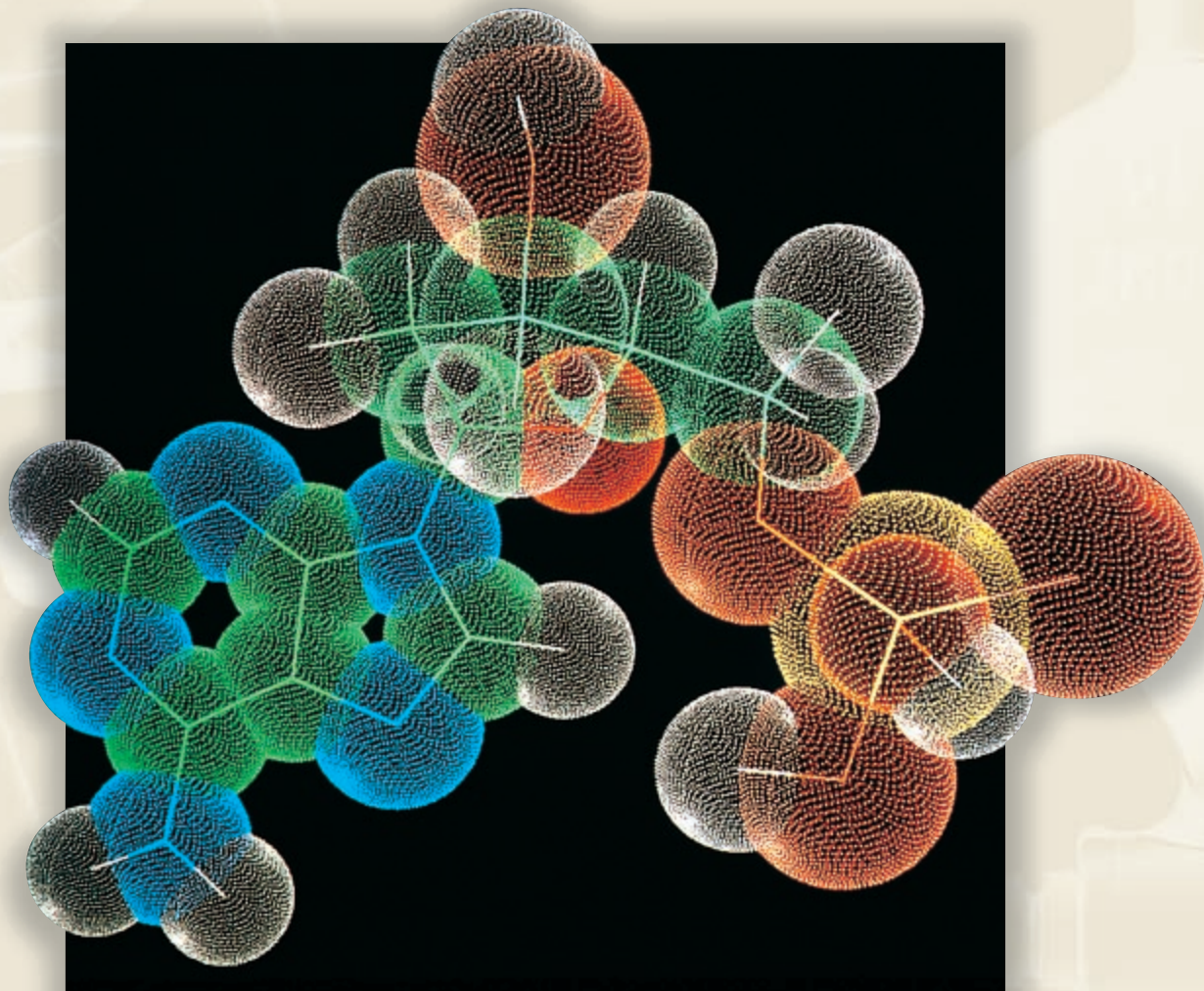


# *Chemical Bonding*

---



*In nature, most atoms are joined  
to other atoms by chemical bonds.*

# Introduction to Chemical Bonding

## SECTION 6-1

### OBJECTIVES

- Define *chemical bond*.
- Explain why most atoms form chemical bonds.
- Describe ionic and covalent bonding.
- Explain why most chemical bonding is neither purely ionic nor purely covalent.
- Classify bonding type according to electronegativity differences.

Atoms seldom exist as independent particles in nature. The oxygen you breathe, the water that makes up most of your body, and nearly all other substances are made up of combinations of atoms that are held together by chemical bonds. A **chemical bond** is a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together.

Why are most atoms chemically bonded to each other? As independent particles, they are at relatively high potential energy. Nature, however, favors arrangements in which potential energy is minimized. This means that most atoms are less stable existing by themselves than when they are combined. By bonding with each other, atoms decrease in potential energy, thereby creating more stable arrangements of matter.

### Types of Chemical Bonding

When atoms bond, their valence electrons are redistributed in ways that make the atoms more stable. The way in which the electrons are redistributed determines the type of bonding. In Chapter 5, you read that main-group metals tend to lose electrons to form positive ions, or cations, and nonmetals tend to gain electrons to form negative ions, or anions. *Chemical bonding that results from the electrical attraction between large numbers of cations and anions is called ionic bonding.* In purely ionic bonding, atoms completely give up electrons to other atoms, as illustrated in Figure 6-1 on page 162. In contrast to atoms joined by ionic bonding, atoms joined by covalent bonding share electrons. **Covalent bonding** results from the sharing of electron pairs between two atoms (see Figure 6-1). In a purely covalent bond, the shared electrons are “owned” equally by the two bonded atoms.

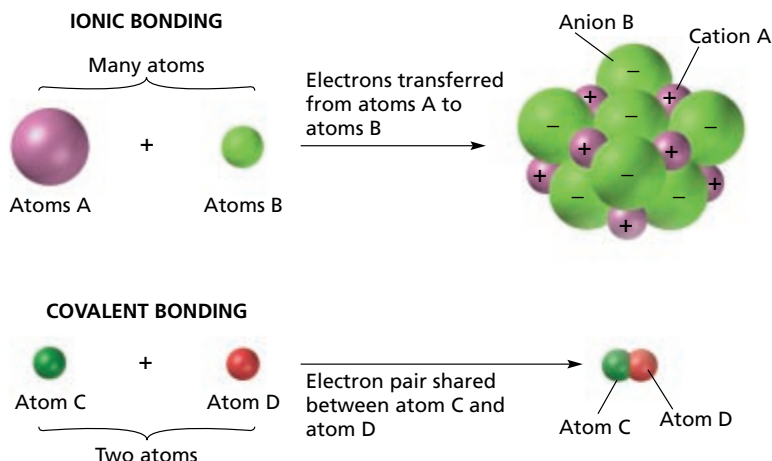
### Ionic or Covalent?

Bonding between atoms of different elements is rarely purely ionic or purely covalent. It usually falls somewhere between these two extremes, depending on how strongly the atoms of each element attract electrons. Recall that electronegativity is a measure of an atom’s ability to attract electrons. The degree to which bonding between atoms of two elements



Module 4: Chemical Bonding

**FIGURE 6-1** In ionic bonding, many atoms transfer electrons. The resulting positive and negative ions combine due to mutual electrical attraction. In covalent bonding, atoms share electron pairs to form independent molecules.



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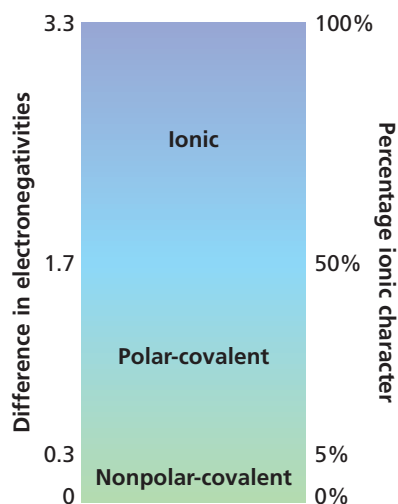
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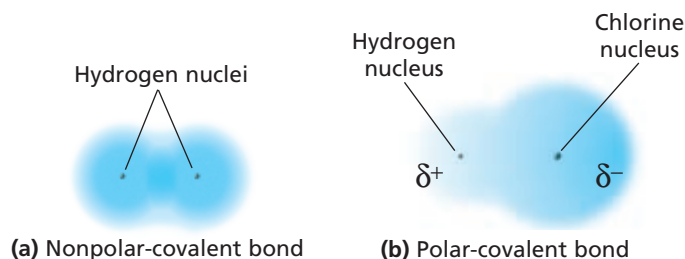
is ionic or covalent can be estimated by calculating the difference in the elements' electronegativities (see Figure 6-2). For example, the electronegativity difference between fluorine, F, and cesium, Cs, is  $4.0 - 0.7 = 3.3$ . (See Figure 5-20 on page 151 for a periodic table of electronegativity values.) So, according to Figure 6-2, cesium-fluorine bonding is ionic. The valence electrons are close to the highly electronegative fluorine atoms, causing the atoms to resemble anions, and far from the barely electronegative cesium atoms, which resemble cations.

Bonding between atoms with an electronegativity difference of 1.7 or less has an ionic character of 50% or less and is classified as covalent. Bonding between two atoms of the same element is completely covalent. Hydrogen, for example, exists in nature not as isolated atoms, but as pairs of atoms held together by covalent bonds. The hydrogen-hydrogen bond has 0% ionic character. It is a **nonpolar-covalent bond**, a covalent bond in which the bonding electrons are shared equally by the bonded atoms, resulting in a balanced distribution of electrical charge. Bonds having 0 to 5% ionic character, corresponding to electronegativity differences of roughly 0 to 0.3, are generally considered nonpolar-covalent bonds. In bonds with significantly different electronegativities, the electrons are more strongly attracted by the more-electronegative atom. Such bonds are **polar**, meaning that they have an uneven distribution of charge. Covalent bonds having 5 to 50% ionic character, corresponding to electronegativity differences of 0.3 to 1.7, are classified as polar. A **polar-covalent bond** is a covalent bond in which the bonded atoms have an unequal attraction for the shared electrons.

Nonpolar- and polar-covalent bonds are compared in Figure 6-3, which illustrates the electron density distribution in hydrogen-hydrogen and hydrogen-chlorine bonds. The electronegativity difference between chlorine and hydrogen is  $3.0 - 2.1 = 0.9$ , indicating a polar-covalent bond. The electrons in this bond are closer to the more-electronegative chlorine atom than to the hydrogen atom, as indicated in Figure 6-3(b). Consequently, the chlorine end of the bond has a partial negative charge, indicated by the symbol  $\delta^-$ . The hydrogen end of the bond then has an equal partial positive charge,  $\delta^+$ .



**FIGURE 6-2** Differences in electronegativities reflect the character of bonding between elements. The electronegativity of the less-electronegative element is subtracted from that of the more-electronegative element. The greater the electronegativity difference, the more ionic is the bonding.



**FIGURE 6-3** Comparison of the electron density in (a) a nonpolar, hydrogen-hydrogen bond and (b) a polar, hydrogen-chlorine bond. Because chlorine is more electronegative than hydrogen, the electron density in the hydrogen-chlorine bond is greater around the chlorine atom.

### SAMPLE PROBLEM 6-1

Use electronegativity differences and Figure 6-2 to classify bonding between sulfur, S, and the following elements: hydrogen, H; cesium, Cs; and chlorine, Cl. In each pair, which atom will be more negative?

#### SOLUTION

From Figure 5-20 on page 151, we know that the electronegativity of sulfur is 2.5. The electronegativities of hydrogen, cesium, and chlorine are 2.1, 0.7, and 3.0, respectively. In each pair, the atom with the larger electronegativity will be the more-negative atom.

Bonding between sulfur and	Electronegativity difference	Bond type	More-negative atom
hydrogen	$2.5 - 2.1 = 0.4$	polar-covalent	sulfur
cesium	$2.5 - 0.7 = 1.8$	ionic	sulfur
chlorine	$3.0 - 2.5 = 0.5$	polar-covalent	chlorine

#### PRACTICE

Use electronegativity differences and Figure 6-2 to classify bonding between chlorine, Cl, and the following elements: calcium, Ca; oxygen, O; and bromine, Br. Indicate the more-negative atom in each pair.

*Answer*

Bonding between chlorine and	Electronegativity difference	Bond type	More-negative atom
calcium	$3.0 - 1.0 = 2.0$	ionic	chlorine
oxygen	$3.5 - 3.0 = 0.5$	polar-covalent	oxygen
bromine	$3.0 - 2.8 = 0.2$	nonpolar-covalent	chlorine

## SECTION REVIEW

- What is the main distinction between ionic and covalent bonding?
  - H and F
  - Cu and S
  - I and Br
- How is electronegativity used in determining the ionic or covalent character of the bonding between two elements?
- What type of bonding would be expected between the following atoms?
  - List the three pairs of atoms referred to in the previous question in order of increasing ionic character of the bonding between them.



## SECTION 6-2

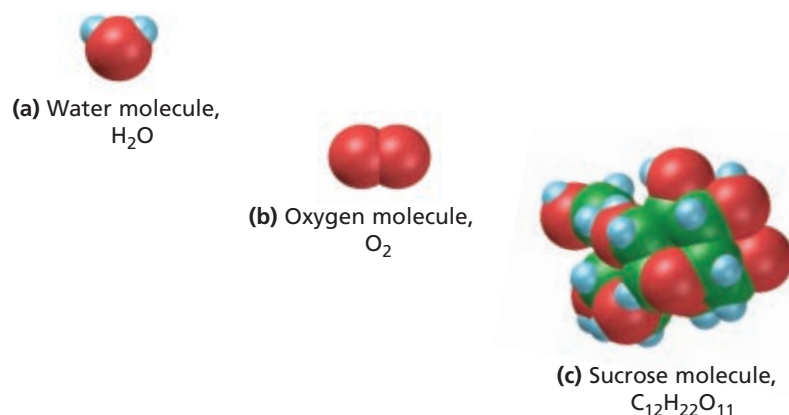
### OBJECTIVES

- Define *molecule* and *molecular formula*.
- Explain the relationships between potential energy, distance between approaching atoms, bond length, and bond energy.
- State the octet rule.
- List the six basic steps used in writing Lewis structures.
- Explain how to determine Lewis structures for molecules containing single bonds, multiple bonds, or both.
- Explain why scientists use resonance structures to represent some molecules.

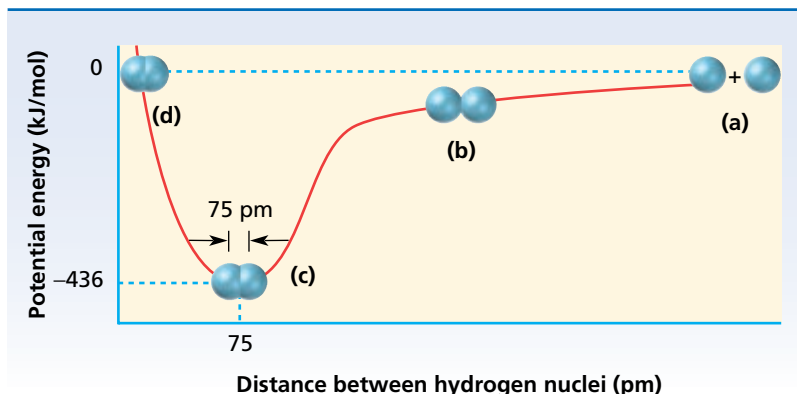
# Covalent Bonding and Molecular Compounds

Many chemical compounds, including most of the chemicals that are in living things and are produced by living things, are composed of molecules. A **molecule** is a neutral group of atoms that are held together by covalent bonds. A single molecule of a chemical compound is an individual unit capable of existing on its own. It may consist of two or more atoms of the same element, as in oxygen, or of two or more different atoms, as in water or sugar (see Figure 6-4 below). A chemical compound whose simplest units are molecules is called a **molecular compound**.

The composition of a compound is given by its chemical formula. A **chemical formula** indicates the relative numbers of atoms of each kind in a chemical compound by using atomic symbols and numerical subscripts. The chemical formula of a molecular compound is referred to as a molecular formula. A **molecular formula** shows the types and numbers of atoms combined in a single molecule of a molecular compound. The molecular formula for water, for example, is  $\text{H}_2\text{O}$ , which reflects the fact that a single water molecule consists of one oxygen atom joined by separate covalent bonds to two hydrogen atoms. A molecule of oxygen,  $\text{O}_2$ , is an example of a diatomic molecule. A **diatomic molecule** is a molecule containing only two atoms.



**FIGURE 6-4** The models for (a) water, (b) oxygen, and (c) sucrose, or table sugar, represent a few examples of the many molecular compounds in and around us. Atoms within molecules may form one or more covalent bonds.



**FIGURE 6-5** Potential energy changes during the formation of a hydrogen-hydrogen bond. (a) The separated hydrogen atoms do not affect each other. (b) Potential energy decreases as the atoms are drawn together by attractive forces. (c) Potential energy is at a minimum when attractive forces are balanced by repulsive forces. (d) Potential energy increases when repulsion between like charges outweighs attraction between opposite charges.

## Formation of a Covalent Bond

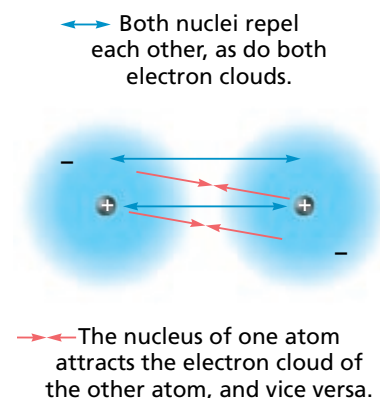
As you read in Section 6-1, nature favors chemical bonding because most atoms are at lower potential energy when bonded to other atoms than they are at as independent particles. In the case of covalent bond formation, this idea is illustrated by a simple example, the formation of a hydrogen-hydrogen bond.

Picture two isolated hydrogen atoms separated by a distance large enough to prevent them from influencing each other. At this distance, the overall potential energy of the atoms is arbitrarily set at zero, as shown in part (a) of Figure 6-5.

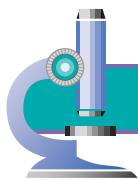
Now consider what happens if the hydrogen atoms approach each other. Each atom has a nucleus containing a single positively charged proton. The nucleus of each atom is surrounded by a negatively charged electron in a spherical  $1s$  orbital. As the atoms near each other, their charged particles begin to interact. As shown in Figure 6-6, the approaching nuclei and electrons are *attracted* to each other, which corresponds to a *decrease* in the total potential energy of the atoms. At the same time, the two nuclei *repel* each other and the two electrons *repel* each other, which results in an *increase* in potential energy.

The relative strength of attraction and repulsion between the charged particles depends on the distance separating the atoms. When the atoms first “see” each other, the electron-proton attraction is stronger than the electron-electron and proton-proton repulsions. Thus, the atoms are drawn to each other and their potential energy is lowered, as shown in part (b) of Figure 6-5.

The attractive force continues to dominate and the total potential energy continues to decrease until, eventually, a distance is reached at which the repulsion between the like charges equals the attraction of the opposite charges. This is shown in part (c) of Figure 6-5. At this point, which is represented by the bottom of the valley in the curve, potential energy is at a minimum and a stable hydrogen molecule forms. A closer approach of the atoms, shown in part (d) of Figure 6-5, results in a sharp rise in potential energy as repulsion becomes increasingly greater than attraction.



**FIGURE 6-6** The arrows indicate the attractive and repulsive forces between the electrons (shown as electron clouds) and nuclei of two hydrogen atoms. Attraction between particles corresponds to a decrease in potential energy of the atoms, while repulsion corresponds to an increase.



# Ultrasonic Toxic-Waste Destroyer

**P**aints, pesticides, solvents, and sulfides—these are just a few components of the 600 million tons of toxic waste that flow out of America's factories every year. Much of this waste ends up in ground water, contaminating our streams and drinking water.

Eliminating hazardous waste is a constant challenge. Unfortunately, today's disposal methods often damage the environment as much as they help it. Incinerators burning certain waste, for example, produce dioxins, one of the most dangerous class of toxins known to man.

Finding new methods to destroy toxic waste is a puzzle. Michael Hoffmann, a professor of environmental chemistry at the California Institute of Technology, thinks that part of the solution lies in sound-wave technology.

According to Hoffmann, the key to eliminating certain chemical wastes from polluted water is a phenomenon called cavitation. Cavitation occurs when the pressure in water is made to fluctuate from slightly above to slightly below normal, causing bubbles. The bubbles are unstable and collapse, creating tiny areas of extremely high pressure and heat. The pressure inside a collapsing bubble can be 1000 times greater than normal, and the temperature reaches about

5000°C—just a bit cooler than the surface of the sun. These conditions are harsh enough to combust most toxic-waste compounds in the water, breaking them down into harmless components.

Professor Hoffmann has employed a device that uses ultrasound—sound waves at frequencies just above the range of human hearing—to create cavitation in polluted water. As water flows between two panels that generate ultrasound at different frequencies, the ultrasonic waves generated by one panel form cavitation bubbles. An instant later, the ultrasound produced by the other panel collapses the bubbles. The intense pressure and heat generated break down the complex toxic compounds into simple, innocuous substances such as carbon dioxide, chloride ions, and hydrogen ions.

“With ultrasound,” says Hoffmann, “we can harness frequencies . . . of about 16 kilohertz up to 1 megahertz, and different . . . compounds are destroyed more readily at one frequency versus another . . . applying a particular frequency range, we can destroy a very broad range of chemical compounds.”

The device destroys simple toxins in a few minutes and other toxins in several hours. Some

compounds must be broken down into intermediate chemicals first and then treated again to destroy them completely. To be sure the waste is totally removed, scientists use sophisticated tracking methods to trace what happens to every single molecule of the toxin.

The ultrasound toxic-waste destroyer treats about 10% of all types of waste, eliminating both organic and inorganic compounds, such as hydrogen cyanide, TNT, and many pesticides. While the device cannot destroy complex mixtures of compounds, such as those found in raw sewage, it does have many advantages over current technologies. Aside from having no harmful environmental side effects, ultrasonic waste destruction is much cheaper and simpler than the process of combustion. By using the destroyer preventively, manufacturers can pre-treat their waste products before they dump them in the sewer, thus stopping a problem before it starts.

*How does Dr. Hoffmann's ultrasound device benefit society?*

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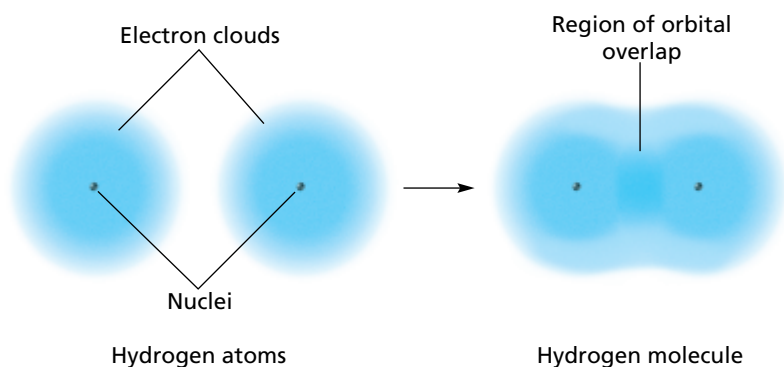
## Characteristics of the Covalent Bond

In Figure 6-5 on page 165, the bottom of the valley in the curve represents the balance between attraction and repulsion in a stable covalent bond. At this point, the electrons of each hydrogen atom of the hydrogen molecule are shared between the nuclei. As shown below in Figure 6-7, the molecule's electrons can be pictured as occupying overlapping orbitals, moving about freely in either orbital.

The bonded atoms vibrate a bit, but as long as their potential energy remains close to the minimum, they are covalently bonded to each other. *The distance between two bonded atoms at their minimum potential energy, that is, the average distance between two bonded atoms, is the **bond length**.* The bond length of a hydrogen-hydrogen bond is 75 pm.

In forming a covalent bond, the hydrogen atoms need to release energy as they change from isolated individual atoms to parts of a molecule. The amount of energy released equals the difference between the potential energy at the zero level (separated atoms) and that at the bottom of the valley (bonded atoms) in Figure 6-5. The same amount of energy must be added to separate the bonded atoms. **Bond energy** is the energy required to break a chemical bond and form neutral isolated atoms. Scientists usually report bond energies in kilojoules per mole (kJ/mol), which indicates the energy required to break one mole of bonds in isolated molecules. For example, 436 kJ of energy is needed to break the hydrogen-hydrogen bonds in one mole of hydrogen molecules and form two moles of separated hydrogen atoms.

The energy relationships described here for the formation of a hydrogen-hydrogen bond apply generally to all covalent bonds. However, bond lengths and bond energies vary with the types of atoms that have combined. Even the energy of a bond between the same two types of atoms varies somewhat, depending on what other bonds the atoms have formed. These facts should be considered in examining the data in Table 6-1 on page 168. The first three columns in the table list bonds, bond lengths, and bond energies of atoms in specific diatomic molecules. The last three columns give average values of specified bonds in many different compounds.



**FIGURE 6-7** The orbitals of the hydrogen atoms in a hydrogen molecule overlap, allowing each electron to feel the attraction of both nuclei. The result is an increase in electron density between the nuclei.



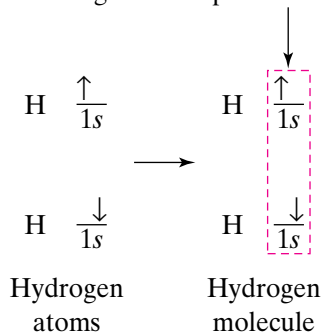
**TABLE 6-1 Bond Lengths and Bond Energies for Selected Covalent Bonds**

Bond	Bond length (pm)	Bond energy (kJ/mol)	Bond	Bond length (pm)	Bond energy (kJ/mol)
H–H	74	436	C–C	154	346
F–F	141	159	C–N	147	305
Cl–Cl	199	243	C–O	143	358
Br–Br	228	193	C–H	109	418
I–I	267	151	C–Cl	177	327
H–F	92	569	C–Br	194	285
H–Cl	127	432	N–N	145	163
H–Br	141	366	N–H	101	386
H–I	161	299	O–H	96	459

All individual hydrogen atoms contain a single, unpaired electron in a  $1s$  atomic orbital. When two hydrogen atoms form a molecule, they share electrons in a covalent bond. As illustrated in Figure 6-8, sharing electrons allows each atom in the hydrogen molecule to experience the effect of the stable electron configuration of helium,  $1s^2$ . This tendency for atoms to achieve noble-gas configurations through covalent bonding extends beyond the simple case of a hydrogen molecule.

**FIGURE 6-8** By sharing electrons in overlapping orbitals, each hydrogen atom in a hydrogen molecule experiences the effect of a stable  $1s^2$  configuration.

Bonding electron pair in overlapping orbitals

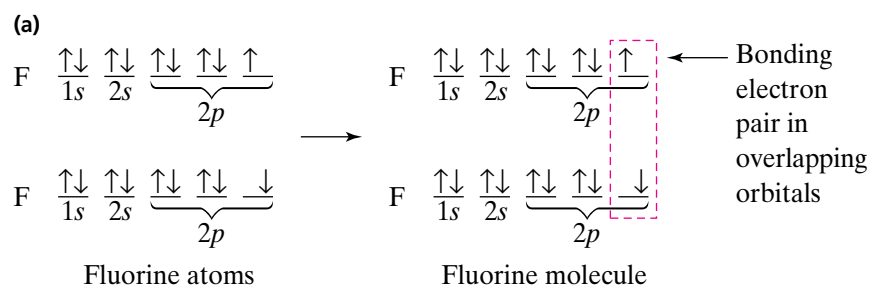


## The Octet Rule

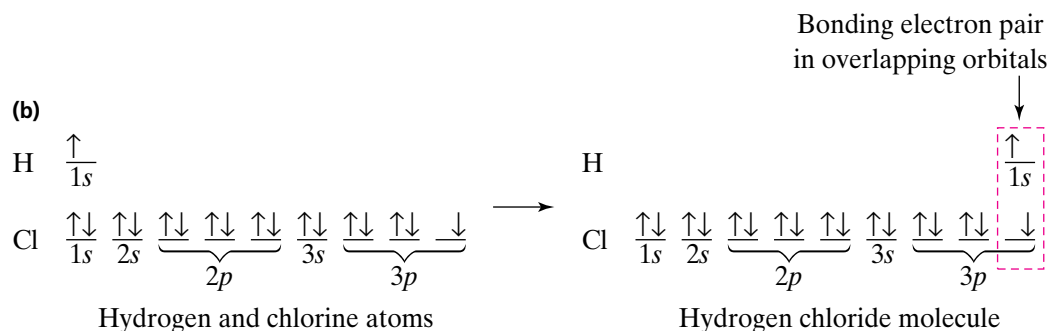
Unlike other atoms, the noble-gas atoms exist independently in nature. They possess a minimum of energy existing on their own because of the special stability of their electron configurations. This stability results from the fact that, with the exception of helium and its two electrons in a completely filled outer shell, the noble-gas atoms' outer  $s$  and  $p$  orbitals are completely filled by a total of eight electrons. Other main-group atoms can effectively fill their outermost  $s$  and  $p$  orbitals with

electrons by sharing electrons through covalent bonding. Such bond formation follows the **octet rule**: *Chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an octet of electrons in its highest occupied energy level.*

Let's examine how the bonding in a fluorine molecule illustrates the octet rule. An independent fluorine atom has seven electrons in its highest energy level ( $[\text{He}]2s^22p^5$ ). Like hydrogen atoms, fluorine atoms bond covalently with each other to form diatomic molecules,  $\text{F}_2$ . When two fluorine atoms bond, each atom shares one of its valence electrons with its partner. The shared electron pair effectively fills each atom's outermost energy level with an octet of electrons, as illustrated in Figure 6-9(a). Figure 6-9(b) shows another example of the octet rule, in which the chlorine atom in a molecule of hydrogen chloride,  $\text{HCl}$ , achieves an outermost octet by sharing an electron pair with an atom of hydrogen.



**FIGURE 6-9** (a) By sharing valence electrons in overlapping orbitals, each atom in a fluorine molecule feels the effect of neon's stable configuration,  $[\text{He}]2s^22p^6$ . (b) In a hydrogen chloride molecule, the hydrogen atom effectively fills its 1s orbital with two electrons, while the chlorine atom experiences the stability of an outermost octet of electrons.



## Exceptions to the Octet Rule

Most main-group elements tend to form covalent bonds according to the octet rule. However, there are exceptions. As you have seen, hydrogen forms bonds in which it is surrounded by only two electrons. Boron, B, has just three valence electrons ( $[\text{He}]2s^22p^1$ ). Because electron pairs are shared in covalent bonds, boron tends to form bonds in which it is surrounded by six electrons. In boron trifluoride,  $\text{BF}_3$ , for example, the boron atom is surrounded by its own three valence electrons plus one from each of the three fluorine atoms bonded to it. Other elements can be surrounded by *more* than eight electrons when they combine with the highly electronegative elements fluorine, oxygen, and chlorine. In these cases of *expanded valence*, bonding involves electrons in *d* orbitals as well as in *s* and *p* orbitals.

Number of valence electrons	Electron-dot notation	Example
1	X·	Na·
2	·X·	·Mg·
3	·X·	·B·
4	·X·	·C·
5	·X·	·N·
6	·X·	·O·
7	·X·	·F·
8	·X·	·Ne·

**FIGURE 6-10** To write an element's electron-dot notation, determine the element's number of valence electrons. Then place a corresponding number of dots around the element's symbol, as shown.

## Electron-Dot Notation

Covalent bond formation usually involves only the electrons in an atom's outermost energy levels, or the atom's valence electrons. To keep track of these electrons, it is helpful to use electron-dot notation.

**Electron-dot notation** is an electron-configuration notation in which only the valence electrons of an atom of a particular element are shown, indicated by dots placed around the element's symbol. The inner-shell electrons are not shown. For example, the electron-dot notation for a fluorine atom (electron configuration  $[\text{He}]2s^2p^5$ ) may be written as follows.



In general, an element's number of valence electrons can be determined by adding the superscripts of the element's noble-gas notation. In this book, the electron-dot notations for elements with 1–8 valence electrons are written as shown in Figure 6-10.

### SAMPLE PROBLEM 6-2

- Write the electron-dot notation for hydrogen.
- Write the electron-dot notation for nitrogen.

#### SOLUTION

- A hydrogen atom has only one occupied energy level, the  $n = 1$  level, which contains a single electron. Therefore, the electron-dot notation for hydrogen is written as follows.



- The group notation for nitrogen's family of elements is  $ns^2np^3$ , which indicates that nitrogen has five valence electrons. Therefore, the electron-dot notation for nitrogen is written as follows.



## Lewis Structures

Electron-dot notation can also be used to represent molecules. For example, a hydrogen molecule,  $\text{H}_2$ , is represented by combining the notations of two individual hydrogen atoms, as follows.

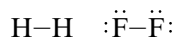


The pair of dots represents the shared electron pair of the hydrogen-hydrogen covalent bond. For a molecule of fluorine,  $F_2$ , the electron-dot notations of two fluorine atoms are combined.



Here also the pair of dots between the two symbols represents the shared pair of a covalent bond. In addition, each fluorine atom is surrounded by three pairs of electrons that are not shared in bonds. *An unshared pair, also called a lone pair, is a pair of electrons that is not involved in bonding and that belongs exclusively to one atom.*

The pair of dots representing a shared pair of electrons in a covalent bond is often replaced by a long dash. According to this convention, hydrogen and fluorine molecules are represented as follows.



These representations are all **Lewis structures**, *formulas in which atomic symbols represent nuclei and inner-shell electrons, dot-pairs or dashes between two atomic symbols represent electron pairs in covalent bonds, and dots adjacent to only one atomic symbol represent unshared electrons*. It is common to write Lewis structures that show only the electrons that are shared, using dashes to represent the bonds. A **structural formula** indicates the kind, number, arrangement, and bonds but not the unshared pairs of the atoms in a molecule. For example,  $F-F$  and  $H-Cl$  are structural formulas.

The Lewis structures (and therefore the structural formulas) for many molecules can be drawn if one knows the composition of the molecule and which atoms are bonded to each other. The following sample problem illustrates the basic steps for writing Lewis structures. The molecule described in this problem contains bonds with single shared electron pairs. A single covalent bond, or a **single bond**, is a covalent bond produced by the sharing of one pair of electrons between two atoms.

### SAMPLE PROBLEM 6-3

**Draw the Lewis structure of iodomethane,  $CH_3I$ .**

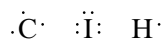
#### SOLUTION

1. Determine the type and number of atoms in the molecule.

The formula shows one carbon atom, one iodine atom, and three hydrogen atoms.

2. Write the electron-dot notation for each type of atom in the molecule.

Carbon is from Group 14 and has four valence electrons. Iodine is from Group 17 and has seven valence electrons. Hydrogen has one valence electron.





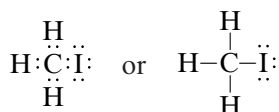
3. Determine the total number of valence electrons in the atoms to be combined.

$$\begin{array}{rcl} \text{C} & 1 \times 4e^- & = 4e^- \\ \text{I} & 1 \times 7e^- & = 7e^- \\ \text{H} & 3 \times 1e^- & = 3e^- \\ \hline & & 14e^- \end{array}$$

4. Arrange the atoms to form a skeleton structure for the molecule. If carbon is present, it is the central atom. Otherwise, the least-electronegative atom is central (except for hydrogen, which is never central). Then connect the atoms by electron-pair bonds.



5. Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons.



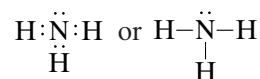
6. Count the electrons in the structure to be sure that the number of valence electrons used equals the number available. Be sure the central atom and other atoms besides hydrogen have an octet.

There are eight electrons in the four covalent bonds and six electrons in the three unshared pairs, giving the correct total of 14 valence electrons.

## PRACTICE

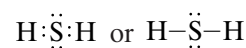
1. Draw the Lewis structure of ammonia,  $\text{NH}_3$ .

Answer



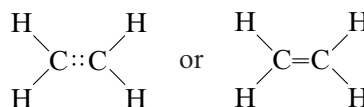
2. Draw the Lewis structure for hydrogen sulfide,  $\text{H}_2\text{S}$ .

Answer



## Multiple Covalent Bonds

Atoms of some elements, especially carbon, nitrogen, and oxygen, can share more than one electron pair. A double covalent bond, or simply a **double bond**, is a covalent bond produced by the sharing of two pairs of electrons between two atoms. A double bond is shown either by two side-by-side pairs of dots or by two parallel dashes. All four electrons in a double bond “belong” to both atoms. In ethene,  $\text{C}_2\text{H}_4$ , for example, two electron pairs are simultaneously shared by two carbon atoms.



A triple covalent bond, or simply a **triple bond**, is a covalent bond produced by the sharing of three pairs of electrons between two atoms. For example, elemental nitrogen,  $N_2$ , like hydrogen and the halogens, normally exists as diatomic molecules. In this case, however, each nitrogen atom, which has five valence electrons, acquires three electrons to complete an octet by sharing three pairs of electrons with its partner. This is illustrated in the Lewis structure and the formula structure for  $N_2$ , as shown below.



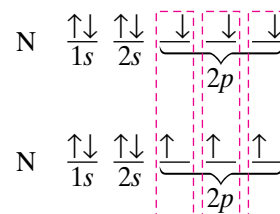
Figure 6-11 represents nitrogen's triple bond through orbital notation. Like the single bonds in hydrogen and halogen molecules, the triple bond in nitrogen molecules is nonpolar.

Carbon forms a number of compounds containing triple bonds. For example, the compound ethyne,  $C_2H_2$ , contains a carbon-carbon triple bond.



Double and triple bonds are referred to as **multiple bonds**, or multiple covalent bonds. Double bonds in general have higher bond energies and are shorter than single bonds. Triple bonds are even stronger and shorter. Table 6-2 compares average bond lengths and bond energies for some single, double, and triple bonds.

In writing Lewis structures for molecules that contain carbon, nitrogen, or oxygen, one must remember that multiple bonds between pairs of these atoms are possible. (A hydrogen atom, on the other hand, has only one electron and therefore always forms a single covalent bond.) The need for a multiple bond becomes obvious if there are not enough valence electrons to complete octets by adding unshared pairs. Sample Problem 6-4 on page 174 illustrates how to deal with this situation.



Nitrogen molecule

**FIGURE 6-11** In a molecule of nitrogen,  $N_2$ , each nitrogen atom is surrounded by six shared electrons plus one unshared pair of electrons. Thus, each nitrogen atom follows the octet rule in forming a triple covalent bond.

**TABLE 6-2** Bond Lengths and Bond Energies for Single and Multiple Covalent Bonds

Bond	Bond length (pm)	Bond energy (kJ/mol)	Bond	Bond length (pm)	Bond energy (kJ/mol)
C—C	154	346	C—O	143	358
C=C	134	612	C=O	120	732
C≡C	120	835	C≡O	113	1072
C—N	147	305	N—N	145	163
C=N	132	615	N=N	125	418
C≡N	116	887	N≡N	110	945

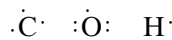
## SAMPLE PROBLEM 6-4

**Draw the Lewis structure for methanal,  $\text{CH}_2\text{O}$ , which is also known as formaldehyde.**

### SOLUTION

1. *Determine the number of atoms of each element present in the molecule.*  
The formula shows one carbon atom, two hydrogen atoms, and one oxygen atom.

2. *Write the electron-dot notation for each type of atom.*  
Carbon from Group 14 has four valence electrons. Oxygen, which is in Group 16, has six valence electrons. Hydrogen has only one electron.



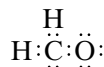
3. *Determine the total number of valence electrons in the atoms to be combined.*

$$\begin{array}{rcl} \text{C} & 1 \times 4e^- & = 4e^- \\ \text{O} & 1 \times 6e^- & = 6e^- \\ 2\text{H} & 2 \times 1e^- & = 2e^- \\ & \hline & 12e^- \end{array}$$

4. *Arrange the atoms to form a skeleton structure for the molecule, and connect the atoms by electron-pair bonds.*



5. *Add unshared pairs of electrons so that each hydrogen atom shares a pair of electrons and each other nonmetal is surrounded by eight electrons.*

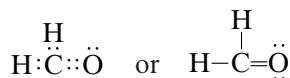


- 6a. *Count the electrons in the Lewis structure to be sure that the number of valence electrons used equals the number available.*

The structure above has six electrons in covalent bonds and eight electrons in four lone pairs, for a total of 14 electrons. The structure has two valence electrons too many.

- 6b. *If too many electrons have been used, subtract one or more lone pairs until the total number of valence electrons is correct. Then move one or more lone electron pairs to existing bonds between non-hydrogen atoms until the outer shells of all atoms are completely filled.*

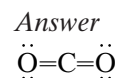
Subtract the lone pair of electrons from the carbon atom. Then move one lone pair of electrons from the oxygen to the bond between carbon and oxygen to form a double bond.



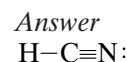
There are eight electrons in covalent bonds and four electrons in lone pairs, for a total of 12 valence electrons.

### PRACTICE

1. Draw the Lewis structure for carbon dioxide,  $\text{CO}_2$ .

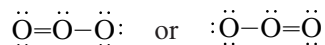


2. Draw the Lewis structure for hydrogen cyanide, which contains one hydrogen atom, one carbon atom, and one nitrogen atom.

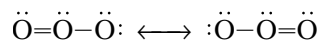


## Resonance Structures

Some molecules and ions cannot be represented adequately by a single Lewis structure. One such molecule is ozone,  $\text{O}_3$ , which can be represented by either of the following Lewis structures.



Notice that each structure indicates that the ozone molecule has two types of O—O bonds, one single and one double. Chemists once speculated that ozone split its time existing as one of these two structures, constantly alternating, or “resonating,” from one to the other. Experiments, however, revealed that the oxygen-oxygen bonds in ozone are identical. Therefore, scientists now say that ozone has a single structure that is the average of these two structures. Together the structures are referred to as *resonance structures* or *resonance hybrids*. **Resonance** refers to bonding in molecules or ions that cannot be correctly represented by a single Lewis structure. To indicate resonance, a double-headed arrow is placed between a molecule’s resonance structures.



## Covalent-Network Bonding

All the covalent compounds that you have read about to this point are molecular. They consist of many identical molecules bound together by forces acting between the molecules. (You will read more about intermolecular forces in Section 6-5.) There are many covalently bonded compounds that do not contain individual molecules, but instead can be pictured as continuous, three-dimensional networks of bonded atoms. You will read more about covalently bonded networks in Chapter 11.

### SECTION REVIEW

1. Define the following:
  - a. bond length
  - b. bond energy
2. State the octet rule.
3. How many pairs of electrons are shared in the following types of covalent bonds?
  - a. a single bond
  - b. a double bond
  - c. a triple bond
4. Draw the Lewis structures for the following molecules:
  - a. IBr
  - b.  $\text{CH}_3\text{Br}$
  - c.  $\text{C}_2\text{HCl}$
  - d.  $\text{SiCl}_4$
  - e.  $\text{F}_2\text{O}$



## SECTION 6-3

### OBJECTIVES

- Compare and contrast a chemical formula for a molecular compound with one for an ionic compound.
- Discuss the arrangements of ions in crystals.
- Define *lattice energy* and explain its significance.
- List and compare the distinctive properties of ionic and molecular compounds.
- Write the Lewis structure for a polyatomic ion given the identity of the atoms combined and other appropriate information.



**FIGURE 6-12** Like most ionic compounds, sodium chloride is a crystalline solid.

# Ionic Bonding and Ionic Compounds

Most of the rocks and minerals that make up Earth's crust consist of positive and negative ions held together by ionic bonding. A familiar example of an ionically bonded compound is sodium chloride, or common table salt, which is found in nature as rock salt. A sodium ion,  $\text{Na}^+$ , has a charge of 1+. A chloride ion,  $\text{Cl}^-$ , has a charge of 1-. In sodium chloride, these ions combine in a one-to-one ratio— $\text{Na}^+\text{Cl}^-$ —so that each positive charge is balanced by a negative charge. Because chemists are aware of this balance of charge, the chemical formula for sodium chloride is usually written simply as  $\text{NaCl}$ .

An **ionic compound** is composed of positive and negative ions that are combined so that the numbers of positive and negative charges are equal. Most ionic compounds exist as crystalline solids (see Figure 6-12). A crystal of any ionic compound is a three-dimensional network of positive and negative ions mutually attracted to one another. As a result, in contrast to a molecular compound, an ionic compound is not composed of independent, neutral units that can be isolated and examined. The chemical formula of an ionic compound merely represents the simplest ratio of the compound's combined ions that gives electrical neutrality.

The chemical formula of an ionic compound shows the ratio of the ions present in a sample of any size. A **formula unit** is the simplest collection of atoms from which an ionic compound's formula can be established. For example, one formula unit of sodium chloride,  $\text{NaCl}$ , is one sodium cation plus one chloride anion. (In naming anions, the *-ine* ending of the element's name is replaced with *-ide*. You'll read more about naming compounds in Chapter 7.)

The ratio of ions in a formula unit depends on the charges of the ions combined. For example, to achieve electrical neutrality in the ionic compound calcium fluoride, two fluoride anions,  $\text{F}^-$ , each with a charge of 1-, must balance the 2+ charge of each calcium cation,  $\text{Ca}^{2+}$ . Therefore, the formula of calcium fluoride is  $\text{CaF}_2$ .

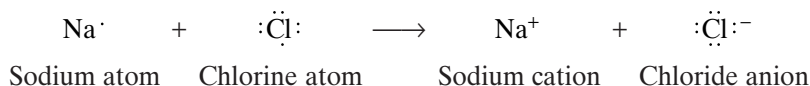
## Formation of Ionic Compounds

Electron-dot notation can be used to demonstrate the changes that take place in ionic bonding. Ionic compounds do not ordinarily form by the combination of isolated ions, but consider for a moment a sodium

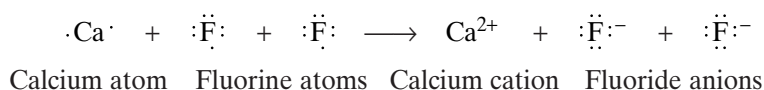
atom and a chlorine atom approaching each other. The two atoms are neutral and have one and seven valence electrons, respectively.



We have already seen that atoms of sodium and the other alkali metals readily lose one electron to form cations. And we have seen that atoms of chlorine and the other halogens readily gain one electron to form anions. The combination of sodium and chlorine atoms to produce one formula unit of sodium chloride can thus be represented as follows.

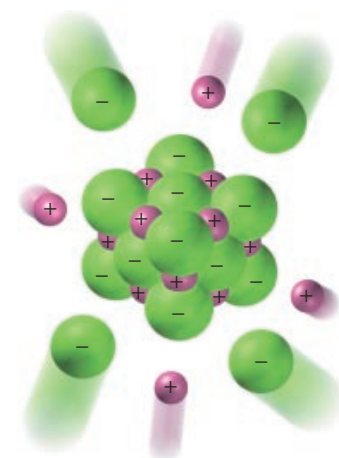
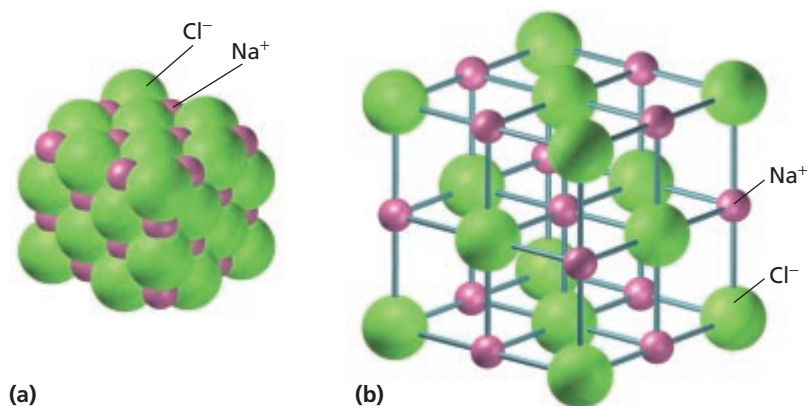


The transfer of an electron from the sodium atom to the chlorine atom transforms each atom into an ion with a noble-gas configuration. In the combination of calcium with fluorine, two fluorine atoms are needed to accept the two valence electrons given up by one calcium atom.



## Characteristics of Ionic Bonding

Recall that nature favors arrangements in which potential energy is minimized. In an ionic crystal, ions minimize their potential energy by combining in an orderly arrangement known as a *crystal lattice* (see Figure 6-13). The attractive forces at work within an ionic crystal include those between oppositely charged ions and those between the nuclei and electrons of adjacent ions. The repulsive forces include those between like-charged ions and those between electrons of adjacent ions. The distances between ions and their arrangement in a crystal represent a balance among all these forces. Sodium chloride's crystal structure is shown in Figure 6-14 below.



**FIGURE 6-13** The ions in an ionic compound lower their potential energy by forming an orderly, three-dimensional array in which the positive and negative charges are balanced. The electrical forces of attraction between oppositely charged ions extend over long distances, causing a large decrease in potential energy.

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**FIGURE 6-14** Two models of the crystal structure of sodium chloride are shown. (a) To illustrate the ions' actual arrangement, the sodium and chloride ions are shown with their electron clouds just touching. (b) In an expanded view, the distances between ions have been exaggerated in order to clarify the positioning of the ions in the structure.

**FIGURE 6-15** The figure shows the ions that most closely surround a chloride anion and a sodium cation within the crystal structure of NaCl. The structure is composed such that (a) six  $\text{Na}^+$  ions surround each  $\text{Cl}^-$  ion. At the same time, (b) six  $\text{Cl}^-$  ions surround each  $\text{Na}^+$  ion (which cannot be seen but whose location is indicated by the dashed outline).

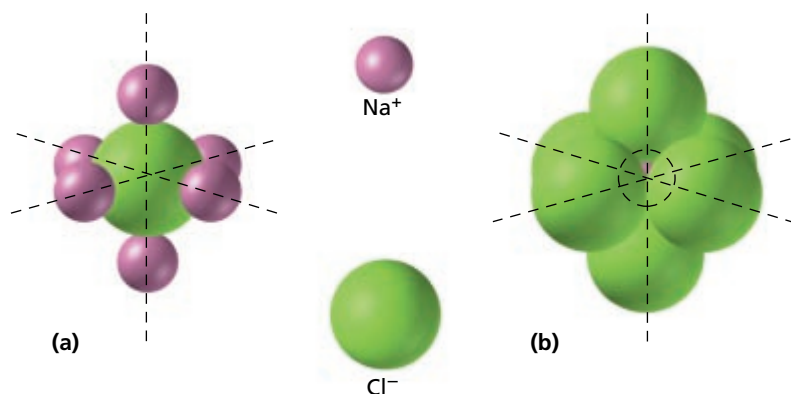
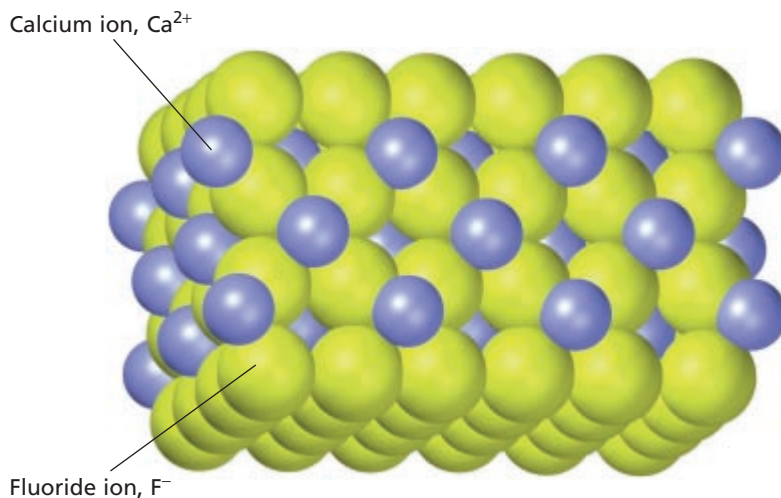


Figure 6-15 shows the crystal structure of sodium chloride in greater detail. Within the arrangement, each sodium cation is surrounded by six chloride anions. At the same time, each chloride anion is surrounded by six sodium cations. Attraction between the adjacent oppositely charged ions is much stronger than repulsion by other ions of the same charge, which are farther away.

The three-dimensional arrangements of ions and the strengths of attraction between them vary with the sizes and charges of the ions and the numbers of ions of different charges. For example, in calcium fluoride, there are two anions for each cation. Each calcium cation is surrounded by eight fluoride anions. At the same time, each fluoride ion is surrounded by four calcium cations, as shown in Figure 6-16.

To compare bond strengths in ionic compounds, chemists compare the amounts of energy released when separated ions in a gas come together to form a crystalline solid. **Lattice energy** is the energy released when one mole of an ionic crystalline compound is formed from gaseous ions. Lattice energy values for a few common ionic compounds are shown in Table 6-3. The negative energy values indicate that energy is released when the crystals are formed.



**FIGURE 6-16** In the crystal structure of calcium fluoride,  $\text{CaF}_2$ , each calcium cation is surrounded by eight fluoride anions and each fluoride ion is surrounded by four calcium cations. This is the closest possible packing of the ions in which the positive and negative charges are balanced.

## A Comparison of Ionic and Molecular Compounds

The force that holds ions together in ionic compounds is a very strong overall attraction between positive and negative charges. In a molecular compound, the covalent bonds of the atoms making up each molecule are also strong. But the forces of attraction *between* molecules are much weaker than the forces of ionic bonding. This difference in the strength of attraction between the basic units of molecular and ionic compounds gives rise to different properties in the two types of compounds.

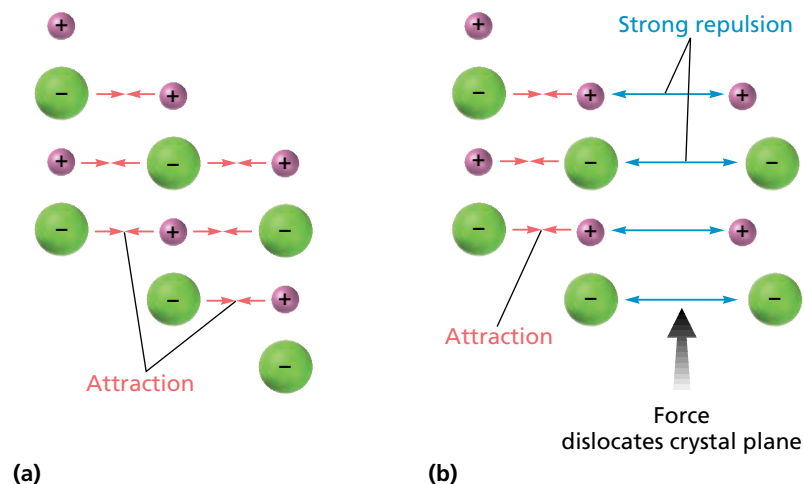
The melting point, boiling point, and hardness of a compound depend on how strongly its basic units are attracted to each other. Because the forces of attraction between individual molecules are not very strong, many molecular compounds melt at low temperatures. In fact, many molecular compounds are already completely gaseous at room temperature. In contrast, the ions in ionic compounds are held together by strong attractive forces, so ionic compounds generally have higher melting and boiling points than do molecular compounds. Further, they do not vaporize at room temperature as many molecular compounds do.

Ionic compounds are hard but brittle. Why? In an ionic crystal, even a slight shift of one row of ions relative to another causes a large buildup of repulsive forces, as shown in Figure 6-17. These forces make it difficult for one layer to move relative to another, causing ionic compounds to be hard. If one layer is moved, however, the repulsive forces make the layers part completely, causing ionic compounds to be brittle.

In the solid state, the ions cannot move, so the compounds are not electrical conductors. In the molten state, ionic compounds are electrical conductors because the ions can move freely to carry electrical current. Many ionic compounds can dissolve in water. When they dissolve, their ions separate from each other and become surrounded by water molecules. These ions are free to move through the solution, so such solutions are electrical conductors. Other ionic compounds do not dissolve in water, however, because the attraction of the water molecules cannot overcome the attractions between the ions.

**TABLE 6-3** Lattice Energies of Some Common Ionic Compounds

Compound	Lattice energy (kJ/mol)
NaCl	-787.5
NaBr	-751.4
CaF <sub>2</sub>	-2634.7
CaO	-3385
LiCl	-861.3
LiF	-1032
MgO	-3760
KCl	-715



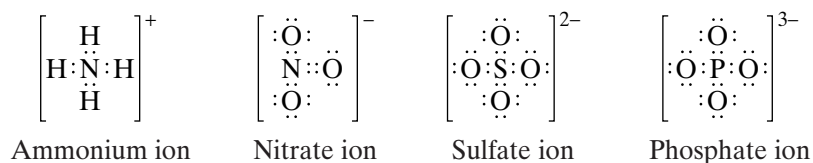
**FIGURE 6-17** (a) The attraction between positive and negative ions in a crystalline ionic compound causes layers of ions to resist motion. (b) When struck with sufficient force, the layers shift so that ions of the same charge approach each other, causing repulsion. As a result, the crystal shatters along the planes.



## Polyatomic Ions

Certain atoms bond covalently with each other to form a group of atoms that has both molecular and ionic characteristics. A *charged group of covalently bonded atoms is known as a polyatomic ion*. Polyatomic ions combine with ions of opposite charge to form ionic compounds. The charge of a polyatomic ion results from an excess of electrons (negative charge) or a shortage of electrons (positive charge). For example, an ammonium ion, a common positively charged polyatomic ion, contains one nitrogen atom and four hydrogen atoms and has a single positive charge. Its formula is  $\text{NH}_4^+$ , sometimes written as  $[\text{NH}_4]^+$  to show that the group of atoms *as a whole* has a charge of 1+. The seven protons in the nitrogen atom plus the four protons in the four hydrogen atoms give the ammonium ion a total positive charge of 11+. An independent nitrogen atom has seven electrons, and four independent hydrogen atoms have a total of four electrons. When these atoms combine to form an ammonium ion, one of their electrons is lost, giving the polyatomic ion a total negative charge of 10–.

Lewis structures for the ammonium ion and some common negative polyatomic ions—the nitrate, sulfate, and phosphate ions—are shown below. To find the Lewis structure for a polyatomic ion, follow the steps of Sample Problem 6-4 on page 174, with the following exception. If the ion is negatively charged, add to the total number of valence electrons a number of  $e^-$  corresponding to the ion's negative charge. If the ion is positively charged, subtract from the total number of valence electrons a number of  $e^-$  corresponding to the ion's positive charge.



### SECTION REVIEW

1. Give two examples of an ionic compound.
2. Use electron-dot notation to demonstrate the formation of ionic compounds involving the following:
  - a. Li and Cl
  - b. Ca and I
3. Distinguish between ionic and molecular compounds in terms of the basic units that each is composed of.
4. Compound B has lower melting and boiling points than compound A. At the same temperature, compound B vaporizes faster and to a greater extent than compound A. If one of these compounds is ionic and the other is molecular, which would you expect to be molecular? ionic? Explain the reasoning behind your choices.

# Metallic Bonding

## SECTION 6-4

### OBJECTIVES

- Describe the electron-sea model of metallic bonding, and explain why metals are good electrical conductors.
- Explain why metal surfaces are shiny.
- Explain why metals are malleable and ductile but ionic-crystalline compounds are not.

### The Metallic-Bond Model

The highest energy levels of most metal atoms are occupied by very few electrons. In *s*-block metals, for example, one or two valence electrons occupy the outermost orbital, whereas all three outermost *p* orbitals, which can hold a total of six electrons, are vacant. In addition to completely vacant outer *p* orbitals, *d*-block metals also possess many vacant *d* orbitals in the energy level just below their highest energy level.

Within a metal, the vacant orbitals in the atoms' outer energy levels overlap. This overlapping of orbitals allows the outer electrons of the atoms to roam freely throughout the entire metal. The electrons are *delocalized*, which means that they do not belong to any one atom but move freely about the metal's network of empty atomic orbitals. These mobile electrons form a *sea of electrons* around the metal atoms, which are packed together in a crystal lattice (see Figure 6-18). *The chemical bonding that results from the attraction between metal atoms and the surrounding sea of electrons is called metallic bonding.*

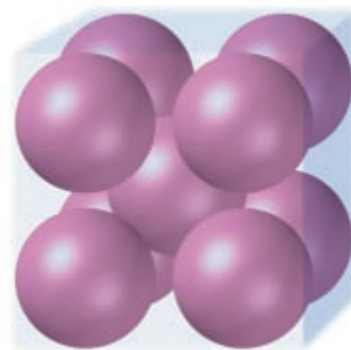
### Metallic Properties

The freedom of electrons to move in a network of metal atoms accounts for the high electrical and thermal conductivity characteristic of all metals. In addition, because they contain many orbitals separated by extremely small energy differences, metals can absorb a wide range of light frequencies. This absorption of light results in the excitation of the metal atoms' electrons to higher energy levels. The electrons immediately fall back down to lower levels, emitting energy in the form of light. This de-excitation is responsible for the shiny appearance of metal surfaces.

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**FIGURE 6-18** The model shows a portion of the crystal structure of solid sodium. The atoms are arranged so that each sodium atom is surrounded by eight other sodium atoms. The atoms are relatively fixed in position, while the electrons are free to move throughout the crystal, forming an electron sea.



**FIGURE 6-19** Unlike ionic crystalline compounds, most metals are malleable. This property allows iron, for example, to be shaped into useful tools.

Most metals are also easy to form into desired shapes. Two important properties related to this characteristic are malleability and ductility. **Malleability** is the ability of a substance to be hammered or beaten into thin sheets. **Ductility** is the ability of a substance to be drawn, pulled, or extruded through a small opening to produce a wire. The malleability and ductility of metals are possible because metallic bonding is the same in all directions throughout the solid. One plane of atoms in a metal can slide past another without encountering any resistance or breaking any bonds. By contrast, recall from Section 6-3 that shifting the layers of an ionic crystal causes the bonds to break and the crystal to shatter.

## Metallic Bond Strength

Metallic bond strength varies with the nuclear charge of the metal atoms and the number of electrons in the metal's electron sea. Both of these factors are reflected in a metal's *heat of vaporization*. When a metal is vaporized, the bonded atoms in the normal (usually solid) state are converted to individual metal atoms in the gaseous state. The amount of heat required to vaporize the metal is a measure of the strength of the bonds that hold the metal together. Some heats of vaporization for metals are given in Table 6-4.

**TABLE 6-4** Heats of Vaporization of Some Metals (kJ/mol)

Period	Element		
Second	Li 147	Be 297	
Third	Na 97	Mg 128	Al 294
Fourth	K 77	Ca 155	Sc 333
Fifth	Rb 76	Sr 137	Y 365
Sixth	Cs 64	Ba 140	La 402

## SECTION REVIEW

1. Describe the electron-sea model of metallic bonding.
2. What is the relationship between metallic bond strength and heat of vaporization?
3. Explain why most metals are malleable and ductile but ionic crystals are not.

# Molecular Geometry

## SECTION 6-5

### OBJECTIVES

- Explain VSEPR theory.
- Predict the shapes of molecules or polyatomic ions using VSEPR theory.
- Explain how the shapes of molecules are accounted for by hybridization theory.
- Describe dipole-dipole forces, hydrogen bonding, induced dipoles, and London dispersion forces.
- Explain what determines molecular polarity.

The properties of molecules depend not only on the bonding of atoms but also on molecular geometry—the three-dimensional arrangement of a molecule’s atoms in space. The polarity of each bond, along with the geometry of the molecule, determines **molecular polarity**, or the *uneven distribution of molecular charge*. As you will read, molecular polarity strongly influences the forces that act *between* molecules in liquids and solids.

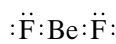
A chemical formula reveals little information about a molecule’s geometry. After performing many tests designed to reveal the shapes of various molecules, chemists developed two different, equally successful theories to explain certain aspects of their findings. One theory accounts for molecular bond angles. The other is used to describe the orbitals that contain the valence electrons of a molecule’s atoms.

### VSEPR Theory

As shown in Figure 6-20, diatomic molecules, like those of hydrogen,  $\text{H}_2$ , and hydrogen chloride,  $\text{HCl}$ , must be linear because they consist of only two atoms. To predict the geometries of more-complicated molecules, one must consider the locations of all electron pairs surrounding the bonded atoms. This is the basis of VSEPR theory.

The abbreviation VSEPR stands for “valence-shell, electron-pair repulsion,” referring to the repulsion between pairs of valence electrons of the atoms in a molecule. **VSEPR theory states that repulsion between the sets of valence-level electrons surrounding an atom causes these sets to be oriented as far apart as possible.** How does the assumption that electrons in molecules repel each other account for molecular shapes? For now let us consider only molecules with no unshared valence electron pairs on the central atom.

Let’s examine the simple molecule  $\text{BeF}_2$ . Recall that beryllium does not follow the octet rule. The beryllium atom forms a covalent bond with each fluorine atom. It is surrounded by only the two electron pairs that it shares with the fluorine atoms.



According to VSEPR, the shared pairs are oriented as far away from each other as possible. As shown in Figure 6-21(a) on page 184, the distance between electron pairs is maximized if the bonds to fluorine are



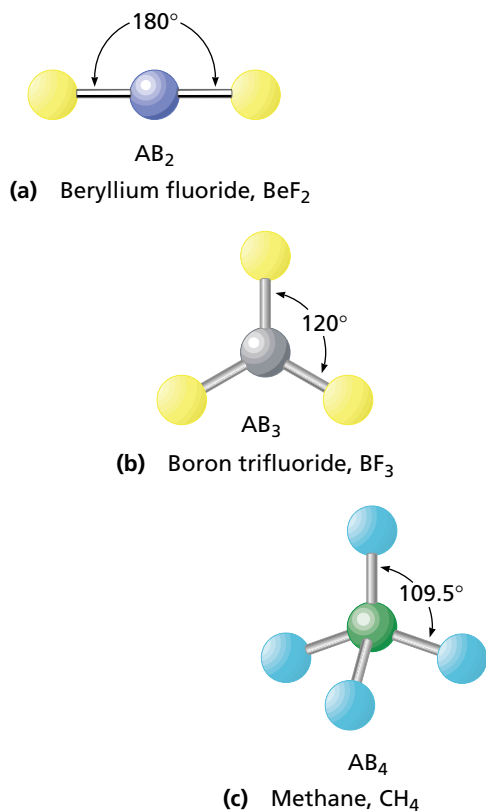
(a) Hydrogen,  $\text{H}_2$



(b) Hydrogen chloride,  $\text{HCl}$

**FIGURE 6-20** Ball-and-stick models illustrate the linearity of diatomic molecules. (a) A hydrogen molecule is represented by two identical balls (the hydrogen atoms) joined by a solid bar (the covalent bond). (b) A hydrogen chloride molecule is composed of dissimilar atoms, but it is still linear.





**FIGURE 6-21** Ball-and-stick models show the shapes of (a)  $\text{AB}_2$ , (b)  $\text{AB}_3$ , and (c)  $\text{AB}_4$  molecules according to VSEPR.

on opposite sides of the beryllium atom,  $180^\circ$  apart. Thus, all three atoms lie on a straight line. The molecule is linear.

If we represent the central atom in a molecule by the letter  $A$  and we represent the atoms bonded to the central atom by the letter  $B$ , then according to VSEPR,  $\text{BeF}_2$  is an example of an  $\text{AB}_2$  molecule, which is linear. Can you determine what an  $\text{AB}_3$  molecule looks like? The three  $A-B$  bonds stay farthest apart by pointing to the corners of an equilateral triangle, giving  $120^\circ$  angles between the bonds. This trigonal-planar geometry is shown in Figure 6-21(b) for the  $\text{AB}_3$  molecule boron trifluoride,  $\text{BF}_3$ .

Unlike  $\text{AB}_2$  and  $\text{AB}_3$  molecules, the central atoms in  $\text{AB}_4$  molecules follow the octet rule by sharing four electron pairs with  $B$  atoms. The distance between electron pairs is maximized if each  $A-B$  bond points to one of four corners of a tetrahedron. This geometry is shown in Figure 6-21(c) for the  $\text{AB}_4$  molecule methane,  $\text{CH}_4$ . The same figure shows that in a tetrahedral molecule, each of the bond angles formed by the  $A$  atom and any two of the  $B$  atoms is equal to  $109.5^\circ$ .

The shapes of various molecules are summarized in Table 6-5 on page 186.  $B$  can represent a single type of atom, a group of identical atoms, or a group of different atoms on the same molecule. The shape of the molecule will still be based on the forms given in the table. However, different sizes of  $B$  groups distort the bond angles, making some bond angles larger or smaller than those given in the table.

### SAMPLE PROBLEM 6-5

Use VSEPR theory to predict the molecular geometry of aluminum trichloride,  $\text{AlCl}_3$ .

#### SOLUTION

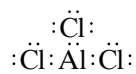
First write the Lewis structure for  $\text{AlCl}_3$ . Aluminum is in Group 13 and has three valence electrons.



Chlorine is in Group 17 and has seven valence electrons.



The total number of available valence electrons is therefore  $24e^-$  ( $3e^-$  from aluminum and  $21e^-$  from chlorine). The following Lewis structure uses all  $24e^-$ .



This molecule is an exception to the octet rule because in this case  $\text{Al}$  forms only three bonds. Aluminum trichloride is an  $\text{AB}_3$  type of molecule. Therefore, according to VSEPR theory, it should have trigonal-planar geometry.

**PRACTICE**

1. Use VSEPR theory to predict the molecular geometry of the following molecules:

- a. HI                      c.  $\text{AlBr}_3$   
b.  $\text{CBr}_4$                 d.  $\text{CH}_2\text{Cl}_2$

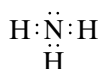
Answer

- a. linear                      c. trigonal-planar  
b. tetrahedral              d. tetrahedral

**VSEPR and Unshared Electron Pairs**

Ammonia,  $\text{NH}_3$ , and water,  $\text{H}_2\text{O}$ , are examples of molecules in which the central atom has both shared and unshared electron pairs (see Table 6-5 for their Lewis structures). How does VSEPR theory account for the geometries of these molecules?

The Lewis structure of ammonia shows that in addition to the three electron pairs it shares with the three hydrogen atoms, the central nitrogen atom has one unshared pair of electrons.



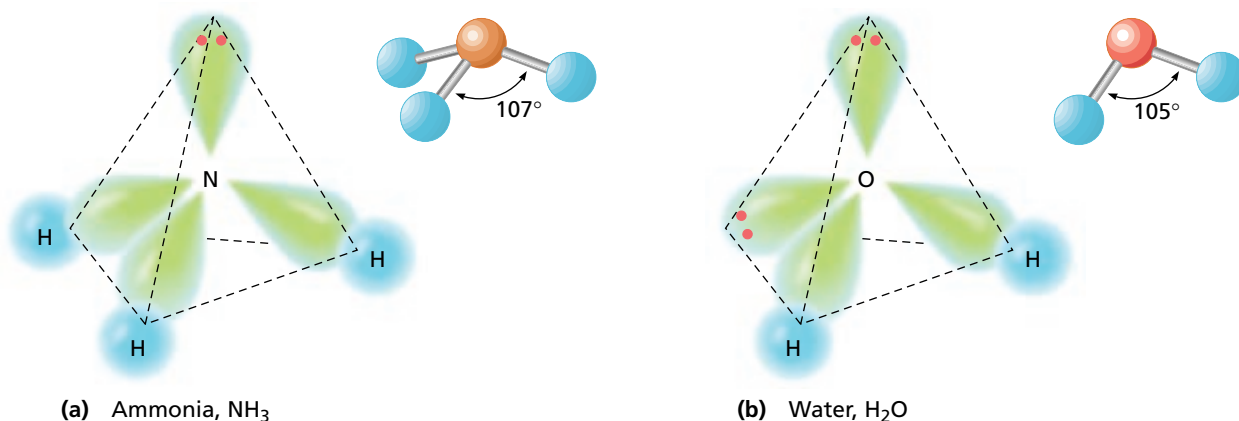
VSEPR theory postulates that the lone pair occupies space around the nitrogen atom just as the bonding pairs do. Thus, as in an  $\text{AB}_4$  molecule, the electron pairs maximize their separation by assuming the four corners of a tetrahedron. Lone pairs do occupy space, but our description of the observed shape of a molecule refers to the *positions of atoms only*. Consequently, as shown in Figure 6-22(a), the molecular geometry of an ammonia molecule is that of a pyramid with a triangular base. The general VSEPR formula for molecules such as ammonia is  $\text{AB}_3\text{E}$ , where E represents the unshared electron pair.

A water molecule has two unshared electron pairs. It is an  $\text{AB}_2\text{E}_2$  molecule. Here, the oxygen atom is at the center of a tetrahedron, with two corners occupied by hydrogen atoms and two by the unshared pairs (Figure 6-22(b)). Again, VSEPR theory states that the lone pairs occupy space around the central atom but that the actual shape of the molecule is determined by the positions of the atoms only. In the case of water, this results in a “bent,” or angular, molecule.

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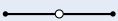
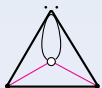
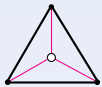


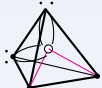
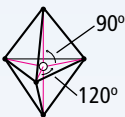
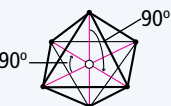
**FIGURE 6-22** The locations of bonds and unshared electrons are shown for molecules of (a) ammonia and (b) water. Although unshared electrons occupy space around the central atoms, the shapes of the molecules depend only on the position of the molecules' atoms, as clearly shown by the ball-and-stick models.

In Figure 6-22(b), note that the bond angles in ammonia and water are somewhat less than the  $109.5^\circ$  bond angles of a perfectly tetrahedral molecule. These angles are smaller because the unshared electron pairs repel electrons more strongly than do bonding electron pairs.

Table 6-5 also includes an example of an  $AB_2E$  type molecule. This type of molecule results when a central atom forms two bonds and retains one unshared electron pair.

Finally, in VSEPR theory, double and triple bonds are treated in the same way as single bonds. And polyatomic ions are treated similarly to molecules. (Remember to consider *all* of the electron pairs present in any ion or molecule.) Thus, Lewis structures and Table 6-5 can be used together to predict the shapes of polyatomic ions as well as molecules with double or triple bonds.

**TABLE 6-5 VSEPR and Molecular Geometry**

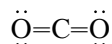
	Molecular shape	Atoms bonded to central atom	Lone pairs of electrons	Type of molecule	Formula example	Lewis structure
Linear		2	0	$AB_2$	$BeF_2$	$\text{:}\ddot{\text{F}}\text{--Be--}\ddot{\text{F}}\text{:}$
Bent or angular		2	1	$AB_2E$	$SnCl_2$	$\text{:}\ddot{\text{Cl}}\text{--}\ddot{\text{Sn}}\text{--}\ddot{\text{Cl}}\text{:}$
Trigonal-planar		3	0	$AB_3$	$BF_3$	$\text{:}\ddot{\text{F}}\text{--}\ddot{\text{B}}\text{--}\ddot{\text{F}}\text{:}$ $\text{:}\ddot{\text{F}}\text{:}$
Tetrahedral		4	0	$AB_4$	$CH_4$	$\begin{array}{c} \text{H} \\   \\ \text{H--C--H} \\   \\ \text{H} \end{array}$
Trigonal-pyramidal		3	1	$AB_3E$	$NH_3$	$\begin{array}{c} \ddot{\text{N}} \\   \\ \text{H--H--H} \end{array}$
Bent or angular		2	2	$AB_2E_2$	$H_2O$	$\begin{array}{c} \ddot{\text{O}} \\   \\ \text{H--O--H} \end{array}$
Trigonal-bipyramidal		5	0	$AB_5$	$PCl_5$	$\begin{array}{c} \ddot{\text{Cl}}\text{:}\ddot{\text{Cl}}\text{:} \\   \quad   \\ \ddot{\text{Cl}}\text{--}\ddot{\text{P}}\text{--}\ddot{\text{Cl}}\text{:} \\   \quad   \\ \ddot{\text{Cl}}\text{:}\ddot{\text{Cl}}\text{:} \end{array}$
Octahedral		6	0	$AB_6$	$SF_6$	$\begin{array}{c} \ddot{\text{F}}\text{:}\ddot{\text{F}}\text{:}\ddot{\text{F}}\text{:} \\   \quad   \quad   \\ \ddot{\text{F}}\text{--}\ddot{\text{S}}\text{--}\ddot{\text{F}}\text{:} \\   \quad   \quad   \\ \ddot{\text{F}}\text{:}\ddot{\text{F}}\text{:}\ddot{\text{F}}\text{:} \end{array}$

## SAMPLE PROBLEM 6-6

- Use VSEPR theory to predict the shape of a molecule of carbon dioxide,  $\text{CO}_2$ .
- Use VSEPR theory to predict the shape of a chlorate ion,  $\text{ClO}_3^-$ .

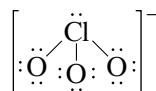
### SOLUTION

- The Lewis structure of carbon dioxide shows two carbon-oxygen double bonds and no unshared electron pairs on the carbon atom. To simplify the molecule's Lewis structure, we represent the covalent bonds with lines instead of dots.



This is an  $\text{AB}_2$  molecule, which is linear.

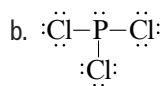
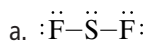
- The Lewis structure of a chlorate ion shows three oxygen atoms and an unshared pair of electrons surrounding a central chlorine atom. Again, lines are used to represent the covalent bonds.



The chlorate ion is an  $\text{AB}_3\text{E}$  type. It has trigonal-pyramidal geometry, with the three oxygen atoms at the base of the pyramid and the chlorine atom at the top.

### PRACTICE

- Use VSEPR theory to predict the molecular geometries of the molecules whose Lewis structures are given below.



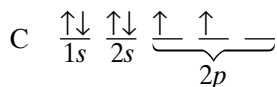
Answer

- bent or angular
- trigonal-pyramidal

## Hybridization

VSEPR theory is useful for explaining the shapes of molecules. However, it does not reveal the relationship between a molecule's geometry and the orbitals occupied by its bonding electrons. To explain how the orbitals of an atom become rearranged when the atom forms covalent bonds, a different model is used. This model is called **hybridization**, which is the mixing of two or more atomic orbitals of similar energies on the same atom to produce new orbitals of equal energies.

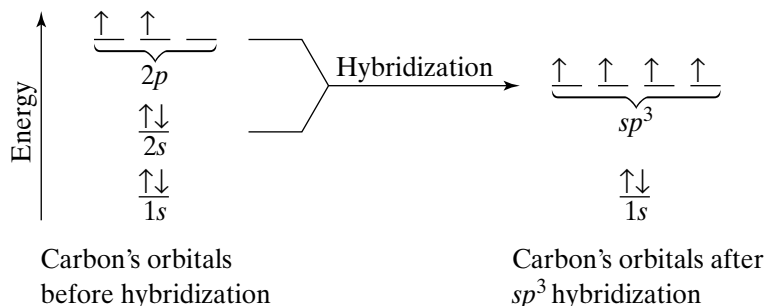
Methane,  $\text{CH}_4$ , provides a good example of how hybridization is used to explain the geometry of molecular orbitals. The orbital notation for a carbon atom shows that it has four valence electrons, two in the  $2s$  orbital and two in  $2p$  orbitals.



We know from experiments that a methane molecule has tetrahedral geometry. How does carbon form four equivalent, tetrahedrally arranged covalent bonds by orbital overlap with four other atoms?

Two of carbon's valence electrons occupy the  $2s$  orbital, and two occupy the  $2p$  orbitals. Recall that the  $2s$  orbital and the  $2p$  orbitals have different shapes. To achieve four equivalent bonds, carbon's  $2s$  and three  $2p$  orbitals *hybridize* to form four new, identical orbitals called  $sp^3$  orbitals. The superscript 3 indicates that three  $p$  orbitals were included in the hybridization; the superscript 1 on the  $s$  is understood. The  $sp^3$  orbitals all have the same energy, which is greater than that of the  $2s$  orbital but less than that of the  $2p$  orbitals, as shown in Figure 6-23.

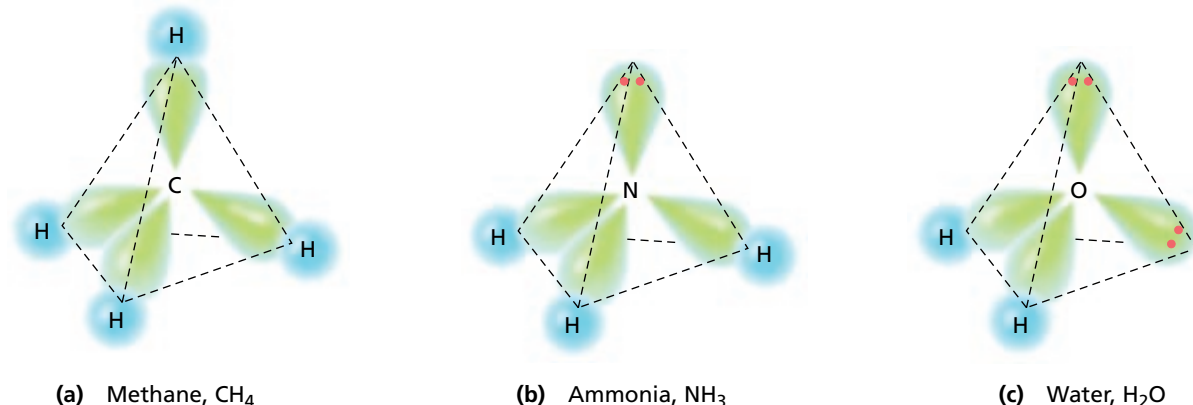
**FIGURE 6-23** The  $sp^3$  hybridization of carbon's outer orbitals combines one  $s$  and three  $p$  orbitals to form four  $sp^3$  hybrid orbitals. Whenever hybridization occurs, the resulting hybrid orbitals are at an energy level between the levels of the orbitals that have combined.



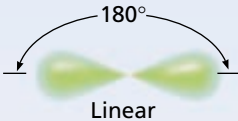
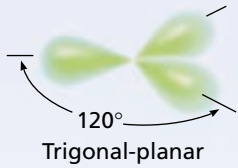
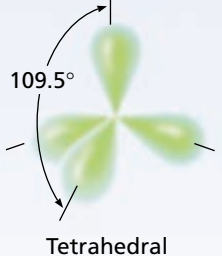
**Hybrid orbitals** are orbitals of equal energy produced by the combination of two or more orbitals on the same atom. The number of hybrid orbitals produced equals the number of orbitals that have combined. Bonding with carbon  $sp^3$  orbitals is illustrated in Figure 6-24(a) for a molecule of methane.

Hybridization also explains the bonding and geometry of many molecules formed by Group 15 and 16 elements. The  $sp^3$  hybridization of a nitrogen atom ( $[\text{He}]2s^22p^3$ ) yields four hybrid orbitals—one orbital containing a pair of electrons and three orbitals that each contain an unpaired electron. Each unpaired electron is capable of forming a single bond, as shown for ammonia in Figure 6-24(b). Similarly, two of the four  $sp^3$  hybrid orbitals on an oxygen atom ( $[\text{He}]2s^22p^4$ ) are occupied by two electron pairs and two are occupied by unpaired electrons. Each unpaired electron can form a single bond, as shown for water in Figure 6-24(c).

**FIGURE 6-24** Bonds formed by the overlap of the  $1s$  orbitals of hydrogen atoms and the  $sp^3$  orbitals of (a) carbon, (b) nitrogen, and (c) oxygen. For the sake of clarity, only the hybrid orbitals of the central atoms are shown.



**TABLE 6-6 Geometry of Hybrid Orbitals**

Atomic orbitals	Type of hybridization	Number of hybrid orbitals	Geometry
$s, p$	$sp$	2	 Linear
$s, p, p$	$sp^2$	3	 Trigonal-planar
$s, p, p, p$	$sp^3$	4	 Tetrahedral

The linear geometry of molecules such as beryllium fluoride,  $\text{BeF}_2$ , (see Table 6-5 on page 186) is made possible by hybridization involving the  $s$  orbital and one available empty  $p$  orbital to yield  $sp$  hybrid orbitals. The trigonal-planar geometry of molecules such as boron fluoride,  $\text{BF}_3$ , is made possible by hybridization involving the  $s$  orbital, one singly occupied  $p$  orbital, and one empty  $p$  orbital to yield  $sp^2$  hybrid orbitals. The geometries of  $sp$ ,  $sp^2$ , and  $sp^3$  hybrid orbitals are summarized in Table 6-6.

## Intermolecular Forces

As a liquid is heated, the kinetic energy of its particles increases. At the boiling point, the energy is sufficient to overcome the force of attraction between the liquid's particles. The particles pull away from each other and enter the gas phase. Boiling point is therefore a good measure of the force of attraction between particles of a liquid. The higher the boiling point, the stronger the forces between particles.

*The forces of attraction between molecules are known as **intermolecular forces**.* Intermolecular forces vary in strength but are generally weaker than bonds that join atoms in molecules, ions in ionic compounds, or metal atoms in solid metals. Compare the boiling points of the metals and ionic compounds in Table 6-7 on page 190 with those of the molecular substances listed. Note that the values for ionic compounds and metals are much higher than those for molecular substances.



**Module 4:** Chemical Bonding



**TABLE 6-7 Boiling Points and Bonding Types**

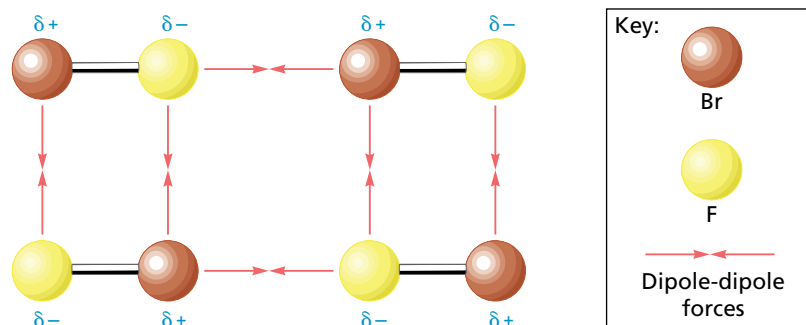
Bonding type	Substance	bp (1 atm, °C)
Nonpolar-covalent (molecular)	H <sub>2</sub>	-253
	O <sub>2</sub>	-183
	Cl <sub>2</sub>	-34
	Br <sub>2</sub>	59
	CH <sub>4</sub>	-164
	CCl <sub>4</sub>	77
	C <sub>6</sub> H <sub>6</sub>	80
Polar-covalent (molecular)	PH <sub>3</sub>	-88
	NH <sub>3</sub>	-33
	H <sub>2</sub> S	-61
	H <sub>2</sub> O	100
	HF	20
	HCl	-85
	ICI	97
Ionic	NaCl	1413
	MgF <sub>2</sub>	2239
Metallic	Cu	2567
	Fe	2750
	W	5660

## Molecular Polarity and Dipole-Dipole Forces

The strongest intermolecular forces exist between polar molecules. Polar molecules act as tiny dipoles because of their uneven charge distribution. A **dipole** is created by equal but opposite charges that are separated by a short distance. The direction of a dipole is from the dipole's positive pole to its negative pole. A dipole is represented by an arrow with a head pointing toward the negative pole and a crossed tail situated at the positive pole. The dipole created by a hydrogen chloride molecule, which has its negative end at the more electronegative chlorine atom, is indicated as follows.



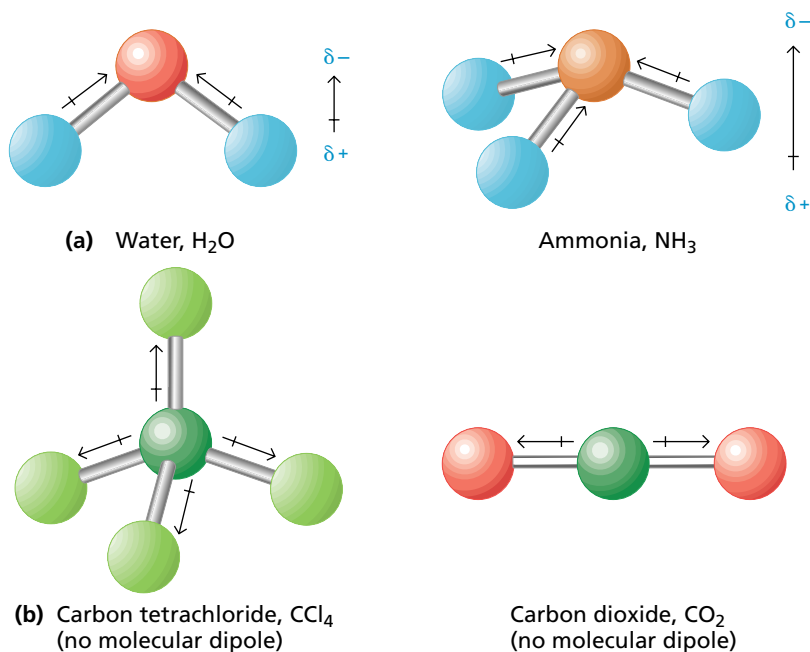
The negative region in one polar molecule attracts the positive region in adjacent molecules, and so on throughout a liquid or solid. *The forces of attraction between polar molecules are known as **dipole-dipole forces**.* These forces are short-range forces, acting only between nearby molecules. The effect of dipole-dipole forces is reflected, for example, by the significant difference between the boiling points of bromine fluoride, Br-F, and fluorine, F-F. The boiling point of polar bromine fluoride is -20°C, whereas that of nonpolar fluorine is only -188°C. The dipole-dipole forces responsible for the relatively high boiling point of BrF are illustrated schematically in Figure 6-25.



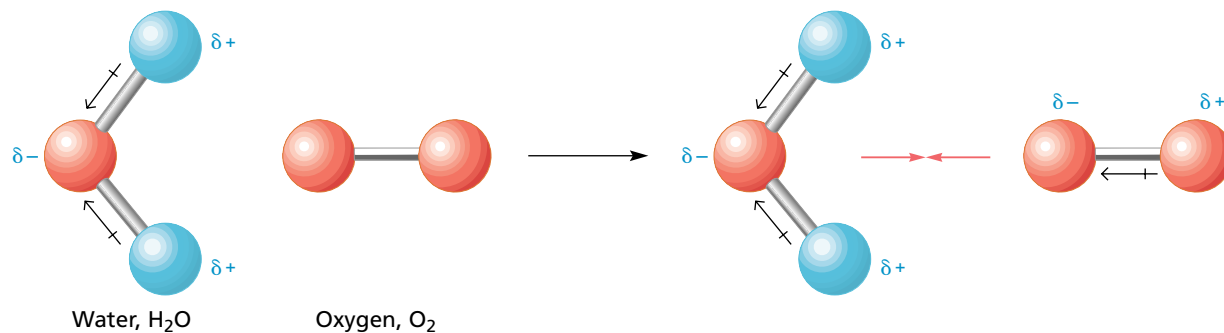
**FIGURE 6-25** Ball-and-stick models illustrate the dipole-dipole forces between molecules of bromine fluoride, BrF. In each molecule, the highly electronegative fluorine atom has a partial negative charge, leaving each bromine atom with a partial positive charge. Consequently, the negative and positive ends of neighboring molecules attract each other.

The polarity of diatomic molecules such as BrF is determined by just one bond. For molecules containing more than two atoms, molecular polarity depends on both the polarity and the orientation of each bond. A molecule of water, for example, has two hydrogen-oxygen bonds in which the more-electronegative oxygen atom is the negative pole of each bond. Because the molecule is bent, the polarities of these two bonds combine to make the molecule highly polar, as shown in Figure 6-26. An ammonia molecule is also highly polar because the dipoles of the three nitrogen-hydrogen bonds are additive, combining to create a net molecular dipole. In some molecules, individual bond dipoles cancel one another, causing the resulting molecular polarity to be zero. Carbon dioxide and carbon tetrachloride are molecules of this type.

A polar molecule can *induce* a dipole in a nonpolar molecule by temporarily attracting its electrons. The result is a short-range intermolecular force that is somewhat weaker than the dipole-dipole force. The force of an induced dipole accounts for the solubility of nonpolar O<sub>2</sub> in water. The positive pole of a water molecule attracts the outer electrons



**FIGURE 6-26** (a) The bond polarities in a water or an ammonia molecule are additive, causing the molecule as a whole to be polar. (b) In molecules of carbon tetrachloride and carbon dioxide, the bond polarities extend equally and symmetrically in different directions, canceling each other's effect and causing each molecule as a whole to be nonpolar.



**FIGURE 6-27** Dipole-induced dipole interaction. The positive pole of a water molecule causes a temporary change in the electron distribution of an oxygen molecule. The negative pole induced in the oxygen molecule is then attracted to the positive pole of the water molecule.

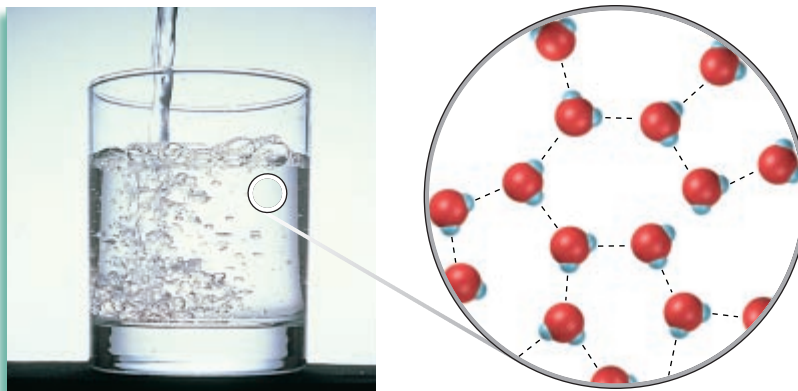
of an adjacent oxygen molecule. The oxygen molecule, then, has an induced negative pole on the side toward the water molecule and an induced positive pole on the opposite side. The result is an attraction to the water molecule, as shown in Figure 6-27.

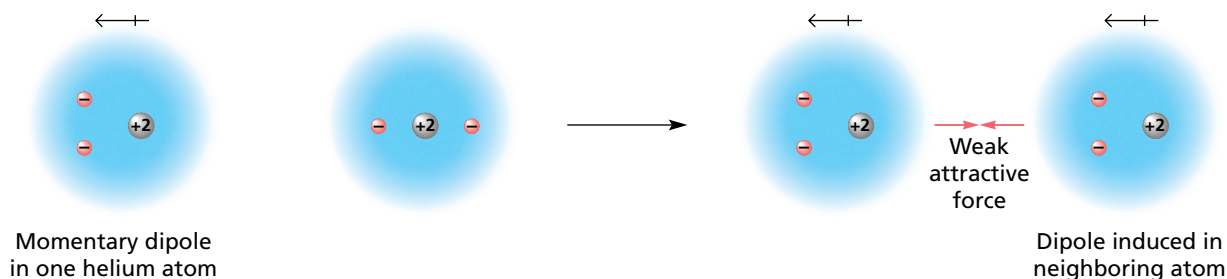
## Hydrogen Bonding

Some hydrogen-containing compounds, such as hydrogen fluoride (HF), water ( $\text{H}_2\text{O}$ ), and ammonia ( $\text{NH}_3$ ), have unusually high boiling points. This is explained by the presence of a particularly strong type of dipole-dipole force. In compounds containing H–F, H–O, or H–N bonds, the large electronegativity differences between hydrogen atoms and fluorine, oxygen, or nitrogen atoms make the bonds connecting them highly polar. This gives the hydrogen atom a positive charge that is almost half as large as that of a proton. Moreover, the small size of the hydrogen atom allows the atom to come very close to an unshared pair of electrons on an adjacent molecule. *The intermolecular force in which a hydrogen atom that is bonded to a highly electronegative atom is attracted to an unshared pair of electrons of an electronegative atom in a nearby molecule is known as **hydrogen bonding**.*

Hydrogen bonds are usually represented by dotted lines connecting the hydrogen-bonded hydrogen to the unshared electron pair of the electronegative atom to which it is attracted, as illustrated for water in Figure 6-28. The effect of hydrogen bonding can be seen by comparing the boiling points in Table 6-7 on page 190. Look at phosphine,  $\text{PH}_3$ , compared with hydrogen-bonded ammonia,  $\text{NH}_3$ . How does hydrogen sulfide,  $\text{H}_2\text{S}$ , compare with strongly hydrogen-bonded water,  $\text{H}_2\text{O}$ ?

**FIGURE 6-28** Space-filling models illustrate hydrogen bonding between water molecules. The dotted lines indicate the attraction between electronegative oxygen atoms and electropositive hydrogen atoms of neighboring molecules.





**FIGURE 6-29** When an instantaneous, temporary dipole develops in a helium atom, it induces a dipole in a neighboring atom.

## London Dispersion Forces

Even noble-gas atoms and molecules that are nonpolar experience a weak intermolecular attraction. In any atom or molecule—polar or nonpolar—the electrons are in continuous motion. As a result, at any instant the electron distribution may be slightly uneven. The momentary, uneven charge creates a positive pole in one part of the atom or molecule and a negative pole in another. This temporary dipole can then induce a dipole in an adjacent atom or molecule. The two are held together for an instant by the weak attraction between the temporary dipoles, as illustrated in Figure 6-29. *The intermolecular attractions resulting from the constant motion of electrons and the creation of instantaneous dipoles are called **London dispersion forces**, after Fritz London, who first proposed their existence in 1930.*

London forces act between all atoms and molecules. But they are the *only* intermolecular forces acting among noble-gas atoms and nonpolar molecules. This fact is reflected in the low boiling points of the noble gases and nonpolar molecular compounds listed in Table 6-7 on page 190. Because London forces are dependent on the motion of electrons, their strength increases with the number of electrons in the interacting atoms or molecules. In other words, London forces increase with increasing atomic or molar mass. This trend can be seen by comparing the boiling points of the gases helium, He, and argon, Ar; hydrogen, H<sub>2</sub>, and oxygen, O<sub>2</sub>; and chlorine, Cl<sub>2</sub>, and bromine, Br<sub>2</sub>.

## SECTION REVIEW

1. What two theories can be used to predict molecular geometry?
2. Draw the Lewis structure, and use the VSEPR theory to predict the molecular geometry of the following molecules:  
a. SO<sub>2</sub>      b. Cl<sub>4</sub>      c. BCl<sub>3</sub>
3. What are some factors that affect the geometry of a molecule?
4. Explain what is meant by  $sp^3$  hybridization.
5. What type of intermolecular force contributes to the high boiling point of water? Explain.

# CHAPTER 6 REVIEW

## CHAPTER SUMMARY

6-1

- Most atoms are chemically bonded to other atoms.
- The three major types of chemical bonding are ionic, covalent, and metallic.

### Vocabulary

chemical bond (161)  
covalent bonding (161)

ionic bonding (161)  
nonpolar-covalent bond (162)

- In general, atoms of metals bond ionically with atoms of nonmetals, atoms of metals bond metallically with each other, and atoms of nonmetals bond covalently with each other.

polar (162)

polar-covalent bond (162)

6-2

- Atoms in molecules are joined by covalent bonds.
- The bond length between two atoms in a molecule is the distance at which the potential energy of the bonded atoms is minimized.
- The octet rule states that many chemical compounds tend to form bonds so that each atom, by gaining, losing, or sharing electrons, shares or has eight electrons in its highest occupied energy level.

### Vocabulary

bond energy (167)  
bond length (167)  
chemical formula (164)  
diatomic molecule (164)  
double bond (172)

electron-dot notation (170)  
Lewis structures (171)  
lone pair (171)  
molecular compound (164)

- A single bond is a covalent bond in which a pair of electrons is shared between two atoms. Covalent bonds in which more than one pair of electrons is shared are called multiple bonds.
- Bonding within many molecules and ions can be indicated by a Lewis structure. Molecules or ions that cannot be correctly represented by a single Lewis structure are represented by resonance structures.

molecular formula (164)  
molecule (164)  
multiple bond (173)  
octet rule (169)  
resonance (175)

single bond (171)  
structural formula (171)  
triple bond (173)  
unshared pair (171)

6-3

- An ionic compound is a three-dimensional network of positive and negative ions mutually attracted to one another.
- Because of the strong attraction between positive and negative ions, ionic compounds tend to

### Vocabulary

formula unit (176)

ionic compound (176)

- be harder and more brittle and to have higher boiling points than materials containing only covalently bonded atoms.
- Polyatomic ions are charged groups of atoms held together by covalent bonds.

lattice energy (178)

polyatomic ion (180)

6-4

- Metallic bonding is a type of chemical bonding that results from the attraction between metal atoms and a surrounding sea of mobile electrons.

### Vocabulary

ductility (182)

malleability (182)

- The electron sea formed in metallic bonding gives metals their properties of high electrical and thermal conductivity, malleability, ductility, and luster.

metallic bonding (181)

## CHAPTER SUMMARY (continued)

- 6-5**
- VSEPR theory is used to predict the shapes of molecules based on the fact that electron pairs strongly repel each other and tend to be oriented as far apart as possible.
  - Hybridization theory is used to predict the shapes of molecules based on the fact that

**Vocabulary**

dipole (190)	hybridization (187)
dipole-dipole forces (190)	hydrogen bonding (192)
hybrid orbitals (188)	

orbitals within an atom can mix to form orbitals of equal energy.

- Intermolecular forces, such as dipole-dipole forces and London dispersion forces, exist between certain types of molecules. Hydrogen bonding is a special case of dipole-dipole forces.

intermolecular forces (189)	molecular polarity (183)
London dispersion forces (193)	VSEPR theory (183)

**REVIEWING CONCEPTS**

- What is a chemical bond? (6-1)
- Identify and define the three major types of chemical bonding. (6-1)
- What is the relationship between electronegativity and the ionic character of a chemical bond? (6-1)
- a. What is the meaning of the term *polar*, as applied to chemical bonding?
  - b. Distinguish between polar-covalent and nonpolar-covalent bonds. (6-1)
- In general, what determines whether atoms will form chemical bonds? (6-1)
- What is a molecule? (6-2)
- a. What determines bond length?
  - b. In general, how are bond energies and bond lengths related? (6-2)
- Describe the general location of the electrons in a covalent bond. (6-2)
- As applied to covalent bonding, what is meant by an unshared or lone pair of electrons? (6-2)
- Describe the octet rule in terms of noble-gas configurations and potential energy. (6-2)
- Determine the number of valence electrons in an atom of each of the following elements:
 

a. H	b. F
c. Mg	d. O
- e. Al
- f. N
- g. C (6-2)
- When drawing Lewis structures, which atom is usually the central atom? (6-2)
- Distinguish between single, double, and triple covalent bonds by defining each and providing an illustration of each type. (6-2)
- In writing Lewis structures, how is the need for multiple bonds generally determined? (6-2)
- a. What is an ionic compound?
  - b. In what form do most ionic compounds occur? (6-3)
- a. What is a formula unit?
  - b. What are the components of one formula unit of  $\text{CaF}_2$ ? (6-3)
- a. What is lattice energy?
  - b. In general, what is the relationship between lattice energy and the strength of ionic bonding? (6-3)
- a. In general, how do ionic and molecular compounds compare in terms of melting points, boiling points, and ease of vaporization?
  - b. What accounts for the observed differences in the properties of ionic and molecular compounds?
  - c. Cite three physical properties of ionic compounds. (6-3)
- a. What is a polyatomic ion?
  - b. Give two examples of polyatomic ions.



- c. In what form do such ions often occur in nature? (6-3)
20. a. How do the properties of metals differ from those of both ionic and molecular compounds?  
b. What specific property of metals accounts for their unusual electrical conductivity? (6-4)
21. What properties of metals contribute to their tendency to form metallic bonds? (6-4)
22. a. What is metallic bonding?  
b. How can the strength of metallic bonding be measured? (6-4)
23. a. How is the VSEPR theory used to classify molecules?  
b. What molecular geometry would be expected for  $F_2$  and  $HF$ ? (6-5)
24. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?  
a.  $AB_2$   
b.  $AB_3$   
c.  $AB_4$   
d.  $AB_5$   
e.  $AB_6$  (6-5)
25. Describe the role of each of the following in predicting molecular geometries:  
a. unshared electron pairs  
b. double bonds (6-5)
26. a. What are hybrid orbitals?  
b. What determines the number of hybrid orbitals produced by an atom? (6-5)
27. a. What are intermolecular forces?  
b. In general, how do these forces compare in strength with those in ionic and metallic bonding?  
c. Where are the strongest intermolecular forces found? (6-5)
28. What is the relationship between electronegativity and the polarity of a chemical bond? (6-5)
29. a. What are dipole-dipole forces?  
b. What determines the polarity of a molecule? (6-5)
30. a. What is meant by an induced dipole?  
b. What is the everyday importance of this type of intermolecular force? (6-5)
31. a. What is hydrogen bonding?  
b. What accounts for its extraordinary strength? (6-5)
32. What are London dispersion forces? (6-5)

## PROBLEMS

### Chemical Bond Character

33. Determine the electronegativity difference, the probable bond type, and the more-electronegative atom with respect to bonds formed between the following pairs of atoms. (Hint: See Sample Problem 6-1.)  
a. H and I  
b. S and O  
c. K and Br  
d. Si and Cl  
e. H and F  
f. Se and S  
g. C and H
34. List the bonding pairs described in item 33 in order of increasing covalent character.
35. Use orbital notation to illustrate the bonding in each of the following molecules:  
a. chlorine,  $Cl_2$   
b. oxygen,  $O_2$   
c. hydrogen fluoride,  $HF$
36. The lattice energy of sodium chloride,  $NaCl$ , is  $-787.5$  kJ/mol. The lattice energy of potassium chloride,  $KCl$ , is  $-715$  kJ/mol. In which compound is the bonding between ions stronger? Why?

### Electron-Dot Notation and Lewis Structures

37. Use electron-dot notation to illustrate the number of valence electrons present in one atom of each of the following elements. (Hint: See Sample Problem 6-2.)  
a. Li  
b. Ca  
c. Cl  
d. O

- e. C  
f. P  
g. Al  
h. S
38. Use electron-dot structures to demonstrate the formation of ionic compounds involving the following elements:  
a. Na and S  
b. Ca and O  
c. Al and S
39. Draw Lewis structures for each of the following molecules. (Hint: See Sample Problem 6-4.)  
a. contains one C and four F atoms  
b. contains two H and one Se atom  
c. contains one N and three I atoms  
d. contains one Si and four Br atoms  
e. contains one C, one Cl, and three H atoms
40. Determine the type of hybrid orbitals formed by the boron atom in a molecule of boron fluoride,  $\text{BF}_3$ . (Hint: See Sample Problems 6-5 and 6-6.)
41. Draw Lewis structures for each of the following molecules. Show resonance structures, if they exist.  
a.  $\text{O}_2$   
b.  $\text{N}_2$   
c. CO  
d.  $\text{SO}_2$
42. Draw Lewis structures for each of the following polyatomic ions. Show resonance structures, if they exist.  
a.  $\text{OH}^-$   
b.  $\text{H}_3\text{C}_2\text{O}_2^-$   
c.  $\text{BrO}_3^-$
- VSEPR Theory and Molecular Geometry**
43. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?  
a.  $\text{AB}_3\text{E}$   
b.  $\text{AB}_2\text{E}_2$   
c.  $\text{AB}_2\text{E}$
44. Use hybridization to explain the bonding in methane,  $\text{CH}_4$ .
45. For each of the following polar molecules, indicate the direction of the resulting dipole:  
a. H—F  
b. H—Cl  
c. H—Br  
d. H—I
46. Determine whether each of the following bonds would be polar or nonpolar:  
a. H—H  
b. H—O  
c. H—F  
d. Br—Br  
e. H—Cl  
f. H—N
47. On the basis of individual bond polarity and orientation, determine whether each of the following molecules would be polar or nonpolar:  
a.  $\text{H}_2\text{O}$   
b.  $\text{I}_2$   
c.  $\text{CF}_4$   
d.  $\text{NH}_3$   
e.  $\text{CO}_2$
48. Draw a Lewis structure for each of the following molecules, and then use the VSEPR theory to predict the molecular geometry of each:  
a.  $\text{SCl}_2$   
b.  $\text{PI}_3$   
c.  $\text{Cl}_2\text{O}$   
d.  $\text{NH}_2\text{Cl}$   
e.  $\text{SiCl}_3\text{Br}$   
f. ONCl
49. Draw a Lewis structure for each of the following polyatomic ions, and then use VSEPR theory to determine the geometry of each:  
a.  $\text{NO}_3^-$   
b.  $\text{NH}_4^+$   
c.  $\text{SO}_4^{2-}$   
d.  $\text{ClO}_2^-$

## MIXED REVIEW

50. Arrange the following pairs from strongest to weakest attraction:  
a. polar molecule and polar molecule  
b. nonpolar molecule and nonpolar molecule  
c. polar molecule and ion  
d. ion and ion

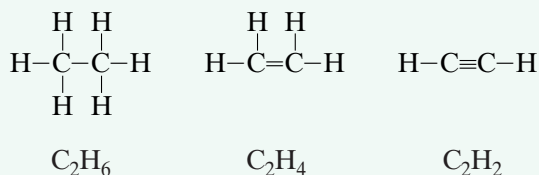
51. Determine the geometry of the following molecules:
  - a.  $\text{CCl}_4$
  - b.  $\text{BeCl}_2$
  - c.  $\text{PH}_3$
52. What types of atoms tend to form the following types of bonding?
  - a. ionic
  - b. covalent
  - c. metallic
53. What happens to the energy level and stability of two bonded atoms when they are separated and become individual atoms?
54. Draw the three resonance structures for sulfur trioxide,  $\text{SO}_3$ .
55. a. How do ionic and covalent bonding differ?  
 b. How does an ionic compound differ from a molecular compound?  
 c. How does an ionic compound differ from a metal?
56. Write the electron-dot notation for each of the following elements:
  - a. He
  - b. Cl
  - c. O
  - d. P
  - e. B
57. Write the structural formula for methanol,  $\text{CH}_3\text{OH}$ .
58. How many  $\text{K}^+$  and  $\text{S}^{2-}$  ions would be in one formula unit of the ionic compound formed by these ions?
59. Explain metallic bonding in terms of the sparsely populated outermost orbitals of metal atoms.
60. Explain the role of molecular geometry in determining molecular polarity.
61. How does the energy level of a hybrid orbital compare with the energy levels of the orbitals it was formed from?
62. Aluminum's heat of vaporization is 284 kJ/mol. Beryllium's heat of vaporization is 224 kJ/mol. In which element is the bonding stronger between atoms?
63. Determine the electronegativity difference, the probable bonding type, and the more-

electronegative atom for each of the following pairs of atoms:

- a. Zn and O
  - b. Br and I
  - c. S and Cl
64. Draw the Lewis structure for each of the following molecules:
    - a.  $\text{PCl}_3$
    - b.  $\text{CCl}_2\text{F}_2$
    - c.  $\text{CH}_3\text{NH}_2$
  65. Write the Lewis structure for  $\text{BeCl}_2$ . (Hint: Beryllium atoms do not follow the octet rule.)
  66. Draw a Lewis structure for each of the following polyatomic ions and determine their geometries:
    - a.  $\text{NO}_2^-$
    - b.  $\text{NO}_3^-$
    - c.  $\text{NH}_4^+$
  67. Why are most atoms chemically bonded to other atoms in nature?

### CRITICAL THINKING

68. **Inferring Relationships** The length of a bond varies depending on the type of bond formed. Predict and compare the lengths of the carbon-carbon bonds in the following molecules. Explain your answer. (Hint: See Table 6-2.)



### TECHNOLOGY & LEARNING

69. **Graphing Calculator** Classify Bonding Type According to Difference in Electronegativity  
 The graphing calculator can run a program that classifies bonding between atoms according to the difference between the atoms' electronegativities. Use this program to determine the electronegativity difference between the bonded atoms and to classify bonding type.  
 Go to Appendix C. If you are using a TI 83 Plus, you can download the program and data sets and run the application as directed. If you are using another calculator, your teacher will

provide you with the keystrokes and data sets to use. Remember that you will need to name the program and check the display, as explained in Appendix C. You will then be ready to run the program. After you have graphed the data, answer these questions.

- Which element pair(s) has/have a pure covalent bond?
- What type of bond does the pair H, O have?
- What type of bond does the pair Ca, O have?



### HANDBOOK SEARCH

- Figure 6-18 on page 181 shows a model for a body-centered cubic crystal. Review the Properties tables for all of the metals in the *Elements Handbook* (pages 728–749). What metals exist in body-centered cubic structures?
- Group 14 of the *Elements Handbook* (pages 754–769) contains a discussion of the band theory of metals. How does this model explain the electrical conductivity of metals?

### RESEARCH & WRITING

- Prepare a report on the work of Linus Pauling.
  - Discuss his work on the nature of the chemical bond.

- Linus Pauling was an advocate of the use of vitamin C as a preventative for colds. Evaluate Pauling's claims. Determine if there is any scientific evidence that indicates whether vitamin C helps prevent colds.

- Covalently bonded solids, such as silicon, an element used in computer components, are harder than pure metals. Research theories that explain the hardness of covalently bonded solids and their usefulness in the computer industry. Present your findings to the class.

### ALTERNATIVE ASSESSMENT

- Devise a set of criteria that will allow you to classify the following substances as ionic or non-ionic:  $\text{CaCO}_3$ , Cu,  $\text{H}_2\text{O}$ , NaBr, and C (graphite). Show your criteria to your instructor.
- Performance Assessment** Identify 10 common substances in and around your home, and indicate whether you would expect these substances to contain ionic, covalent, or metallic bonds.