unpaired electron. (a) What formal charge would the carbon atom have? (b) What total charge would the species have? (c) Given that the shape of this species is trigonal planar, what would you expect the hybridization state of the carbon atom to be?

1.46 Draw a three-dimensional orbital representation for each of the following molecules, indicate whether each bond in it is a σ or π bond, and provide the hybridization for each non-hydrogen atom.

(a) CH_2O (b) $H_2C=CHCH=CH_2$ (c) $H_2C=C=C=CH_2$
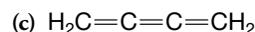
1.47 Ozone (O_3) is found in the upper atmosphere where it absorbs highly energetic ultraviolet (UV) radiation and thereby provides the surface of Earth with a protective screen (cf. Section 10.11E). One possible resonance structure for ozone is the following:
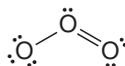

(a) Assign any necessary formal charges to the atoms in this structure. (b) Write another equivalent resonance structure for ozone. (c) What do these resonance structures predict about the relative lengths of the two oxygen–oxygen bonds of ozone? (d) In the structure above, and the one you have written, assume an angular shape for the ozone molecule. Is this shape consistent with VSEPR theory? Explain your answer.

1.48 Write resonance structures for the azide ion, N_3^-. Explain how these resonance structures account for the fact that both bonds of the azide ion have the same length.

1.49 Write structural formulas of the type indicated: (a) bond-line formulas for seven constitutional isomers with the formula $C_4H_{10}O$; (b) condensed structural formulas for two constitutional isomers with the formula C_2H_7N; (c) condensed structural formulas for four constitutional isomers with the formula C_3H_9N; (d) bond-line formulas for three constitutional isomers with the formula C_5H_{12}.

1.50 Define the relationship between the members of the following pairs. Are they constitutional isomers, the same, or something else (specify)?

(a)

(b) $CH_3CH_2CH_2CH(CH_3)_2$

(c)

(d)

(e)

(f)
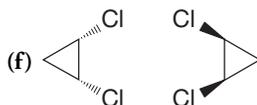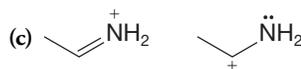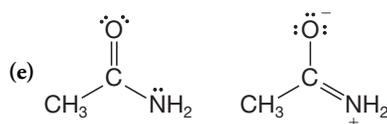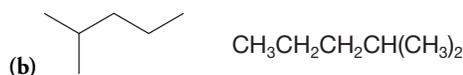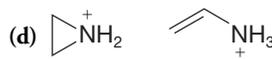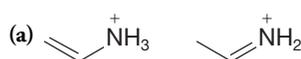
CHALLENGE PROBLEMS

1.51 In Chapter 15 we shall learn how the nitronium ion, NO_2^+, forms when concentrated nitric and sulfuric acids are mixed. (a) Write a Lewis structure for the nitronium ion. (b) What geometry does VSEPR theory predict for the NO_2^+ ion? (c) Give a species that has the same number of electrons as NO_2^+.
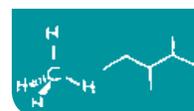
1.52 Given the following sets of atoms, write bond-line formulas for all of the possible constitutionally isomeric compounds or ions that could be made from them. Show all unshared electron pairs and all formal charges, if any.

Set	C atoms	H atoms	Other
A	3	6	2 Br atoms
B	3	9	1 N atom and 1 O atom (not on same C)
C	3	4	1 O atom
D	2	7	1 N atom and 1 proton
E	3	7	1 extra electron

1.53 **(a)** Consider a carbon atom in its ground state. Would such an atom offer a satisfactory model for the carbon of methane? If not, why not? (*Hint:* Consider whether a ground state carbon atom could be tetravalent, and consider the bond angles that would result if it were to combine with hydrogen atoms.)

(b) Consider a carbon atom in the excited state:

$$\text{C} \quad \underline{1\!\!\downarrow} \quad \underline{1} \quad \underline{1} \quad \underline{1} \quad \underline{1}$$
$$1s \quad 2s \quad 2p_x \quad 2p_y \quad 2p_z$$

Excited state of a carbon atom

Would such an atom offer a satisfactory model for the carbon of methane? If not, why not?

1.54 Open computer molecular models for dimethyl ether, dimethylacetylene, and *cis*-1,2-dichloro-1,2-difluoroethene 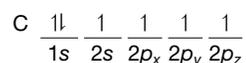from the 3D Molecular Models section of the book's website. By interpreting the computer molecular model for each one, draw **(a)** a dash formula, **(b)** a bond-line formula, and **(c)** a three-dimensional dashed-wedge formula. Draw the models in whatever perspective is most convenient—generally the perspective in which the most atoms in the chain of a molecule can be in the plane of the paper.

1.55 Boron is a group IIIA element. Open the molecular model for boron trifluoride from the 3D Molecular Models section of the book's website. Near the boron atom, above and below the plane of the atoms in BF_3, are two relatively large lobes. Considering the position of boron in the periodic table and the three-dimensional and electronic structure of BF_3, what type of orbital does this lobe represent? Is it a hybridized orbital or not?

1.56 There are two contributing resonance structures for an anion called acetaldehyde enolate, whose condensed molecular formula is CH_2CHO^-. Draw the two resonance contributors and the resonance hybrid, then consider the map of electrostatic potential (MEP) shown below for this anion. Comment on whether the MEP is consistent or not with predominance of the resonance contributor you would have predicted to be represented most strongly in the hybrid.
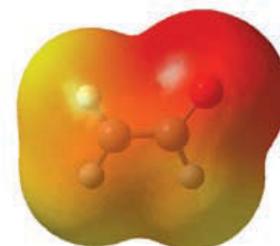
LEARNING GROUP PROBLEMS

Consider the compound with the following condensed molecular formula:

$$CH_3CHOHCH{=}CH_2$$

1. Write a full dash structural formula for the compound.

2. Show all nonbonding electron pairs on your dash structural formula.

3. Indicate any formal charges that may be present in the molecule.

4. Label the hybridization state at every carbon atom and the oxygen.

5. Draw a three-dimensional perspective representation for the compound showing approximate bond angles as clearly as possible. Use ordinary lines to indicate bonds in the plane of the paper, solid wedges for bonds in front of the paper, and dashed wedges for bonds behind the paper.

6. Label all the bond angles in your three-dimensional structure.

7. Draw a bond-line formula for the compound.

8. Devise two structures, each having two *sp*-hybridized carbons and the molecular formula C_4H_6O. Create one of these structures such that it is linear with respect to all carbon atoms. Repeat parts 1–7 above for both structures.

[HELPFUL HINT]

Your instructor will tell you how to work these problems as a Learning Group.

[CONCEPT MAP] ▶ WileyPLUS

Organic Molecules

↓ have

can be predicted by ← **Three-dimensional shape** → can be predicted by

VSEPR Theory (Section 1.16)

Quantum mechanics (Section 1.9)

↓ requires creation of

↓ utilizes

Proper Lewis structures (Section 1.3) ← must be ― **Resonance structures** (Section 1.8)

show all

Wave functions

are used to generate

↓ show all   ↓ show all

Valence electrons

Formal charges (Section 1.7)

Atomic orbitals (Section 1.10)

of 2nd row elements consist of

↓ include all

↓ are averaged in the

Bonding and nonbonding electrons

Resonance hybrid (Section 1.8)

↓ repel each other to achieve

Maximum separation in 3-D space

One 2s

and three 2p orbitals

may become

of two groups* of electrons leads to → **Linear geometry** → is present in → **Alkynes** (Section 1.14)

π Bond
σ Bond
H
C   C
H
π Bond

—C≡C—

are at each triple-bonded carbon of

Two sp hybrid and two p orbitals

p Orbitals
sp Orbital
C
sp Orbital

of three groups* of electrons leads to → **Trigonal planar geometry** → is present in → **Alkenes** (Section 1.13)

Overlap
H
C   C
H
H   H

C=C

are at each double-bonded carbon of

Three sp² hybrid and one p orbital

y
sp² Orbital
sp² Orbital   z
p Orbital
sp² Orbital
x

of four groups* of electrons leads to → **Tetrahedral geometry** → is present in → **Alkanes** (Section 1.12)

H
109.5°
H
C
H
H

C

are at each single-bonded carbon of

Four sp³ hybrid orbitals

109.5°   109.5°
ψ(+)
ψ(+)   109.5°
ψ(+)
109.5°
ψ(+)
109.5°

*A single bond, a double bond, a triple bond, and a nonbonding electron pair each represent a single 'group' of electrons.