

CHAPTER 6

Chemical Bonding

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Chemical Bonding

Introduction to Chemical Bonding

Key Terms

chemical bond	nonpolar-covalent bond
ionic bonding	polar
covalent bonding	polar-covalent bond

Atoms seldom exist as independent particles in nature. The oxygen you breathe, the water you drink, and nearly all other substances consist 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, most atoms are at relatively high potential energy. Nature, however, favors arrangements in which potential energy is minimized. Most atoms are less stable existing by themselves than when they are combined. By bonding with each other, atoms decrease in potential energy, creating more stable arrangements of matter.

▶ MAIN IDEA

Atoms form compounds by gaining, losing, or sharing electrons.

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. As discussed in the chapter “The Periodic Law,” 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 cations and anions is called ionic bonding.** In purely ionic bonding, atoms completely give up electrons to other atoms, as illustrated in **Figure 1.1** on the next page. 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 1.1**). 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 is ionic or covalent can be estimated by calculating the difference in the elements’ electronegativities (see **Figure 1.2** on the next page).

Main Ideas

▶ **Atoms form compounds by gaining, losing, or sharing electrons.**

▶ VIRGINIA STANDARDS

CH.3.d The student will investigate and understand how conservation of energy and matter is expressed in chemical formulas and balanced equations. Key concepts include: bonding types.

CH.3.EKS-9



FIGURE 1.1

Ionic Bonding and Covalent Bonding

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.

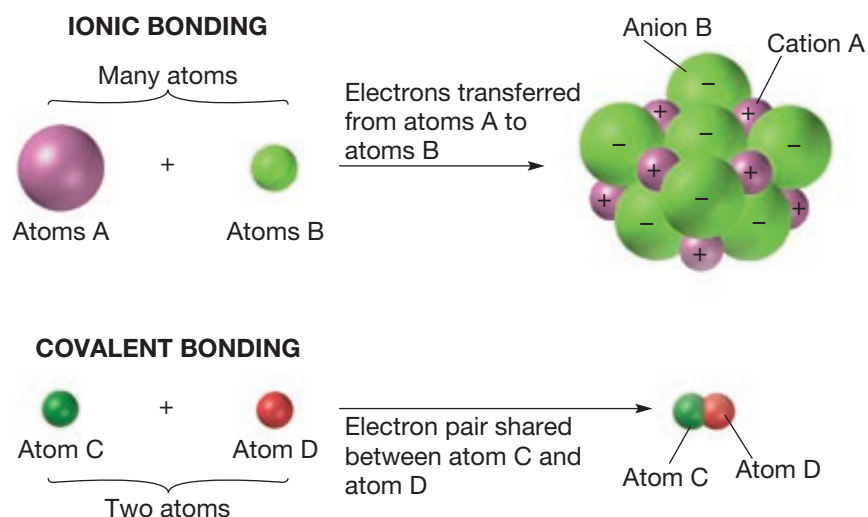
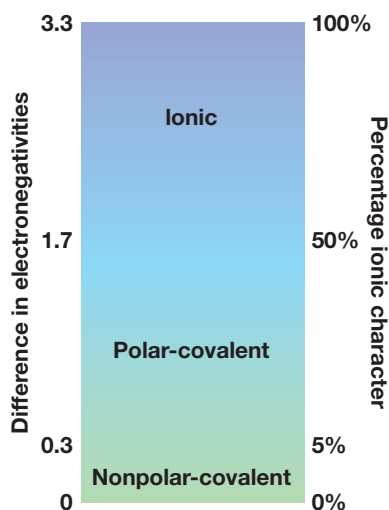


FIGURE 1.2

Bonding and Electronegativity

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.



For example, the electronegativity difference between fluorine, F, and cesium, Cs, is $4.0 - 0.7 = 3.3$. So, according to **Figure 1.2**, cesium-fluorine bonding is ionic. Fluorine atoms, which are highly electronegative, gain valence electrons, causing the atoms to become anions. Cesium atoms, which are less electronegative, lose valence electrons, causing the atoms to become cations.

Bonding between atoms with an electronegativity difference of 1.7 or less has an ionic character of 50% or less. These compounds are typically 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 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.**

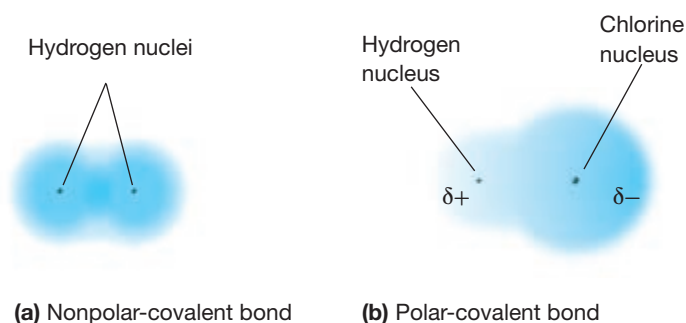
Nonpolar- and polar-covalent bonds are compared in **Figure 1.3**, which illustrates the electron density distribution in hydrogen-hydrogen and hydrogen-chlorine bonds. The electronegativity difference between chlorine and hydrogen is $3.0 - 2.1 = 0.9$, indicating a polar-covalent bond. The electrons in this bond are closer to the more-electronegative chlorine atom than to the hydrogen atom. Thus, the chlorine end of the bond has a partial negative charge, indicated by the symbol δ^- . The hydrogen end of the bond then has an equal partial positive charge, δ^+ .

FIGURE 1.3

Electron Density 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.

CRITICAL THINKING

Explain Why is the density of the electron cloud greater around the chlorine atom in the polar hydrogen-chlorine bond?



Classifying Bonds

Sample Problem A Use electronegativity differences and Figure 1.2 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?

SOLVE

From the Periodic Table of Electronegativities in the chapter “The Periodic Law,” 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

Answers in Appendix E

Use electronegativity differences and Figure 1.2 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.

SECTION 1 FORMATIVE ASSESSMENT

Reviewing Main Ideas

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

Critical Thinking

5. **INTERPRETING CONCEPTS** Compare the following two pairs of atoms: Cu and Cl; I and Cl.
 - a. Which pair would have a bond with a greater percent ionic character?
 - b. In which pair would Cl have the greater negative charge?
6. **INFERRING RELATIONSHIPS** The isolated K atom is larger than the isolated Br atom.
 - a. What type of bond is expected between K and Br?
 - b. Which ion in the compound KBr is larger?

SECTION 2

Main Ideas

- ▶ Covalent bonds form from shared electrons.
- ▶ Bond lengths and energy vary from molecule to molecule.
- ▶ Atoms tend to form bonds to follow the octet rule.
- ▶ Dots placed around an element's symbol can represent valence electrons.
- ▶ Electron-dot notations can represent compounds.
- ▶ Some atoms can share multiple pairs of electrons.
- ▶ Resonance structures show hybrid bonds.
- ▶ Some compounds are networks of bonded atoms.

VIRGINIA STANDARDS

CH.1.j The student will investigate and understand that experiments in which variables are measured, analyzed, and evaluated produce observations and verifiable data. Key concepts include: the use of current applications to reinforce chemistry concepts.

CH.3 The student will investigate and understand how conservation of energy and matter is expressed in chemical formulas and balanced equations. Key concepts include:

CH.3.c writing chemical formulas.

CH.3.d bonding types.

CH.3.EKS-7

Covalent Bonding and Molecular Compounds

Key Terms

molecule	Lewis structure
molecular compound	structural formula
chemical formula	single bond
molecular formula	multiple bond
bond energy	resonance
electron-dot notation	

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 two or more different atoms, as in water or sugar (see **Figure 2.1** 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 H_2O . A single water molecule consists of one oxygen atom joined by separate covalent bonds to two hydrogen atoms. A molecule of oxygen, O_2 , is an example of a diatomic molecule. A *diatomic molecule* contains only two atoms.

FIGURE 2.1

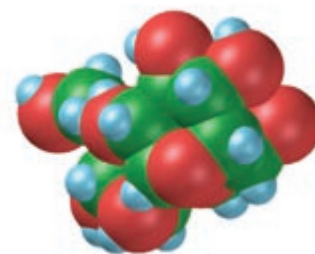
Covalently Bonded Molecules The models for (a) water, (b) oxygen, and (c) sucrose, or table sugar, represent a few examples of the many molecular compounds in and around us. Atoms within molecules may form one or more covalent bonds.



(a) Water molecule,
 H_2O



(b) Oxygen molecule,
 O_2

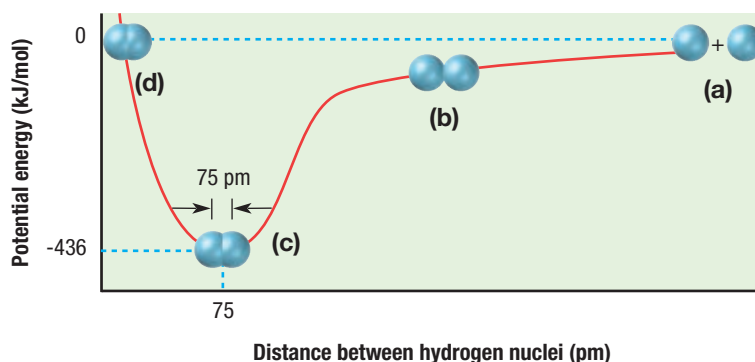


(c) Sucrose molecule,
 $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

FIGURE 2.2

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.



MAIN IDEA

Covalent bonds form from shared electrons.

As you read in Section 1, nature favors chemical bonding because most atoms have lower potential energy when they are bonded to other atoms than they have when they are 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 2.2.

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 2.3, 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 “sense” 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 2.2.

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 2.2. 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 2.2, results in a sharp rise in potential energy as repulsion becomes increasingly greater than attraction.

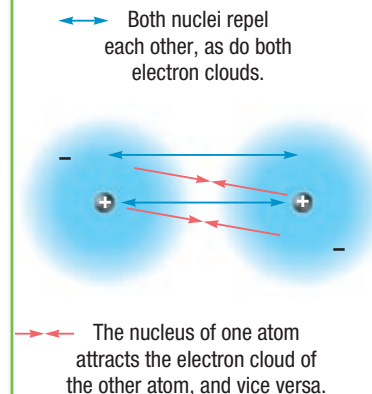
FIGURE 2.3

Attractive and Repulsive Forces

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.

CRITICAL THINKING

Explain How do covalently-bonded compounds stay together if both the nuclei and the electrons of the atoms involved repel each other?



▶ MAIN IDEA

Bond lengths and energy vary from molecule to molecule.

In **Figure 2.2**, 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 2.4**, 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 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 2.2**. 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 when examining the data in **Figure 2.5** on the next page. 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.

✓ CHECK FOR UNDERSTANDING

Apply Does electronegativity play a role in the formation of covalent bonds? Explain.

FIGURE 2.4

Overlapping Orbitals 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.

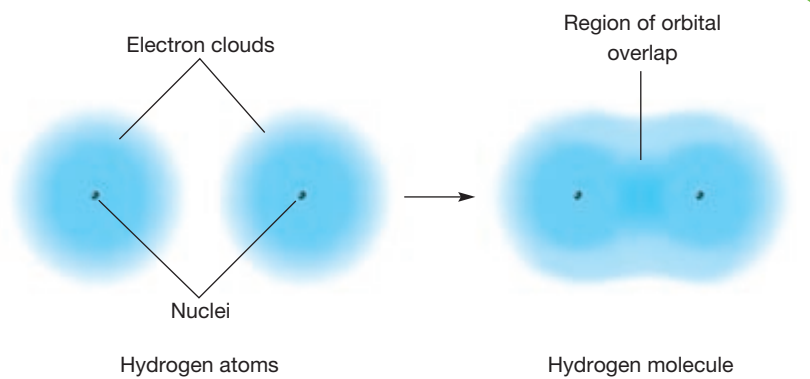


FIGURE 2.5

BOND LENGTHS AND BOND ENERGIES FOR SELECTED COVALENT BONDS

Bond	Average bond length (pm)	Average bond energy (kJ/mol)	Bond	Average bond length (pm)	Average bond energy (kJ/mol)
H—H	75	436	C—C	154	346
F—F	142	159	C—N	147	305
Cl—Cl	199	243	C—O	143	358
Br—Br	229	193	C—H	109	418
I—I	266	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

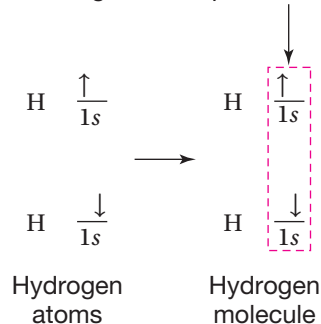
All individual hydrogen atoms contain a single, unpaired electron in a $1s$ atomic orbital. When two hydrogen atoms form a molecule, they share electrons in a covalent bond. As **Figure 2.6** shows, sharing electrons allows each atom to have the stable electron configuration of helium, $1s^2$. This tendency for atoms to achieve noble-gas configurations by bonding covalently extends beyond the simple case of a hydrogen molecule.

FIGURE 2.6

Bond Length and Stability

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

**MAIN IDEA****Atoms tend to form bonds to follow 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, 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 2.7a**.

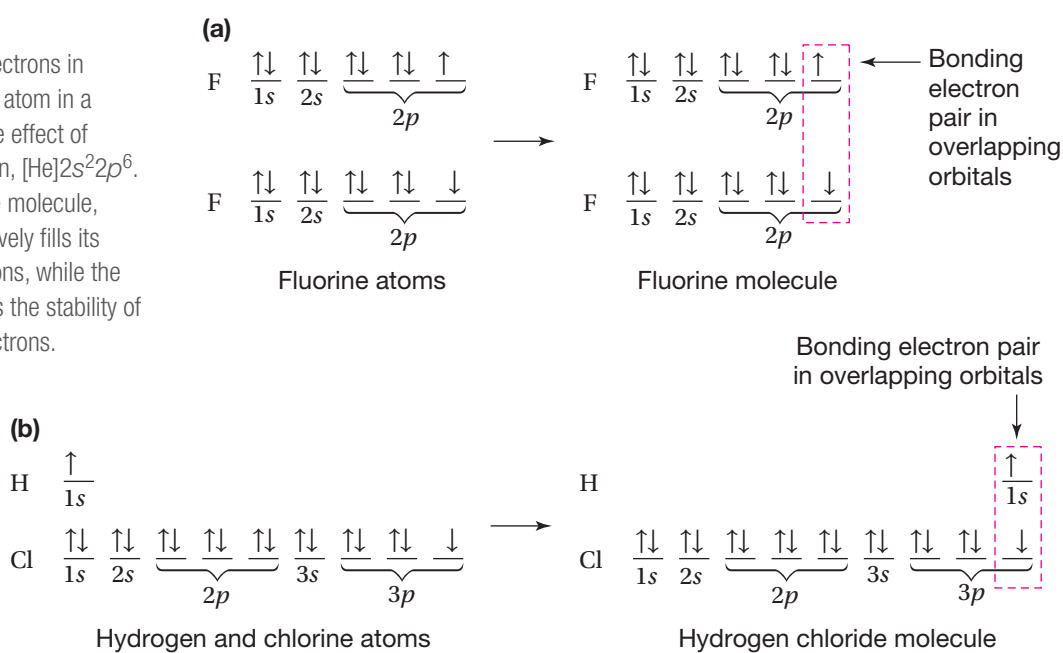
Figure 2.7b shows another example of the octet rule, in which the chlorine atom in a molecule of hydrogen chloride, HCl , achieves an outermost octet by sharing an electron pair with an atom of hydrogen.

FIGURE 2.7

Octet Rule

(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, 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. Examples of compounds that have an expanded valence include PCl_5 and SF_6 , as shown in **Figure 5.4** (in Section 5).

FIGURE 2.8

Writing Electron-Dot Notations 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.

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·

MAIN IDEA

Dots placed around an element's symbol can represent valence electrons.

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 $[\text{He}]2s^22p^5$) 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 2.8**.

PREMIUM CONTENT



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Electron-Dot Notation

- Sample Problem B**
- Write the electron-dot notation for hydrogen.
 - Write the electron-dot notation for nitrogen.

SOLVE

- 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.



MAIN IDEA

Electron-dot notations can represent compounds.

Electron-dot notation can also be used to represent molecules. For example, a hydrogen molecule, H_2 , is represented by combining the notations of two individual hydrogen atoms, as follows.

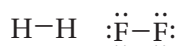


The pair of dots represents the shared electron pair of the hydrogen-hydrogen covalent bond. For a molecule of fluorine, F_2 , the electron-dot notations of two fluorine atoms are combined.



Here, too, 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 in which one pair of electrons is shared between two atoms.

PREMIUM CONTENT



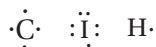
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Lewis Structures

Sample Problem C Draw the Lewis structure of iodomethane, CH_3I .

SOLVE

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.



Continued

Lewis Structures (continued)

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

$$\text{C} \quad 1 \times 4e^- = 4e^-$$

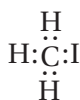
$$\text{I} \quad 1 \times 7e^- = 7e^-$$

$$\text{3H} \quad 3 \times 1e^- = 3e^-$$

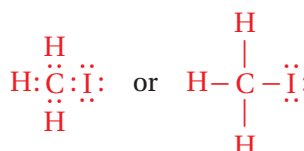
$$\underline{\hspace{1.5cm}} \quad \underline{\hspace{1.5cm}} \quad \underline{\hspace{1.5cm}}$$

$$\hspace{1.5cm} 14e^-$$

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 to each nonmetal atom (except hydrogen) such that each 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.

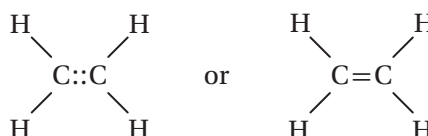
Practice

1. Draw the Lewis structure for ammonia, NH_3 .
2. Draw the Lewis structure for hydrogen sulfide, H_2S .
3. Draw the Lewis structure for silane, SiH_4 .
4. Draw the Lewis structure for phosphorus trifluoride, PF_3 .

MAIN IDEA

Some atoms can share multiple pairs of electrons.

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 in which two pairs of electrons are shared 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, C_2H_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 in which three pairs of electrons are shared 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 2.9 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.

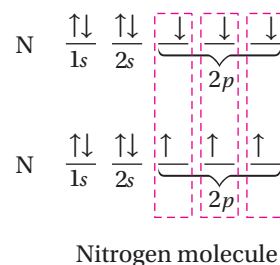


Double and triple bonds are referred to as multiple bonds, or multiple covalent bonds. Double bonds in general have greater bond energies and are shorter than single bonds. Triple bonds are even stronger and shorter. **Figure 2.10** compares average bond lengths and bond energies for some single, double, 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 D on the next page shows how to deal with this situation.

FIGURE 2.9

Forming Triple Bonds 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.



✓ CHECK FOR UNDERSTANDING

Explain Although silicon is in the same periodic group and shares many properties with carbon, it has a significantly greater bond length. Explain why this would make carbon a better building block than silicon for living organisms.

FIGURE 2.10

BOND LENGTHS AND BOND ENERGIES FOR SINGLE AND MULTIPLE COVALENT BONDS

Bond	Average bond length (pm)	Average bond energy (kJ/mol)	Bond	Average bond length (pm)	Average 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

Lewis Structures

Sample Problem D Draw the Lewis structure for methanal, CH_2O , which is also known as formaldehyde.

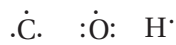
SOLVE

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 is from Group 14 and 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 available in the atoms to be combined.

$$\text{C} \quad 1 \times 4e^- = 4e^-$$

$$\text{O} \quad 1 \times 6e^- = 6e^-$$

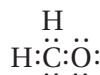
$$\text{2H} \quad 2 \times 1e^- = 2e^-$$

$$\underline{\hspace{1.5cm}} \quad 12e^-$$

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 to each nonmetal atom (except hydrogen) such that each is surrounded by eight electrons.

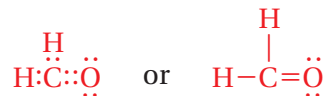


- 6a. Count the electrons in the Lewis structure to be sure that the number of valence electrons used equals the number available.

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.

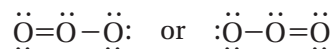
Practice

- Draw the Lewis structure for carbon dioxide, CO_2 .
- Draw the Lewis structure for hydrogen cyanide, which contains one hydrogen atom, one carbon atom, and one nitrogen atom.

▶ MAIN IDEA

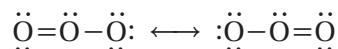
Resonance structures show hybrid bonds.

Some molecules and ions cannot be represented adequately by a single Lewis structure. One such molecule is ozone, 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.



▶ MAIN IDEA

Some compounds are networks of bonded atoms.

The covalent compounds that you have read about so far consist of many identical molecules held together by forces acting between the molecules. (You will read more about these intermolecular forces in Section 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 the chapter “Chemical Formulas and Chemical Compounds.”



SECTION 2 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

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. CH_3Br
- c. C_2HCl
- d. $SiCl_4$
- e. OF_2

✔ Critical Thinking

5. **APPLYING MODELS** Compare the molecules H_2NNH_2 and $HNNH$. Which molecule has the stronger N–N bond?

SECTION 3

Main Ideas

- ▶ Ionic bonds form from attractions between positive and negative ions.
- ▶ Differences in attraction strength give ionic and molecular compounds different properties.
- ▶ Multiple atoms can bond covalently to form a single ion.

VIRGINIA STANDARDS

CH.3 The student will investigate and understand how conservation of energy and matter is expressed in chemical formulas and balanced equations. Key concepts include:

CH.3.c writing chemical formulas.

CH.3.d bonding types.

CH.3.EKS-9

FIGURE 3.1

Ionic Compounds Sodium chloride (common table salt) is an ionic compound.

CRITICAL THINKING

Explain How is the structure of sodium chloride typical of ionic compounds?



Ionic Bonding and Ionic Compounds

Key Terms

ionic compound
formula unit

lattice energy
polyatomic ion

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, Na^+ , has a charge of $1+$. A chloride ion, Cl^- , has a charge of $1-$. There is an electrical force of attraction between oppositely charged ions. In sodium chloride, these ions combine in a one-to-one ratio— Na^+Cl^- —so that each positive charge is balanced by a negative charge. The chemical formula for sodium chloride is usually written simply as 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 3.1**). 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 written.** For example, one formula unit of sodium chloride, NaCl , is one sodium cation plus one chloride anion. (In the naming of a monatomic anion, the ending of the element's name becomes *-ide*.)

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, F^- , each with a charge of $1-$, must balance the $2+$ charge of each calcium cation, Ca^{2+} . Therefore, the formula of calcium fluoride is CaF_2 .

MAIN IDEA

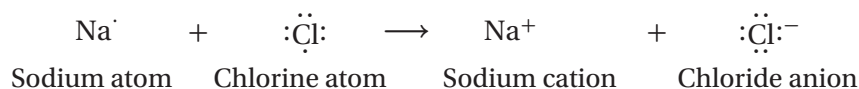
Ionic bonds form from attractions between positive and negative ions.

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.

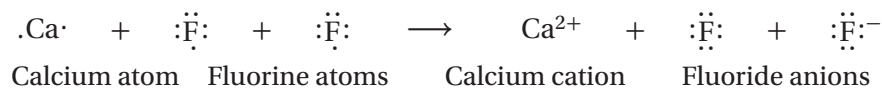


We have already seen that atoms of sodium and the other alkali metals readily lose one electron to form cations. And we have seen that atoms of chlorine and the other halogens readily gain one electron to form anions.

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 3.2**). 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 3.3** below.

FIGURE 3.2

Ions and Electrical Forces 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.

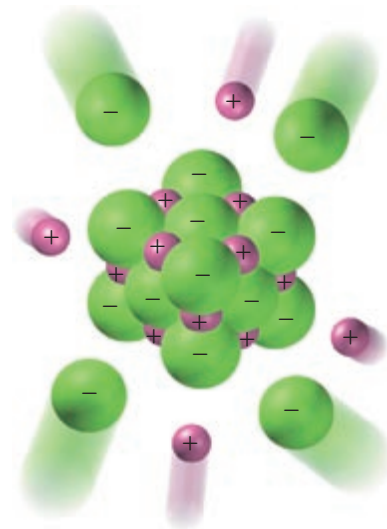
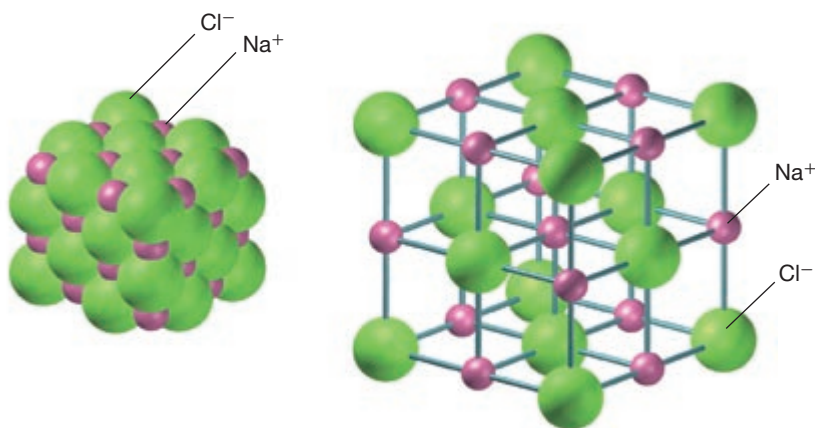


FIGURE 3.3

Crystal Structure of NaCl 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 3.4

Crystal Structure of NaCl The figure shows the ions that most closely surround a chloride anion and a sodium cation within the crystal structure of NaCl.

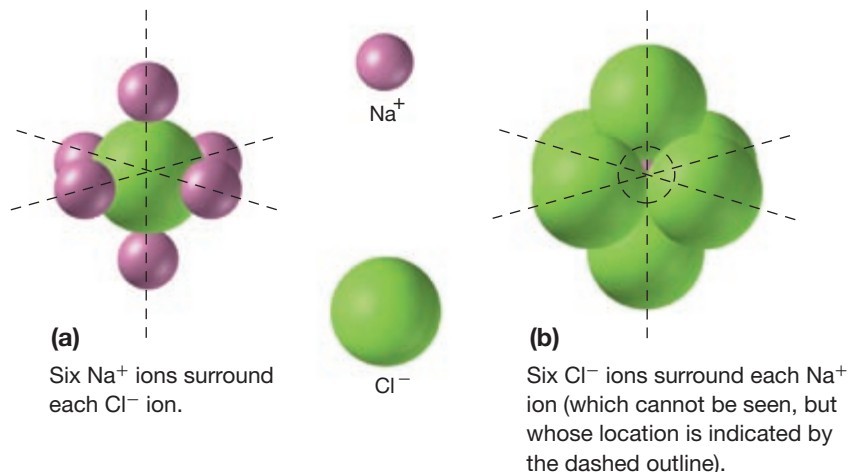


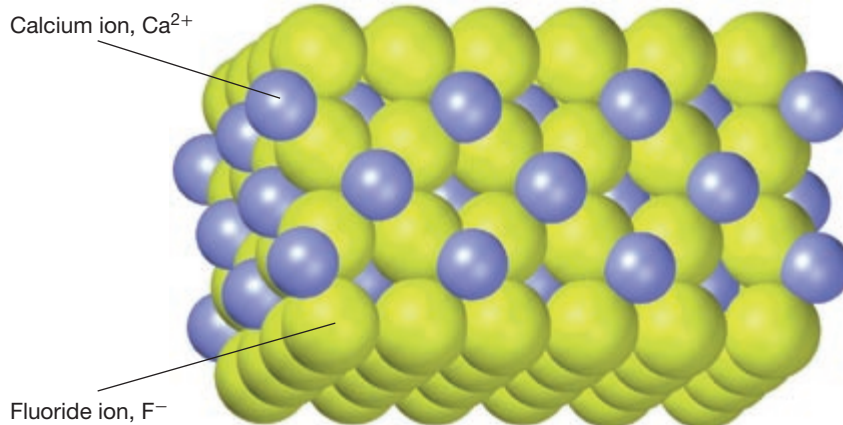
Figure 3.4 shows the crystal structure of sodium chloride in greater detail. Within the arrangement, each sodium cation is surrounded by six chloride anions. At the same time, each chloride anion is surrounded by six sodium cations. Attraction between the adjacent, oppositely charged ions is much stronger 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 3.5**.

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 **Figure 3.6** (on the next page). The negative energy values indicate that energy is *released* when the crystals are formed.

FIGURE 3.5

Crystal Structure of CaF_2 In the crystal structure of calcium fluoride, 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.



MAIN IDEA

Differences in attraction strength give ionic and molecular compounds different properties.

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 among formula units in 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.

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 3.7**. 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 attractions between the water molecules and the ions cannot overcome the attractions between the ions.

FIGURE 3.6

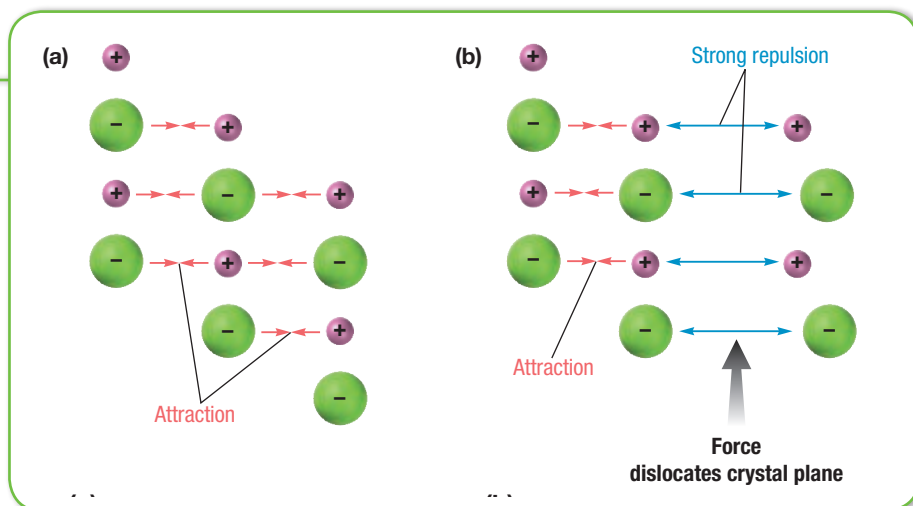
LATTICE ENERGIES OF SOME COMMON IONIC COMPOUNDS

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

FIGURE 3.7

Ionic Properties (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.

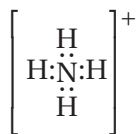


▶ MAIN IDEA

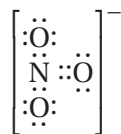
Multiple atoms can bond covalently to form a single ion.

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 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–.

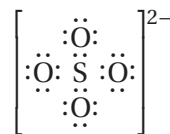
Lewis structures for the ammonium ion and some common negative polyatomic ions—the nitrate, sulfate, and phosphate ions—are shown below. To find the Lewis structure for a polyatomic ion, follow the steps of Sample Problem D, with the following exception. If the ion is negatively charged, add to the total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



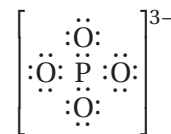
Ammonium ion



Nitrate ion



Sulfate ion



Phosphate ion

 CHECK FOR UNDERSTANDING

Why is it necessary to add or subtract electrons from the total number of valence electrons for polyatomic ions?

SECTION 3 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

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 make up each.

4. Compound B has lower melting and boiling points than compound A. At the same temperature, compound B vaporizes faster than compound A. If one of these compounds is ionic and the other is molecular, which would you expect to be molecular? ionic? Explain your reasoning.

 Critical Thinking

5. **ANALYZING DATA** The melting points for the compounds Li_2S , Rb_2S , and K_2S are 900°C , 530°C , and 840°C , respectively. List these three compounds in order of increasing lattice energy.

▶ Metal electrons move freely in empty, overlapping orbitals.

Metallic Bonding

Key Terms

metallic bonding
malleability
ductility

Chemical bonding is different in metals than it is in ionic, molecular, or covalent-network compounds. This difference is reflected in the unique properties of metals. They are excellent electrical conductors in the solid state—much better conductors than even molten ionic compounds. This property is due to the highly mobile valence electrons of the atoms that make up a metal. Such mobility is not possible in molecular compounds, in which valence electrons are localized in electron-pair bonds between neutral atoms. Nor is it possible in solid ionic compounds, in which electrons are bound to individual ions that are held in place in crystal structures.

▶ MAIN IDEA

Metal electrons move freely in empty, overlapping orbitals.

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, and 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 4.1**). **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, metals are both strong absorbers and reflectors of light. 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. However, in metals the electrons immediately fall back down to lower levels, emitting energy in the form of light at a frequency similar to the absorbed frequency. This re-radiated (or reflected) light is responsible for the metallic appearance or luster of metal surfaces.

▶ VIRGINIA STANDARDS

CH.3.d The student will investigate and understand how conservation of energy and matter is expressed in chemical formulas and balanced equations. Key concepts include: bonding types.

FIGURE 4.1

Crystal Structure of Solid Sodium

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 4.2

Shaping Metals 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 (see Figure 4.2). **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. When struck, one plane of atoms in a metal can slide past another without encountering resistance or breaking bonds. By contrast, recall from Section 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 *enthalpy of vaporization*. The amount of energy as heat required to vaporize the metal is a measure of the strength of the bonds that hold the metal together. The enthalpy of vaporization is defined as the amount of energy absorbed as heat when a specified amount of a substance vaporizes at constant pressure. Some enthalpies of vaporization for metals are given in Figure 4.3.

FIGURE 4.3

ENTHALPIES 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 4 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

- Describe the electron-sea model of metallic bonding.
- What is the relationship between metallic bond strength and enthalpy of vaporization?

- Explain why most metals are malleable and ductile but ionic crystals are not.

✔ Critical Thinking

- ORGANIZING IDEAS** Explain why metals are good electrical conductors.

Molecular Geometry

Key Terms

VSEPR theory
hybridization

hybrid orbitals
dipole

hydrogen bonding
London dispersion forces

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.

▶ MAIN IDEA

Negative particles repel and move away from each other.

As shown in **Figure 5.1**, diatomic molecules, like those of hydrogen, H_2 , and hydrogen chloride, 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 BeF_2 . The beryllium atom forms a covalent bond with each fluorine atom and does not follow the octet rule. It is surrounded by only the two electron pairs that it shares with the fluorine atoms.



According to VSEPR theory, the shared pairs will be as far away from each other as possible. As shown in **Figure 5.2a** on the next page, the distance between electron pairs is maximized if the bonds to fluorine are on opposite sides of the beryllium atom, 180° apart. Thus, all three atoms lie on a straight line. The molecule is linear.

Main Ideas

- ▶ Negative particles repel and move away from each other.
- ▶ Multiple orbitals can combine to form hybrid orbitals.
- ▶ Weak forces exist between molecules.

▶ VIRGINIA STANDARDS

CH.3.c The student will investigate and understand how conservation of energy and matter is expressed in chemical formulas and balanced equations. Key concepts include: writing chemical formulas.
CH.3.EKS-3; CH.3.EKS-7; CH.3.EKS-8

FIGURE 5.1

Linear Molecules Ball-and-stick models illustrate the linearity of diatomic molecules.



(a) Hydrogen, H_2

(a) A hydrogen molecule is represented by two identical balls (the hydrogen atoms) joined by a solid bar (the covalent bond).

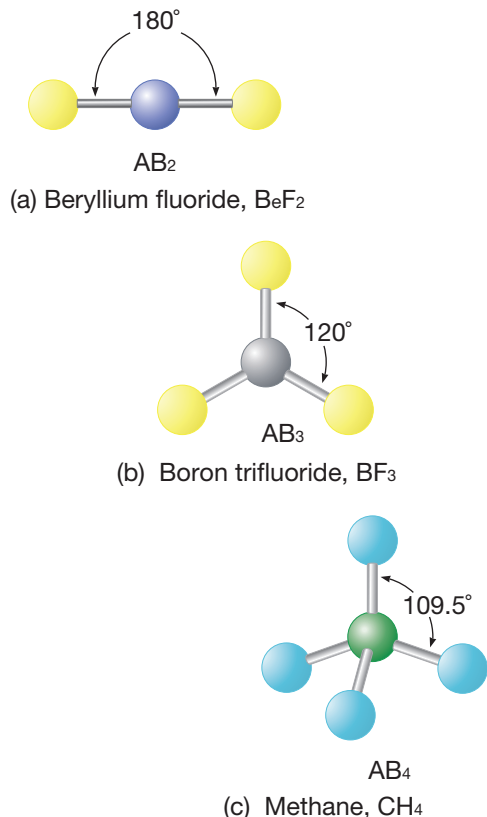


(b) Hydrogen chloride, HCl

(b) A hydrogen chloride molecule is composed of dissimilar atoms, but it is still linear.

FIGURE 5.2

Molecular Geometry Ball-and-stick models show the shapes of molecules according to VSEPR theory.



If we represent the central atom in a molecule by the letter A and the atoms bonded to the central atom by the letter B, then according to VSEPR theory, BeF_2 is an example of an AB_2 molecule, which is linear. Can you determine what an AB_3 molecule looks like? The three A—B bonds stay farthest apart by pointing to the corners of an equilateral triangle, giving 120° angles between the bonds. This trigonal-planar geometry is shown in **Figure 5.2b** for the AB_3 molecule boron trifluoride, BF_3 .

The central atoms in AB_4 molecules follow the octet rule by sharing four electron pairs with B atoms, for a total of eight shared electrons. 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 5.2c** for the AB_4 molecule methane, 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° .

The shapes of various molecules are summarized in the table on the next spread (**Figure 5.4**). B can represent a single type of atom, a group of identical atoms, or a group of different atoms in 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.

PREMIUM CONTENT

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VSEPR Theory and Molecular Geometry

Sample Problem E Use VSEPR theory to predict the molecular geometry of boron trichloride, BCl_3 .

SOLVE

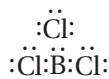
First write the Lewis structure for BCl_3 . Boron is in Group 13 and has three valence electrons.



Chlorine is in Group 17, so each chlorine atom has seven valence electrons.



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



This molecule is an exception to the octet rule because in this case B forms only three bonds. Boron trichloride is an AB_3 type of molecule. Therefore, according to VSEPR theory, it should have **trigonal-planar geometry**.

Practice

Answers in Appendix E

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

- a. HI b. CBr_4 c. CH_2Cl_2

VSEPR Theory and Unshared Electron Pairs

Ammonia, NH_3 , and water, H_2O , are examples of molecules in which the central atom has both shared and unshared electron pairs (see **Figure 5.4** on the next page 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 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 5.3a**, 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 AB_3E , where E represents the unshared electron pair.

A water molecule has two unshared electron pairs. It is an AB_2E_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 5.3b**). 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. In **Figure 5.3b**, the bond angles in ammonia and water are somewhat less than the 109.5° bond angles of a perfectly tetrahedral molecule, because the unshared electron pairs repel electrons more strongly than do bonding electron pairs.

FIGURE 5.3

Molecular Shape 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.

CRITICAL THINKING

Explain Why would unshared electrons affect the geometry of a molecule?

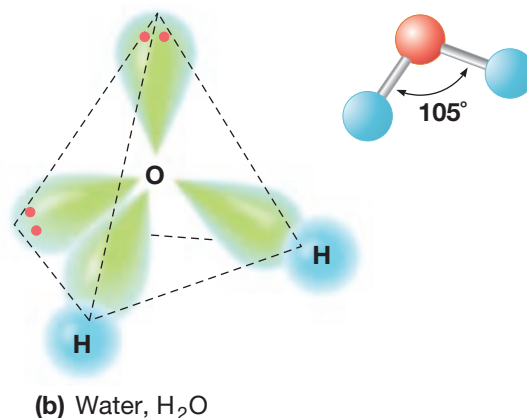
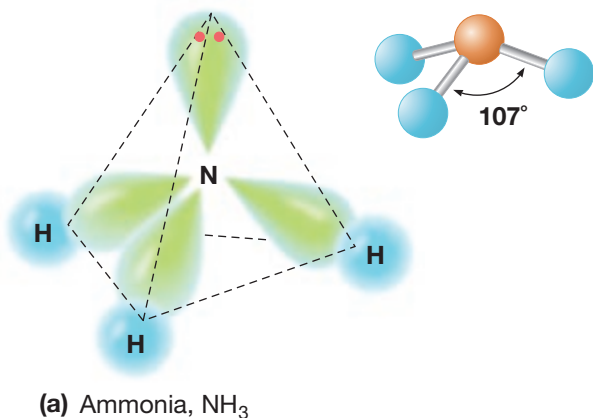
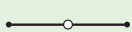
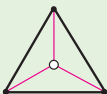





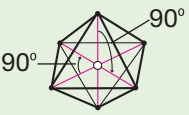


Figure 5.4 also includes an example of an AB_2E type molecule. This type of molecule results when a central atom forms two bonds and retains one unshared electron pair.

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 Figure 5.4 can be used together to predict the shapes of polyatomic ions as well as molecules with double or triple bonds.

FIGURE 5.4

VSEPR THEORY 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	$:\ddot{F}-Be-\ddot{F}:$
Trigonal-planar		3	0	AB_3	BF_3	$\begin{array}{c} :\ddot{F} \quad \ddot{F}: \\ \diagdown \quad / \\ B \\ \\ :\ddot{F}: \end{array}$
Bent or Angular		2	1	AB_2E	ONF	$\begin{array}{c} \ddot{N} \\ // \quad \backslash \\ \ddot{O} \quad \ddot{F}: \end{array}$
Tetrahedral		4	0	AB_4	CH_4	$\begin{array}{c} H \\ \\ H-C-H \\ \\ H \end{array}$
Trigonal-pyramidal		3	1	AB_3E	NH_3	$\begin{array}{c} \ddot{N} \\ / \quad \backslash \\ H \quad H \quad H \end{array}$
Bent or Angular		2	2	AB_2E_2	H_2O	$\begin{array}{c} \ddot{O} \\ / \quad \backslash \\ H \quad H \end{array}$
Trigonal-bipyramidal		5	0	AB_5	PCl_5	$\begin{array}{c} :\ddot{Cl}:\ddot{Cl}: \\ / \quad \backslash \\ :\ddot{Cl}-P-\ddot{Cl}: \\ \\ :\ddot{Cl}:\ddot{Cl}: \end{array}$
Octahedral		6	0	AB_6	SF_6	$\begin{array}{c} :\ddot{F}:\ddot{F}:\ddot{F}: \\ / \quad \quad \backslash \\ :\ddot{F}-S-\ddot{F}: \\ \\ :\ddot{F}:\ddot{F}: \end{array}$

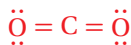
VSEPR Theory and Molecular Geometry

Sample Problem F

- Use VSEPR theory to predict the shape of a molecule of carbon dioxide, CO_2 .
- Use VSEPR theory to predict the shape of a chlorate ion, ClO_3^- .

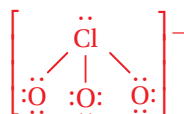
SOLVE

- 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 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.

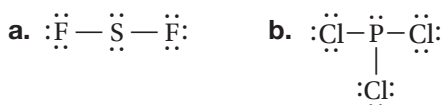
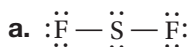


The chlorate ion is an AB_3E type. It has trigonal-pyramidal geometry, with the three oxygen atoms at the base of the pyramid and the chlorine atom at the top.

Practice

Answers in Appendix E

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



MAIN IDEA

Multiple orbitals can combine to form hybrid orbitals.

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 become rearranged when an 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 hybrid atomic orbitals of equal energies.** Methane, 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 the $2p$ orbitals.

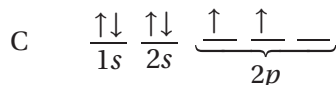
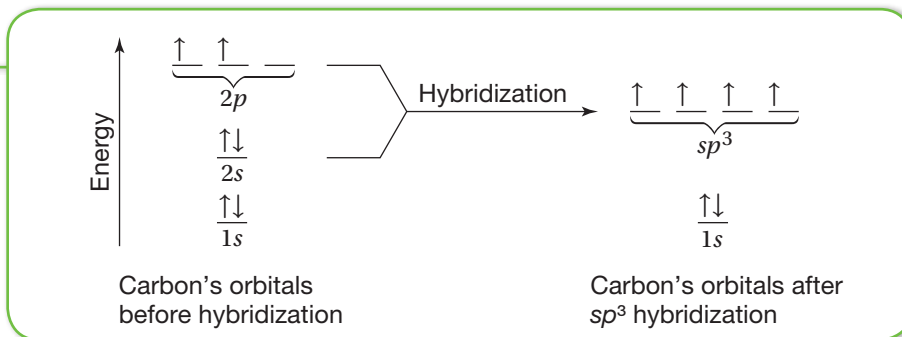


FIGURE 5.5

Hybridization of Carbon 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.



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 5.5**.

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 shown in **Figure 5.6a** 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 5.6b**. Similarly, two of the four sp^3 hybrid orbitals of 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 5.6c**.

FIGURE 5.6

Hybrid Orbitals 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.

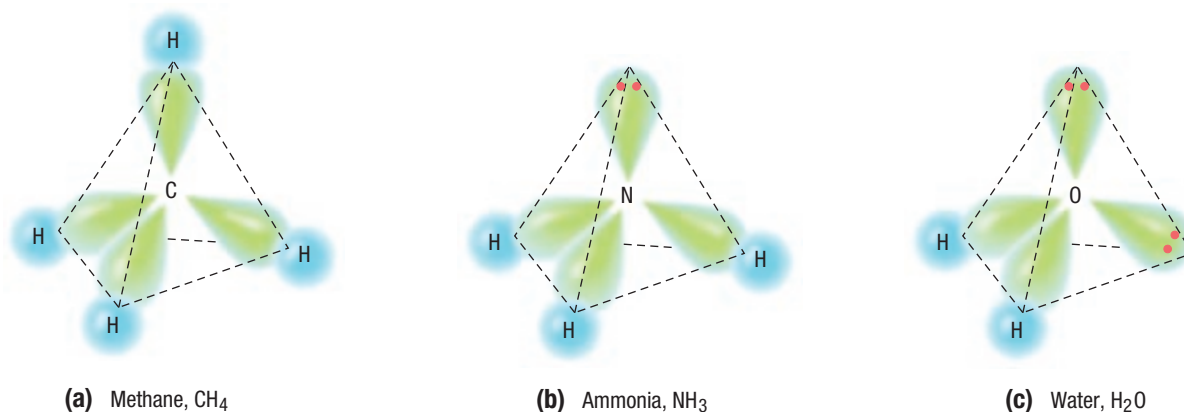
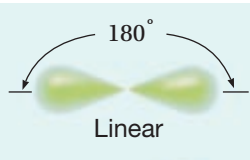
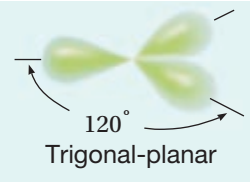
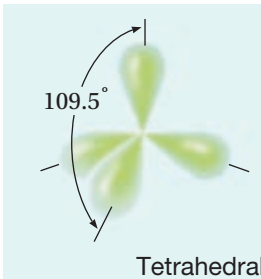


FIGURE 5.7

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, BeF_2 , 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, 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 (see **Figure 5.7**).

▶ MAIN IDEA

Weak forces exist between molecules.

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 **Figure 5.8** (on the next page) with those of the molecular substances listed. Note that the values for ionic compounds and metals are much higher than those for molecular substances.

FIGURE 5.8

BOILING POINTS AND BONDING TYPES

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

CAREERS IN CHEMISTRY

Computational
Chemist

S.T.E.M.

Computational chemistry is the study of molecules, their properties, and the interactions between them, using mathematical equations that are based on the laws of quantum mechanics and which describe the motion of the electrons. Today, widely-available software packages exist that allow chemists to solve these equations for molecules under study.

Computational chemists combine their expertise in mathematics, their computer skills, and their love of chemistry. Computational chemistry has been used in industry to aid in the discovery of new pharmaceutical drugs and new catalysts. Computational chemists are employed in all areas of chemistry and work closely with experimental chemists.

Molecular Polarity and Dipole-Dipole Forces

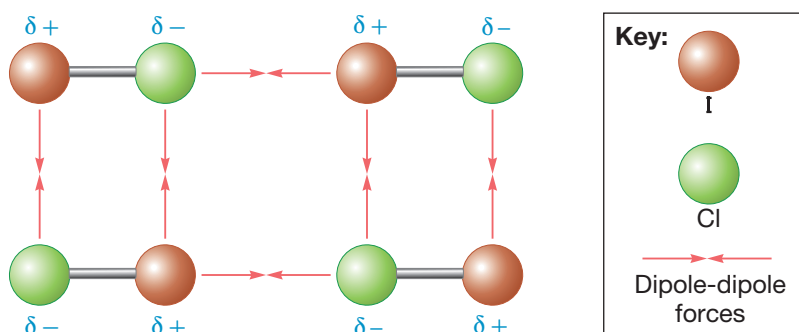
The strongest intermolecular forces exist between polar molecules. Polar molecules act as tiny dipoles because of their uneven charge distribution. **A dipole is created by equal but opposite charges that are separated by a short distance.** The direction of a dipole is from the dipole's positive pole 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 iodine chloride, I—Cl, and bromine, Br—Br. The boiling point of polar iodine chloride is 97°C, whereas that of nonpolar bromine is only 59°C. The dipole-dipole forces responsible for the relatively high boiling point of ICl are illustrated schematically in **Figure 5.9** (on the next page).

FIGURE 5.9

Dipole-Dipole Forces Ball-and-stick models illustrate the dipole-dipole forces between molecules of iodine chloride, ICl. In each molecule, the highly electronegative chlorine atom has a partial negative charge, leaving each iodine 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 ICl 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 5.10**. 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 O₂ in water. The positive pole of a water molecule attracts the outer electrons

FIGURE 5.10

Bond Polarities (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.

CRITICAL THINKING

Explain What explanation can you give for the fact that the boiling point of H₂O is significantly higher than the boiling point of either H₂ (g) or O₂ (g) alone?

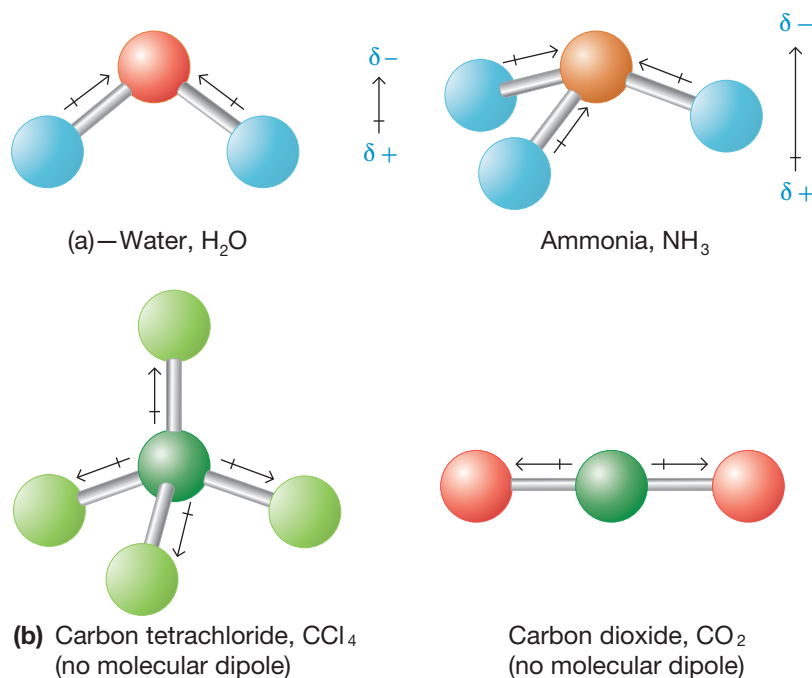
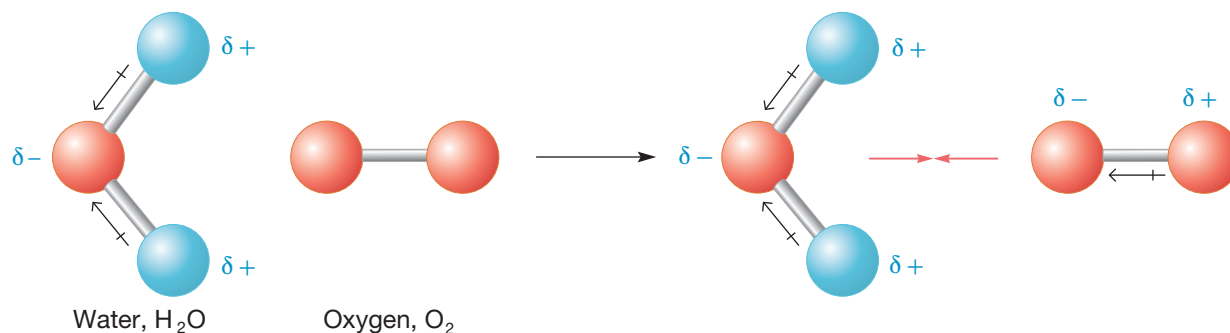


FIGURE 5.11

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.



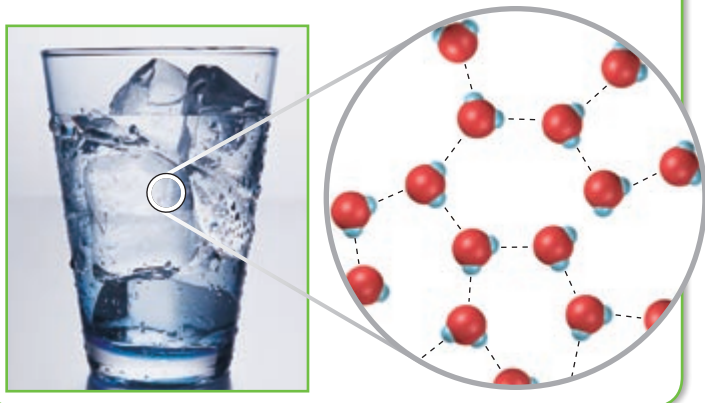
of an adjacent oxygen molecule. The oxygen molecule, then, has an induced negative pole on the side toward the water molecule and an induced positive pole on the opposite side. The result is an attraction to the water molecule, as shown in **Figure 5.11**.

Hydrogen Bonding

Some hydrogen-containing compounds, such as hydrogen fluoride (HF), water (H₂O), and ammonia (NH₃), 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.**

FIGURE 5.12

Hydrogen Bonding 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.

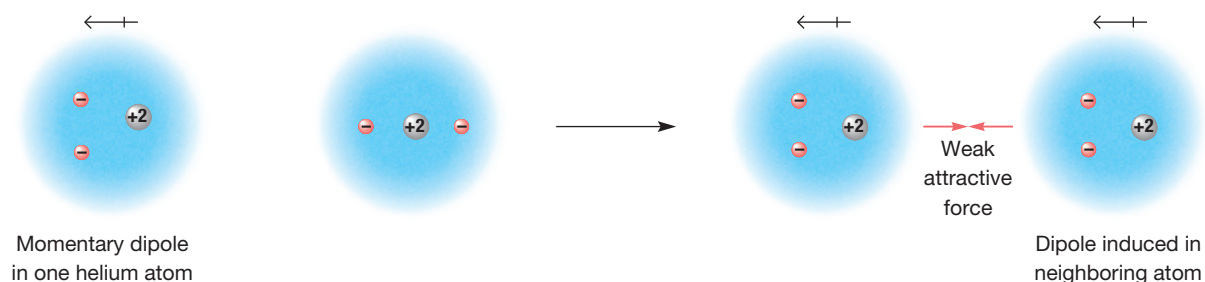


Hydrogen bonds are usually represented by dotted lines connecting the hydrogen-bonded hydrogen to the unshared electron pair of the electronegative atom to which it is attracted, as illustrated for water in **Figure 5.12**. The effect of hydrogen bonding can be seen by comparing the boiling points in **Figure 5.8**. Look at phosphine, PH₃, compared with hydrogen-bonded ammonia, NH₃. How does hydrogen sulfide, H₂S, compare with hydrogen-bonded water, H₂O?

In living organisms, hydrogen bonds play an extremely important role: that of stabilizing the structure of deoxyribonucleic acid (DNA). Hydrogen bonds are individually very weak, but the sum of millions of these bonds forms a very strong force holding two DNA strands together.

FIGURE 5.13

Temporary Dipoles 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 5.13**. **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 **Figure 5.8**. 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, H₂, and oxygen, O₂; and chlorine, Cl₂, and bromine, Br₂.



SECTION 5 FORMATIVE ASSESSMENT

▶ Reviewing Main Ideas

1. What two theories can be used to predict molecular geometry?
2. Draw the Lewis structure and predict the molecular geometry of the following molecules:
 - a. SO₂
 - b. Cl₄
 - c. BCl₃
3. What factors 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.

✔ Critical Thinking

6. **INFERRING RELATIONSHIPS** What experimental property directly correlates with the strength of the intermolecular forces? Briefly explain your answer.

Drawing Lewis dot structures can help you understand how valence electrons participate in bonding. Dots are placed around the symbol of an element to represent the element's valence electrons. For example, carbon has four valence electrons, and its Lewis dot structure is usually written as $\cdot\dot{\text{C}}\cdot$. An atom of fluorine has seven valence electrons. Fluorine's Lewis dot structure can be written as $:\ddot{\text{F}}:$. When Lewis

structures for covalently bonded atoms are written, the dots may be placed as needed to show the electrons shared in each bond. Most atoms bond in a way that gives them a stable octet of *s* and *p* electrons in the highest energy level. So, whenever possible, dots should be arranged in a way that represents a stable octet around each atom.

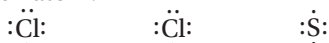
Problem-Solving TIPS

- Hydrogen is an exception to the octet rule, because hydrogen has only one electron and becomes stable with two electrons.
- Some elements, such as boron, can bond without achieving an octet, because they have three or fewer electrons to share.

Sample Problem

Draw the Lewis dot structure for a molecule of sulfur dichloride, SCl_2 .

First, write the electron dot notation for each atom.

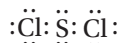


Next, determine the total number of valence electrons in the atoms.

S	$1 \times 6e^-$	=	$6e^-$
2Cl	$2 \times 7e^-$	=	$14e^-$
	Total e^-	=	$20e^-$

Arrange the atoms to form a skeleton structure for the molecule, and place electron pairs between atoms to represent covalent bonds. You can predict the arrangement of atoms by figuring out how many covalent bonds each atom must form in order to achieve a stable octet. Each chlorine atom, which has 7 valence electrons, must form a single covalent bond. Sulfur, which has 6 valence electrons, must form two covalent bonds. The only possible structure is $\text{Cl}-\text{S}-\text{Cl}$.

Finally, insert dots representing the remaining electrons (16 in this case), in order to give each atom an octet.



Practice

1. Draw the electron dot notations for a silicon atom and a strontium atom.
2. Draw Lewis structures for hydrogen sulfide, H_2S , and formic acid, HCO_2H .

CHAPTER 6 Summary

PREMIUM CONTENT



Interactive Review
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Review Games
Concept Maps

SECTION 1 Introduction to Chemical Bonding

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

KEY TERMS

chemical bond
ionic bonding
covalent bonding

nonpolar-covalent bond
polar
polar-covalent bond

SECTION 2 Covalent Bonding and Molecular Compounds

- Atoms in molecules are joined by covalent bonds. In a covalent bond, two atoms share one or more pairs of electrons.
- The octet rule states that many chemical compounds tend to form bonds so that each atom shares or has eight electrons in its highest occupied energy level.
- 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.

KEY TERMS

molecule
molecular compound
chemical formula
molecular formula
bond energy
electron-dot notation

Lewis structure
structural formula
single bond
multiple bond
resonance

SECTION 3 Ionic Bonding and Ionic Compounds

- An ionic compound is a three-dimensional network of positive and negative ions mutually attracted to one another.
- Ionic compounds tend to be harder and more brittle and have higher boiling points than materials containing only covalently bonded atoms.

KEY TERMS

ionic compound
formula unit
lattice energy
polyatomic ion

SECTION 4 Metallic Bonding

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

KEY TERMS

metallic bonding
malleability
ductility

SECTION 5 Molecular Geometry

- VSEPR theory is used to predict the shapes of molecules based on the fact that electron pairs strongly repel each other.
- Hybridization theory is used to predict the shapes of molecules, based on the fact that orbitals within an atom can mix to form orbitals of equal energy.
- Intermolecular forces include dipole-dipole forces and London dispersion forces. Hydrogen bonding is a special case of dipole-dipole forces.

KEY TERMS

VSEPR theory
hybridization
hybrid orbitals
dipole
hydrogen bonding
London dispersion forces

CHAPTER 6 Review

SECTION 1

Introduction to Chemical Bonding

REVIEWING MAIN IDEAS

1. What is a chemical bond?
2. Identify and define the three major types of chemical bonding.
3. What is the relationship between electronegativity and the ionic character of a chemical bond?
4.
 - a. What is the meaning of the term polar, as applied to chemical bonding?
 - b. Distinguish between polar-covalent and nonpolar-covalent bonds.
5. In general, what determines whether atoms will form chemical bonds?

PRACTICE PROBLEMS

6. 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 A.)
 - a. H and I
 - b. S and O
 - c. K and Br
 - d. Si and Cl
 - e. K and Cl
 - f. Se and S
 - g. C and H
7. List the bonding pairs described in item 6 in order of increasing covalent character.
8. 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
9. 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?

SECTION 2

Covalent Bonding and Molecular Compounds

REVIEWING MAIN IDEAS

10. What is a molecule?
11.
 - a. What determines bond length?
 - b. In general, how are bond energies and bond lengths related?
12. Describe the general location of the electrons in a covalent bond.
13. As applied to covalent bonding, what is meant by an unshared or lone pair of electrons?
14. Describe the octet rule in terms of noble-gas configurations and potential energy.
15. 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
16. In a Lewis structure, which atom is usually the central atom?
17. Distinguish between single, double, and triple covalent bonds by defining each and providing an illustration of each type.
18. For Lewis structures, how is the need for multiple bonds generally determined?

PRACTICE PROBLEMS

19. 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 B.)

a. Li	e. C
b. Ca	f. P
c. Cl	g. Al
d. O	h. S

20. Use electron-dot structures to demonstrate the formation of ionic compounds involving the following elements:
- Na and S
 - Ca and O
 - Al and S
21. Draw Lewis structures for each of the following molecules. (Hint: See Sample Problem D.)
- contains one C and four F atoms
 - contains two H and one Se atom
 - contains one N and three I atoms
 - contains one Si and four Br atoms
 - contains one C, one Cl, and three H atoms
22. Determine the type of hybrid orbitals formed by the boron atom in a molecule of boron fluoride, BF_3 .
23. Draw Lewis structures for each of the following molecules. Show resonance structures, if they exist.
- O_2
 - N_2
 - CO
 - SO_2
24. Draw Lewis structures for each of the following polyatomic ions. Show resonance structures, if they exist.
- OH^-
 - $\text{H}_3\text{C}_2\text{O}_2^-$
 - BrO_3^-

SECTION 3

Ionic Bonding and Ionic Compounds

REVIEWING MAIN IDEAS

25. a. What is an ionic compound?
b. In what form do most ionic compounds occur?
26. a. What is a formula unit?
b. What are the components of one formula unit of CaF_2 ?
27. a. What is lattice energy?
b. In general, what is the relationship between lattice energy and the strength of ionic bonding?

28. 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.
29. a. What is a polyatomic ion?
b. Give two examples of polyatomic ions.
c. In what form do such ions often occur in nature?

SECTION 4

Metallic Bonding

REVIEWING MAIN IDEAS

30. 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?
31. What properties of metals contribute to their tendency to form metallic bonds?
32. a. What is metallic bonding?
b. How can the strength of metallic bonding be measured?

SECTION 5

Molecular Geometry

REVIEWING MAIN IDEAS

33. a. How is the VSEPR theory used to classify molecules?
b. What molecular geometry would be expected for F_2 and HF?
34. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?
- AB_2
 - AB_3
 - AB_4
 - AB_5
 - AB_6
35. Describe the role of each of the following in predicting molecular geometries:
- unshared electron pairs
 - double bonds

36. a. What are hybrid orbitals?
b. What determines the number of hybrid orbitals produced by the hybridization of an atom?
37. a. What are intermolecular forces?
b. In general, how do these forces compare in strength with those in ionic and metallic bonding?
c. What types of molecules have the strongest intermolecular forces?
38. What is the relationship between electronegativity and the polarity of a chemical bond?
39. a. What are dipole-dipole forces?
b. What determines the polarity of a molecule?
40. a. What is meant by an induced dipole?
b. What is the everyday importance of this type of intermolecular force?
41. a. What is hydrogen bonding?
b. What accounts for its extraordinary strength?
42. What are London dispersion forces?
47. On the basis of individual bond polarity and orientation, determine whether each of the following molecules would be polar or nonpolar:
a. H_2O
b. I_2
c. CF_4
d. NH_3
e. 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. SCl_2
b. PI_3
c. Cl_2O
d. NH_2Cl
e. SiCl_3Br
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. NO_3^-
b. NH_4^+
c. SO_4^{2-}
d. ClO_2^-

PRACTICE PROBLEMS

43. According to the VSEPR theory, what molecular geometries are associated with the following types of molecules?
a. AB_3E
b. AB_2E_2
c. AB_2E
44. Use hybridization to explain the bonding in methane, 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

Mixed Review

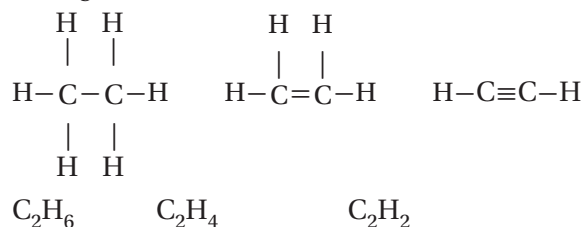
REVIEWING MAIN IDEAS

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. CCl_4
b. BeCl_2
c. 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, 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, CH_3OH .
58. How many K^+ and 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 from which it was formed?
62. Aluminum's enthalpy of vaporization is 284 kJ/mol. Beryllium's enthalpy 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. PCl_3
b. CCl_2F_2
c. CH_3NH_2
65. Draw the Lewis structure for 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. NO_2^-
b. NO_3^-
c. NH_4^+
67. Why do most atoms tend to be chemically bonded to other atoms?

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 Figure 2.10)



69. Why does F generally form covalent bonds with great polarity?
70. Explain what is wrong with the following Lewis structures, and then correct each one.
- a. $\text{H}-\text{H}-\ddot{\text{S}}:$
 $:\text{O}:$
- b. $\text{H}-\overset{\parallel}{\text{C}}=\ddot{\text{O}}-\text{H}$
 $:\ddot{\text{Cl}}:$
- c. $\overset{\parallel}{\text{N}}$
 $:\ddot{\text{Cl}} \quad \ddot{\text{Cl}}:$
71. Ionic compounds tend to have higher boiling points than covalent substances do. Both ammonia, NH_3 , and methane, CH_4 , are covalent compounds, yet the boiling point of ammonia is 130°C higher than that of methane. What might account for this large difference?

USING THE HANDBOOK

72. Figure 4.1 shows a model for a body-centered cubic crystal. Review the Properties tables for all of the metals in the *Elements Handbook* (Appendix A). What metals exist in body-centered cubic structures?

73. Group 14 of the *Elements Handbook* (Appendix A) contains a discussion of semiconductors and the band theory of metals. How does this model explain the electrical conductivity of metals?

RESEARCH AND WRITING

74. 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.
75. 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.
76. Natural rubber consists of long chains of carbon and hydrogen atoms covalently bonded together. When Charles Goodyear accidentally dropped a mixture of sulfur and rubber on a hot stove, the energy from the stove joined these chains together to make vulcanized rubber (named for Vulcan, the Roman god of fire). The carbon-hydrogen chains in vulcanized rubber are held together by two sulfur atoms that form covalent bonds between the chains. These covalent bonds are commonly called disulfide bridges. Explore other molecules that have such disulfide bridges. Present your findings to the class.
77. Searching for the perfect artificial sweetener—great taste with no Calories—has been the focus of chemical research for some time. Molecules such as sucralose, aspartamine, and saccharine owe their sweetness to their size and shape. One theory holds that any sweetener must have three sites that fit into the proper taste buds on the tongue. This theory is appropriately known as the “triangle theory.” Research artificial sweeteners to develop a model to show how the triangle theory operates.

ALTERNATIVE ASSESSMENT

78. Devise a set of criteria that will allow you to classify the following substances as ionic or non-ionic: CaCO_3 , Cu, H_2O , NaBr, and C (graphite). Show your criteria to your instructor.
79. **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.

Standards-Based Assessment

Answer the following items on a separate piece of paper.

MULTIPLE CHOICE

- A chemical bond results from the mutual attraction of the nuclei for
 - electrons.
 - neutrons.
 - protons.
 - dipoles.
- A polar covalent bond is likely to form between two atoms that
 - are similar in electronegativity.
 - are of similar size.
 - differ in electronegativity.
 - have the same number of electrons.
- The Lewis structure of HCN contains
 - one double bond and one single bond.
 - one triple bond and one single bond.
 - two single bonds.
 - two double bonds.
- According to VSEPR theory, the molecular geometry for CH_3^+ is
 - tetrahedral.
 - trigonal-pyramidal.
 - bent or angular.
 - None of the above
- Which molecule contains a double bond?
 - COCl_2
 - C_2H_6
 - CF_4
 - SF_2
- Which molecule is polar?
 - CCl_4
 - CO_2
 - SO_3
 - none of these
- What is the hybridization of the carbon atoms in C_2H_2 ?
 - sp
 - sp^2
 - sp^3
 - The carbon atoms do not hybridize in C_2H_2 .

- Which of the following compounds is predicted to have the highest boiling point?
 - HCl
 - CH_3COOH (Note: The two oxygen atoms bond to the carbon.)
 - Cl_2
 - SO_2
- An unknown substance is an excellent electrical conductor in the solid state and is malleable. What type of chemical bonding does this substance exhibit?
 - ionic bonding
 - molecular bonding
 - metallic bonding
 - cannot determine from the information given

SHORT RESPONSE

- What does the hybridization model help explain?
- Explain why ionic crystals are brittle.

EXTENDED RESPONSE

- Naphthalene, C_{10}H_8 , is a nonpolar molecule and has a boiling point of 218°C . Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, is a polar molecule and has a boiling point of 118°C . Which substance has the stronger intermolecular forces? Briefly explain your answer.
- Describe and explain the potential energy changes that occur during the formation of a covalent bond.



Test Tip

When several questions refer to the same graph, table, drawing, or passage, answer the questions you are sure of first.