8

BASIC CONCEPTS OF CHEMICAL BONDING

Whenever two atoms or ions are strongly held together, we say there is a **chemical bond** between them. There are three general types of chemical bonds: *ionic, covalent*, and *metallic*. These three types of bonds are in the substances illustrated in **Figure 8.1**: We add table salt to water using a stainless steel spoon.

Table salt is sodium chloride, NaCl, which consists of sodium ions, Na^+, and chloride ions, Cl^-. The structure is held together by **ionic bonds**, which are due to the electrostatic attractions between oppositely charged ions. The water consists mainly of H_2O molecules. The hydrogen and oxygen atoms are bonded to one another through **covalent bonds**, in which molecules are formed by the sharing of electrons between atoms. The spoon consists mainly of iron metal, in which Fe atoms are connected to one another by **metallic bonds**, which are formed by electrons that are relatively free to move from one atom to another. These different substances—NaCl, H_2O, and Fe metal—behave as they do because of the ways in which their constituent atoms are connected to one another. For example, NaCl readily dissolves in water, but Fe metal does not.

What determines the type of bonding in any substance? How do the characteristics of these bonds give rise to different physical and chemical properties? The keys to answering the first question are found in the electronic structure of the atoms involved, as discussed in Chapters 6 and 7. In this chapter and the next, we examine the relationship between the electronic structure of atoms and the ionic and covalent chemical bonds they form. We will discuss metallic bonding in Chapter 12.

New! Full-page chapter opener photos and captions spark student interest.

◀ **GIANT CRYSTALS.** These gypsum crystals, large enough for people to walk on, are composed of $CaSO_4 \cdot 2H_2O$. The ionic bonding between calcium and sulfate ions at the atomic scale leads to the characteristic crystal shape at the human scale.

New! What's Ahead sidebar provides an at-a-glance outline of the chapter to.

WHAT'S AHEAD

8.1 ▶ **Lewis Symbols and the Octet Rule** Learn about the three main types of chemical bonds: *ionic*, *covalent*, and *metallic*. In evaluating bonding, *Lewis symbols* provide a useful shorthand for keeping track of valence electrons. We learn that atoms usually follow the *octet rule*.

8.2 ▶ **Ionic Bonding** Explore ionic substances, substances in which atoms are held together by the electrostatic attractions between ions of opposite charge. Analyze the energetics of forming ionic substances and describe the *lattice energy* of these substances.

8.3 ▶ **Covalent Bonding** Examine the bonding in molecular substances, in which atoms bond by sharing one or more electron pairs. In general, the electrons are shared in such a way that each atom attains an octet of electrons.

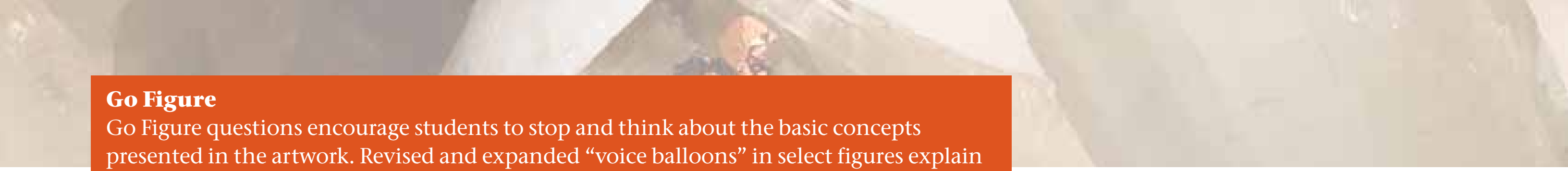
8.4 ▶ **Bond Polarity and Electronegativity** Learn that *electronegativity* is the ability of an atom in a compound to attract electrons to itself. In general, electron pairs are shared unequally between atoms with different electronegativities, leading to *polar covalent bonds*.

8.5 ▶ **Drawing Lewis Structures** Learn that *Lewis structures* are a simple yet powerful way of predicting covalent bonding patterns in molecules. In addition to the octet rule, see how the concept of *formal charge* can be used to identify the dominant Lewis structure.

8.6 ▶ **Resonance Structures** Learn that in some cases, more than one equivalent Lewis structure can be drawn for a molecule or polyatomic ion. The bonding description in such cases is a blend of two or more *resonance structures*.

8.7 ▶ **Exceptions to the Octet Rule** Recognize that the octet rule is more of a guideline than an absolute rule. Exceptions to the rule include molecules with an odd number of electrons, molecules where large differences in electronegativity prevent an atom from completing its octet, and molecules where an element from period 3 or below in the periodic table attains more than an octet of electrons.

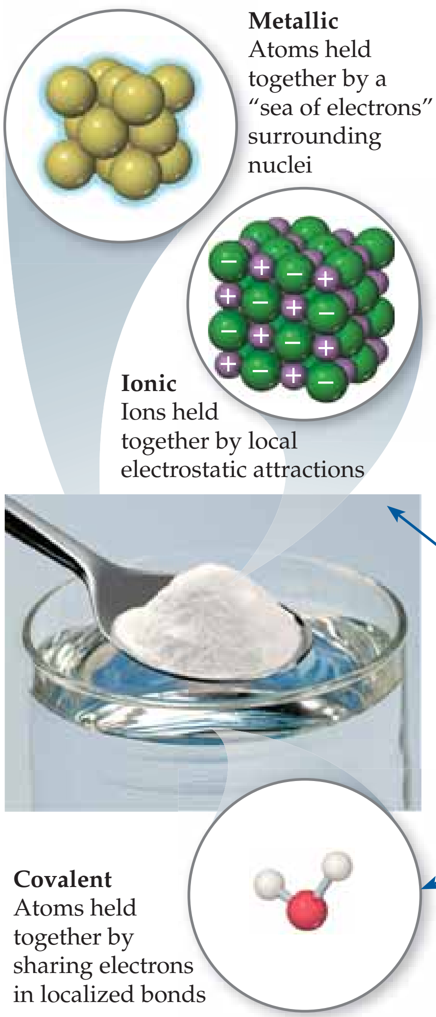
8.8 ▶ **Strengths and Lengths of Covalent Bonds** Observe that bond strengths and lengths vary with the number of shared electron pairs as well as other factors.



Go Figure
Go Figure questions encourage students to stop and think about the basic concepts presented in the artwork. Revised and expanded "voice balloons" in select figures explain important details and help break the figure down into easy-to-understand components.

Go Figure

If the white powder were sugar, $C_{12}H_{22}O_{11}$, how would we have to change this picture?



▲ **Figure 8.1 Ionic, covalent, and metallic bonds.** The three different substances shown here are held together by different types of chemical bonds.

8.1 | Lewis Symbols and the Octet Rule

The electrons involved in chemical bonding are the *valence electrons*, which, for most atoms, are those in the outermost occupied shell. ∞∞ (Section 6.8) The American chemist G. N. Lewis (1875–1946) suggested a simple way of showing the valence electrons in an atom and tracking them during bond formation, using what are now known as either *Lewis electron-dot symbols* or simply Lewis symbols.

The **Lewis symbol** for an element consists of the element's chemical symbol plus a dot for each valence electron. Sulfur, for example, has the electron configuration $[Ne]3s^23p^4$ and therefore six valence electrons. Its Lewis symbol is

·S̤̈·

The dots are placed on the four sides of the symbol—top, bottom, left, and right—and each side can accommodate up to two electrons. All four sides are equivalent, which means that the choice of sides for placement of two electrons rather than one electron is arbitrary. In general, we spread out the dots as much as possible. In the Lewis symbol for S, for instance, we prefer the dot arrangement shown rather than the arrangement having two electrons on three of the sides and none on the fourth.

The electron configurations and Lewis symbols for the main-group elements of periods 2 and 3 are shown in **Figure 8.2**. Notice that the number of valence electrons in any representative element is the same as the element's group number. For example, the Lewis symbols for oxygen and sulfur, members of group 6A, both show six dots.

Give It Some Thought

Are all these Lewis symbols for Cl correct?

:C̤̈l·   :C̣̈l: :Ċ̣l·

Give It Some Thought (GIST) questions
These informal, sharply-focused exercises allow students to gauge whether they are "getting it" as they read the text.

For 14e, all figures and figure captions were carefully examined and revised when needed, to improve clarity and teaching focus.

The Octet Rule

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table. The noble gases have very stable electron arrangements, as evidenced by their high ionization energies, low affinity for additional electrons, and general lack of chemical reactivity. ∞∞ (Section 7.8) Because all the noble gases except He have eight valence electrons, many atoms undergoing reactions end up with eight valence electrons. This observation has led to a guideline known as the **octet rule**: *Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons.*

An octet of electrons consists of full *s* and *p* subshells in an atom. In a Lewis symbol, an octet is shown as four pairs of valence electrons arranged around the element symbol, as in the Lewis symbols for Ne and Ar in Figure 8.2. There are exceptions to the octet rule, as we will see in Section 8.7, but it provides a useful framework for introducing many

1A	2A	3A	4A	5A	6A	7A	8A
Li $[He]2s^1$ Li·	**Be** $[He]2s^2$ ·Be·	**B** $[He]2s^22p^1$ ·Ḃ·	**C** $[He]2s^22p^2$ ·Ċ̣·	**N** $[He]2s^22p^3$ ·Ṇ̇:	**O** $[He]2s^22p^4$:Ọ̇:	**F** $[He]2s^22p^5$ ·F̤̈:	**Ne** $[He]2s^22p^6$:N̤̈e:
Na $[Ne]3s^1$ Na·	**Mg** $[Ne]3s^2$ ·Mg·	**Al** $[Ne]3s^23p^1$ ·Ȧl·	**Si** $[Ne]3s^23p^2$ ·Ṩi·	**P** $[Ne]3s^23p^3$ ·Ṗ̣:	**S** $[Ne]3s^23p^4$:Ṩ:	**Cl** $[Ne]3s^23p^5$ ·C̤̈l:	**Ar** $[Ne]3s^23p^6$:Ä̤r:

▲ **Figure 8.2 Lewis symbols.**

important concepts of bonding. The octet rule mostly applies to atoms that have *s* and *p* valence electrons; compounds of the transition metals, having valence *d* electrons, will be examined in Chapter 23.

8.2 | Ionic Bonding

Ionic substances generally result from the interaction of metals on the left side of the periodic table with nonmetals on the right side (excluding the noble gases, group 8A). For example, when sodium metal, Na(*s*), is brought into contact with chlorine gas, $Cl_2(g)$, a violent reaction ensues (**Figure 8.3**). The product of this very exothermic reaction is sodium chloride, NaCl(*s*):

$$\mathrm{Na}(s) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ = -410.9\ \mathrm{kJ} \qquad [8.1]$$

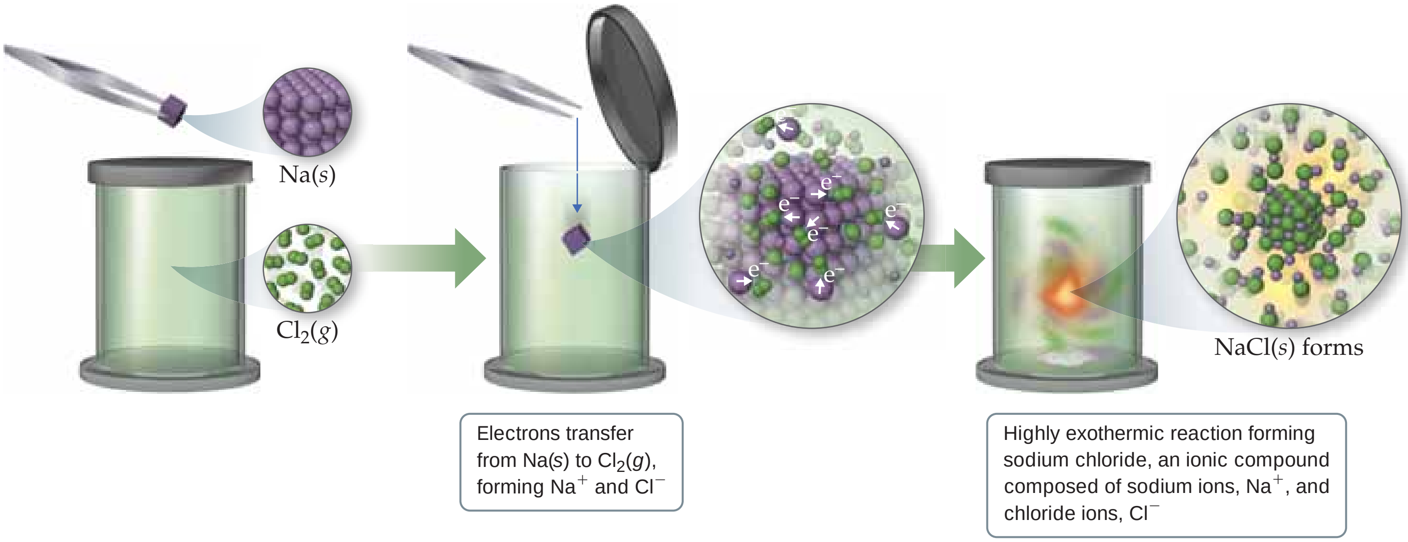
Sodium chloride is composed of Na^+ and Cl^- ions arranged in a three-dimensional array (**Figure 8.4**).

The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom—we say there has been an *electron transfer* from the Na atom to the Cl atom. Two of the atomic properties discussed in Chapter 7 give us an indication of how readily electron transfer occurs: ionization energy, which indicates how easily an electron can be removed from an atom; and electron affinity, which measures how much an atom wants to gain an electron. ∞ (Sections 7.4 and 7.5) Electron transfer to form oppositely charged ions occurs when one atom readily gives up an electron (low ionization energy) and another atom readily gains an electron (high electron affinity). Thus, NaCl is a typical ionic compound because it consists of a metal of low ionization energy and a nonmetal of high electron affinity. Using Lewis electron-dot symbols (and showing a chlorine atom rather than the Cl_2 molecule), we can represent this reaction as

$$\mathrm{Na}\cdot + \cdot\overset{..}{\underset{..}{\mathrm{Cl}}}\!: \longrightarrow \mathrm{Na}^+ + [:\overset{..}{\underset{..}{\mathrm{Cl}}}:]^- \qquad [8.2]$$

The arrow indicates the transfer of an electron from the Na atom to the Cl atom. Each ion has an octet of electrons, the Na^+ octet being the $2s^22p^6$ electrons that lie below the single 3*s* valence electron of the Na atom. We have put a bracket around the chloride ion to emphasize that all eight electrons are located on it.

Go Figure Do you expect a similar reaction between potassium metal and elemental bromine?



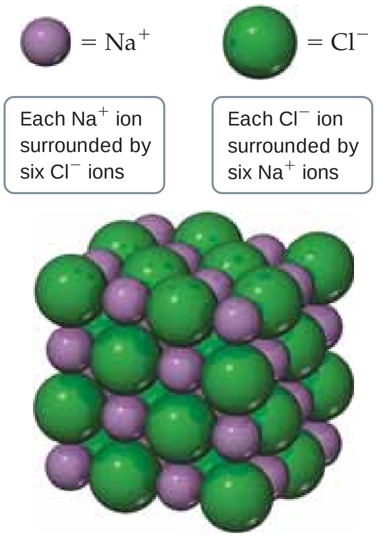
Electrons transfer from Na(*s*) to $Cl_2(g)$, forming Na^+ and Cl^-

Highly exothermic reaction forming sodium chloride, an ionic compound composed of sodium ions, Na^+, and chloride ions, Cl^-

▲ **Figure 8.3 Reaction of sodium metal with chlorine gas to form the ionic compound sodium chloride.**

Go Figure

If no color key were provided, how would you know which color ball represented Na^+ and which represented Cl^-?



▲ **Figure 8.4** **The crystal structure of sodium chloride.**

Ionic substances possess several characteristic properties. They are usually brittle substances with high melting points. They are usually crystalline. Furthermore, ionic crystals often can be cleaved; that is, they break apart along smooth, flat surfaces. These characteristics result from electrostatic forces that maintain the ions in a rigid, well-defined, three-dimensional arrangement such as that shown in Figure 8.4.

Energetics of Ionic Bond Formation

The formation of sodium chloride from sodium and chlorine is *very* exothermic, as indicated by the large negative enthalpy of formation value given in Equation 8.1, $\Delta H_f^\circ = -410.9$ kJ. Appendix C shows that the heat of formation of other ionic substances is also quite negative. What factors make the formation of ionic compounds so exothermic?

In Equation 8.2, we represented the formation of NaCl as the transfer of an electron from Na to Cl. Recall from Section 7.4 that the loss of electrons from an atom is always an endothermic process. Removing an electron from $Na(g)$ to form $Na^+(g)$ for instance, requires 496 kJ/mol. Recall from Section 7.5 that when a nonmetal gains an electron, the process is generally exothermic, as seen from the negative electron affinities of the elements. Adding an electron to $Cl(g)$, for example, releases 349 kJ/mol. From the magnitudes of these energies, we can see that the transfer of an electron from an Na atom to a Cl atom would not be exothermic—the overall process would be an endothermic process that requires $496 - 349 = 147$ kJ/mol. This endothermic process corresponds to the formation of sodium and chloride ions that are infinitely far apart—in other words, the positive energy change assumes that the ions do not interact with each other, which is quite different from the situation in ionic solids.

The principal reason ionic compounds are stable is the attraction between ions of opposite charge. This attraction draws the ions together, releasing energy and causing many ions to form a solid array, or lattice, such as that shown in Figure 8.4. A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid is given by the **lattice energy**, which is *the energy required to completely separate one mole of a solid ionic compound into its gaseous ions*.

To envision this process for NaCl, imagine that the structure in Figure 8.4 expands from within, so that the distances between the ions increase until the ions are very far apart. This process requires 788 kJ/mol, which is the value of the lattice energy:

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{\text{lattice}} = +788 \text{ kJ/mol} \qquad [8.3]$$

Notice that this process is highly endothermic. The reverse process—the coming together of $Na^+(g)$ and $Cl^-(g)$ to form $NaCl(s)$—is therefore highly exothermic ($\Delta H = -788$ kJ/mol).

Table 8.1 lists the lattice energies for a number of ionic compounds. The large positive values indicate that the ions are strongly attracted to one another in ionic solids.

Revised Visuals for Clarity: Restyled tables clearly showcase two columns of values.

TABLE 8.1 Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2526
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

The energy released by the attraction between ions of unlike charge more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process. The strong attractions also cause most ionic materials to be hard and brittle with high melting points—for example, NaCl melts at 801 °C.

Give It Some Thought

If you were to perform the reaction $KCl(s) \longrightarrow K^+(g) + Cl^-(g)$, would energy be released?

The magnitude of the lattice energy of an ionic solid depends on the charges of the ions, their sizes, and their arrangement in the solid. We saw in Section 5.1 that the electrostatic potential energy of two interacting charged particles is given by

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \qquad [8.4]$$

In this equation Q_1 and Q_2 are the charges on the particles in Coulombs, with their signs; d is the distance between their centers in meters; and κ is a constant, 8.99×10^9 J-m/C^2. Equation 8.4 indicates that the attractive interaction between two oppositely charged ions increases as the magnitudes of their charges increase and as the distance between their centers decreases. Thus, *for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease*. The variation in the magnitude of lattice energies depends more on ionic charge than on ionic radius because ionic radii vary over only a limited range compared to charges.

Sample Exercise 8.1

Magnitudes of Lattice Energies

Without consulting Table 8.1, arrange the ionic compounds NaF, CsI, and CaO in order of increasing lattice energy.

SOLUTION

Analyze From the formulas for three ionic compounds, we must determine their relative lattice energies.

Plan We need to determine the charges and relative sizes of the ions in the compounds. We then use Equation 8.4 qualitatively to determine the relative energies, knowing that (**a**) the larger the ionic charges, the greater the energy and (**b**) the farther apart the ions are, the lower the energy.

Solve NaF consists of Na^+ and F^- ions, CsI of Cs^+ and I^- ions, and CaO of Ca^{2+} and O^{2-} ions. Because the product Q_1Q_2 appears in the numerator of Equation 8.4, the lattice energy increases dramatically when the charges increase. Thus, we expect the lattice energy of CaO, which has 2+ and 2− ions, to be the greatest of the three.

The ionic charges are the same in NaF and CsI. The difference in their lattice energies thus depends on the difference in the distance between ions in the lattice. Because ionic size increases as we go down a group in the periodic table (Section 7.3), we know that Cs^+ is larger than Na^+ and I^- is larger than F^-. Therefore, the distance between Na^+ and F^- ions in NaF is less than the distance between the Cs^+ and I^- ions in CsI. As a result, the lattice energy of NaF should be greater than that of CsI. In order of increasing energy, therefore, we have CsI < NaF < CaO.

Check Table 8.1 confirms our predicted order is correct.

Practice Exercise 1

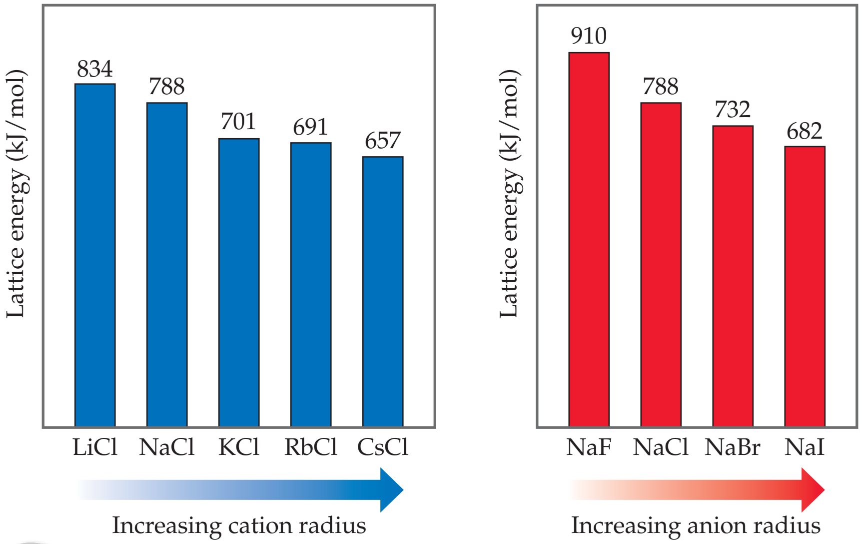
Without looking at Table 8.1, predict which one of the following orderings of lattice energy is correct for these ionic compounds.
(**a**) NaCl > MgO > CsI > ScN (**b**) ScN > MgO > NaCl > CsI
(**c**) NaCl > CsI > ScN > CaO (**d**) MgO > NaCl > ScN > CsI
(**e**) ScN > CsI > NaCl > MgO

Practice Exercise 2

Which substance do you expect to have the greatest lattice energy: MgF_2, CaF_2, or ZrO_2?

Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius shown in Figure 7.8. In particular, because ionic radius increases as we go down a group of the periodic table, we find that, for a given type of ionic compound, lattice energy decreases as we go down a group. **Figure 8.5** illustrates this trend for the alkali chlorides MCl (M = Li, Na, K, Rb, Cs) and the sodium halides NaX (X = F, Cl, Br, I).

Go Figure Using this figure, find the most likely range of values for the lattice energy of KF.



▲ **Figure 8.5** **Periodic trends in lattice energy as a function of cation or anion radius.**

New! Interactive Figures, which appear in select chapters, use animation and narration to bring important concepts to life.

Electron Configurations of Ions of the *s*- and *p*-Block Elements

The energetics of ionic bond formation helps explain why many ions tend to have noble-gas electron configurations. For example, sodium readily loses one electron to form Na^+, which has the same electron configuration as Ne:

$$\begin{array}{lll} \text{Na} & 1s^22s^22p^63s^1 & = [\text{Ne}]3s^1 \\ \text{Na}^+ & 1s^22s^22p^6 & = [\text{Ne}] \end{array}$$

Even though lattice energy increases with increasing ionic charge, we never find ionic compounds that contain Na^{2+} ions. The second electron removed would have to come from an inner shell of the sodium atom, and removing electrons from an inner shell requires a very large amount of energy. ∞ (Section 7.4) The increase in lattice energy is not enough to compensate for the energy needed to remove an inner-shell electron. Thus, sodium and the other group 1A metals are found in ionic substances only as 1+ ions.

Similarly, adding electrons to nonmetals is either exothermic or only slightly endothermic as long as the electrons are added to the valence shell. Thus, a Cl atom easily adds an electron to form Cl^-, which has the same electron configuration as Ar:

$$\begin{array}{ll} \text{Cl} & 1s^22s^22p^63s^23p^5 = [\text{Ne}]3s^23p^5 \\ \text{Cl}^- & 1s^22s^22p^63s^23p^6 = [\text{Ne}]3s^23p^6 = [\text{Ar}] \end{array}$$

To form a Cl^{2-} ion, the second electron would have to be added to the next higher shell of the Cl atom, an addition that is energetically very unfavorable. Therefore, we never observe Cl^{2-} ions in ionic compounds. We thus expect ionic compounds of the representative metals from groups 1A, 2A, and 3A to contain 1+, 2+, and 3+ cations, respectively, and we usually expect ionic compounds of the representative nonmetals of groups 5A, 6A, and 7A to contain 3−, 2−, and 1− anions, respectively.

A CLOSER LOOK Calculation of Lattice Energies: The Born–Haber Cycle

Lattice energies cannot be determined directly by experiment. They can, however, be calculated by envisioning the formation of an ionic compound as occurring in a series of well-defined steps. We can then use Hess's law (Section 5.6) to combine the steps in a way that gives the lattice energy for the compound. By so doing, we construct a **Born–Haber cycle**, a thermochemical cycle named after the German scientists Max Born (1882–1970) and Fritz Haber (1868–1934), who introduced it to analyze the factors contributing to the stability of ionic compounds.

Let's use NaCl as an example. In Equation 8.3, which defines lattice energy, $\mathrm{NaCl}(s)$ is the reactant, and the gas-phase ions $\mathrm{Na}^+(g)$ and $\mathrm{Cl}^-(g)$ are the products. This equation is our target as we apply Hess's Law.

In seeking a set of other equations that can be added up to give our target equation, we can use the heat of formation for NaCl (Section 5.7):

$$\mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{NaCl}(s) \qquad \Delta H_f^\circ[\mathrm{NaCl}(s)] = -411\ \mathrm{kJ} \qquad [8.5]$$

Of course, we will have to turn this equation around so that we have $\mathrm{NaCl}(s)$ as the reactant as we do in the equation for the lattice energy. We can use two other equations to arrive at our target, as shown below:

$$\begin{array}{lll}
1. & \mathrm{NaCl}(s) \longrightarrow \mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) & \Delta H_1 = -\Delta H_f^\circ[\mathrm{NaCl}(s)] \\
 & & \quad = +411\ \mathrm{kJ} \\
2. & \mathrm{Na}(s) \longrightarrow \mathrm{Na}^+(g) + e^- & \Delta H_2 = ?? \\
3. & e^- + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}^-(g) & \Delta H_3 = ??? \\
\hline
4. & \mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) & \Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3 \\
 & & \quad = \Delta H_{\mathrm{lattice}}
\end{array}$$

Step 2 involves the formation of sodium ion from solid sodium, which is just the heat of formation for sodium gas and the first ionization energy for sodium (Appendix C and Figure 7.10 list numbers for these processes):

$$\mathrm{Na}(s) \longrightarrow \mathrm{Na}(g) \qquad \Delta H = \Delta H_f^\circ[\mathrm{Na}(g)] = 108\ \mathrm{kJ} \qquad [8.6]$$

$$\mathrm{Na}(g) \longrightarrow \mathrm{Na}^+(g) + e^- \qquad \Delta H = I_1(\mathrm{Na}) = 496\ \mathrm{kJ} \qquad [8.7]$$

The sum of these two processes gives us the required energy for Step 2 (above), which is 604 kJ.

Similarly, for Step 3, we have to create chlorine atoms, and then anions, from the Cl_2 molecule, in two steps. The enthalpy changes for these two steps are the sum of the enthalpy of formation of $\mathrm{Cl}(g)$ and the electron affinity of chlorine, $EA(\mathrm{Cl})$:

$$\tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}(g) \qquad \Delta H = \Delta H_f^\circ[\mathrm{Cl}(g)] = 122\ \mathrm{kJ} \qquad [8.8]$$

$$e^- + \mathrm{Cl}(g) \longrightarrow \mathrm{Cl}^-(g) \qquad \Delta H = EA(\mathrm{Cl}) = -349\ \mathrm{kJ} \qquad [8.9]$$

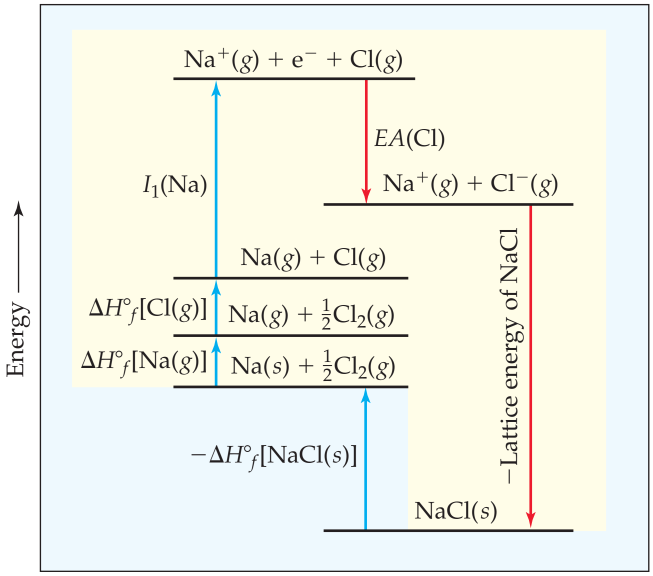
The sum of these two processes gives us the required energy for Step 3 (above), which is -227 kJ.

Finally, when we put it all together, we have:

$$\begin{array}{lll}
1. & \mathrm{NaCl}(s) \longrightarrow \mathrm{Na}(s) + \tfrac{1}{2}\mathrm{Cl}_2(g) & \Delta H_1 = -\Delta H_f^\circ[\mathrm{NaCl}(s)] \\
 & & \quad = +411\ \mathrm{kJ} \\
2. & \mathrm{Na}(s) \longrightarrow \mathrm{Na}^+(g) + e^- & \Delta H_2 = 604\ \mathrm{kJ} \\
3. & e^- + \tfrac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}^-(g) & \Delta H_3 = -227\ \mathrm{kJ} \\
\hline
4. & \mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) & \Delta H_4 = 788\ \mathrm{kJ} = \Delta H_{\mathrm{lattice}}
\end{array}$$

This process is described as a "cycle" because it corresponds to the scheme in **Figure 8.6**, which shows how all the quantities we have just calculated are related. The sum of all the blue "up" arrow energies has to be equal to the sum of all the red "down" arrow energies in this cycle. Born and Haber recognized that if we know the value of every quantity in the cycle except the lattice energy, we can calculate it from this cycle.

Related Exercises: 8.28–8.30, 8.83



▲ **Figure 8.6 Born–Haber cycle for formation of NaCl.** This Hess's law representation shows the energetic relationships in the formation of the ionic solid from its elements.

Transition Metal Ions

Because ionization energies increase rapidly for each successive electron removed, the lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only three electrons from atoms. Thus, we find cations with charges of 1+, 2+, or 3+ in ionic compounds. Most transition metals, however, have more than three electrons beyond a noble-gas core. Silver, for example, has a $[\mathrm{Kr}]4d^{10}5s^1$ electron configuration. Metals of group 1B (Cu, Ag, Au) often occur as 1+ ions (as in CuBr and AgCl). In forming Ag^+, the $5s$ electron is lost, leaving a completely filled $4d$ subshell. As in this example, transition metals generally do not form ions that have a noble-gas configuration. The octet rule, although useful, is clearly limited in scope.

Sample Exercise 8.2

Charges on Ions

Predict the ion generally formed by (**a**) Sr, (**b**) S, (**c**) Al.

SOLUTION

Analyze We must decide how many electrons are most likely to be gained or lost by atoms of Sr, S, and Al.

Plan In each case, we can use the element's position in the periodic table to predict whether the element forms a cation or an anion. We can then use its electron configuration to determine the most likely ion formed.

Solve

(**a**) Strontium is a metal in group 2A and therefore forms a cation. Its electron configuration is $[\mathrm{Kr}]5s^2$, and so we expect that the two valence electrons will be lost to give an Sr^{2+} ion.

(**b**) Sulfur is a nonmetal in group 6A and will thus tend to be found as an anion. Its electron configuration ($[\mathrm{Ne}]3s^23p^4$) is two electrons short of a noble-gas configuration. Thus, we expect that sulfur will form S^{2-} ions.

(**c**) Aluminum is a metal in group 3A. We therefore expect it to form Al^{3+} ions.

Check The ionic charges we predict here are confirmed in Tables 2.4 and 2.5.

Practice Exercise 1

Which of these elements is most likely to form ions with a 2+ charge?
(**a**) Li (**b**) Ca (**c**) O (**d**) P (**e**) Cl

Practice Exercise 2

Predict the charges on the ions formed when magnesium reacts with nitrogen.

Recall from Section 7.4 that when a positive ion forms from an atom, electrons are always lost first from the subshell having the largest value of n. Thus, *in forming ions, transition metals lose the valence-shell* s *electrons first, then as many* d *electrons as required to reach the charge of the ion*. For instance, in forming Fe^{2+} from Fe, which has the electron configuration $[\mathrm{Ar}]3d^64s^2$, the two 4*s* electrons are lost, leading to an $[\mathrm{Ar}]3d^6$ configuration. Removal of an additional electron gives Fe^{3+}, whose electron configuration is $[\mathrm{Ar}]3d^5$.

Give It Some Thought

Which element forms a 3+ ion that has the electron configuration $[\mathrm{Kr}]4d^6$?

8.3 | Covalent Bonding

The vast majority of chemical substances do not have the characteristics of ionic materials. Most of the substances with which we come into daily contact—such as water—tend to be gases, liquids, or solids with low melting points. Many, such as gasoline, vaporize readily. Many are pliable in their solid forms—for example, plastic bags and wax.

For the very large class of substances that do not behave like ionic substances, we need a different model to describe the bonding between atoms. G. N. Lewis reasoned that atoms might acquire a noble-gas electron configuration by sharing electrons with other atoms. A chemical bond formed by sharing a pair of electrons is a *covalent bond*.

The hydrogen molecule, H_2, provides the simplest example of a covalent bond. When two hydrogen atoms are close to each other, the two positively charged nuclei repel each other, the two negatively charged electrons repel each other, and the nuclei and electrons attract each other, as shown in **Figure 8.7**(**a**). Because the molecule is stable, we know that the attractive forces must overcome the repulsive ones. Let's take a closer look at the attractive forces that hold this molecule together.

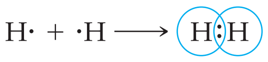
By using quantum mechanical methods analogous to those used for atoms in Section 6.5, we can calculate the distribution of electron density in molecules. Such a calculation for H_2 shows that the attractions between the nuclei and the electrons cause electron density to concentrate between the nuclei, as shown in Figure 8.7(b). As a result, the overall electrostatic interactions are attractive. Thus, the atoms in H_2 are held together principally because the two positive nuclei are attracted to the concentration of negative charge between them. In essence, the shared pair of electrons in any covalent bond acts as a kind of "glue" to bind atoms together.

Give It Some Thought

Ionizing an H_2 molecule to H_2^+ changes the strength of the bond. Based on the description of covalent bonding given previously, do you expect the H—H bond in H_2^+ to be weaker or stronger than the H—H bond in H_2?

Lewis Structures

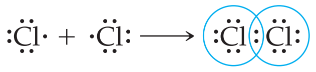
The formation of covalent bonds can be represented with Lewis symbols. The formation of the H_2 molecule from two H atoms, for example, can be represented as



$$\mathrm{H}\cdot + \cdot\mathrm{H} \longrightarrow \mathrm{H}{:}\mathrm{H}$$

In forming the covalent bond, each hydrogen atom acquires a second electron, achieving the stable, two-electron, noble-gas electron configuration of helium.

Formation of a covalent bond between two Cl atoms to give a Cl_2 molecule can be represented in a similar way:



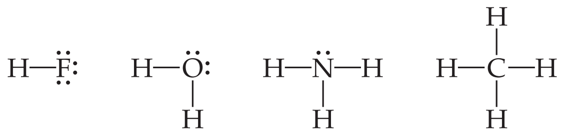
$$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{:}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

By sharing the bonding electron pair, each chlorine atom has eight electrons (an octet) in its valence shell, thus achieving the noble-gas electron configuration of argon.

The structures shown here for H_2 and Cl_2 are **Lewis structures**, or *Lewis dot structures*. While these structures show circles to indicate electron sharing, the more common convention is to show each shared electron pair or **bonding pair**, as a line and any unshared electron pairs (also called **lone pairs** or **nonbonding pairs**) as dots. Written this way, the Lewis structures for H_2 and Cl_2 are

$$\mathrm{H{-}H} \qquad :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}{-}\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

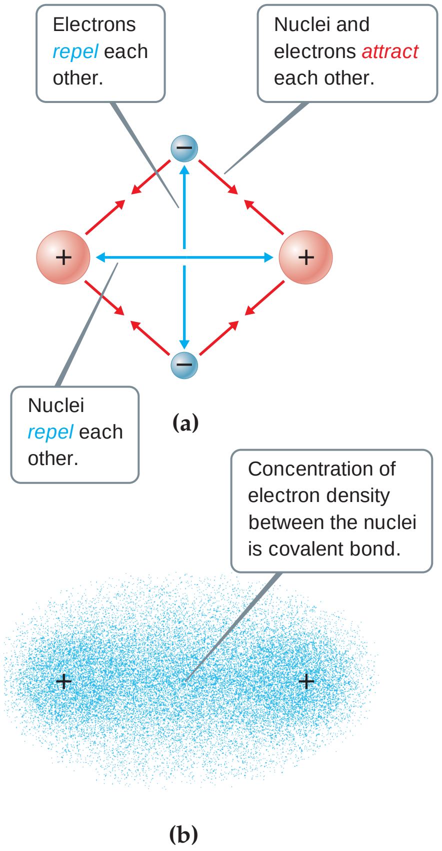
For nonmetals, the number of valence electrons in a neutral atom is the same as the group number. Therefore, one might predict that 7A elements, such as F, would form one covalent bond to achieve an octet; 6A elements, such as O, would form two covalent bonds; 5A elements, such as N, would form three; and 4A elements, such as C, would form four. These predictions are borne out in many compounds, as in, for example, the compounds with hydrogen of the nonmetals of the second row of the periodic table:



$$\mathrm{H{-}}\ddot{\underset{\cdot\cdot}{\mathrm{F}}}: \qquad \mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\ddot{\mathrm{O}}}: \qquad \mathrm{H{-}}\underset{\underset{\mathrm{H}}{|}}{\ddot{\mathrm{N}}}\mathrm{{-}H} \qquad \mathrm{H{-}}\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}\mathrm{{-}H}$$

Go Figure

What would happen to the concentration of electron density between the nuclei in (b) if you pulled the nuclei further apart?



▲ **Figure 8.7 The covalent bond in H_2.** (**a**) The attractions and repulsions among electrons and nuclei in the hydrogen molecule. (**b**) Electron distribution in the H_2 molecule.

Sample Exercise 8.3

Lewis Structure of a Compound

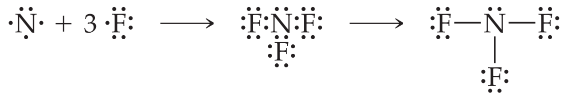
Given the Lewis symbols for nitrogen and fluorine in Figure 8.2, predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine and draw its Lewis structure.

SOLUTION

Analyze The Lewis symbols for nitrogen and fluorine reveal that nitrogen has five valence electrons and fluorine has seven.

Plan We need to find a combination of the two elements that results in an octet of electrons around each atom. Nitrogen requires three additional electrons to complete its octet, and fluorine requires one. Sharing a pair of electrons between one N atom and one F atom will result in an octet of electrons for fluorine but not for nitrogen. We therefore need to figure out a way to get two more electrons for the N atom.

Solve Nitrogen must share a pair of electrons with three fluorine atoms to complete its octet. Thus, the binary compound these two elements form must be NF_3:



Check The Lewis structure in the center shows that each atom is surrounded by an octet of electrons. Once you are accustomed to thinking of each line in a Lewis structure as representing *two* electrons, you can just as easily use the structure on the right to check for octets.

Practice Exercise 1

Which of these molecules has the same number of shared electron pairs as unshared electron pairs?
(a) HCl **(b)** H_2S **(c)** PF_3 **(d)** CCl_2F_2 **(e)** Br_2

Practice Exercise 2

Compare the Lewis symbol for neon with the Lewis structure for methane, CH_4. How many valence electrons are in each structure? How many bonding pairs and how many nonbonding pairs does each structure have?

Multiple Bonds

A shared electron pair constitutes a single covalent bond, generally referred to simply as a **single bond**. In many molecules, atoms attain complete octets by sharing more than one pair of electrons. When two electron pairs are shared by two atoms, two lines are drawn in the Lewis structure, representing a **double bond**. In carbon dioxide, for example, bonding occurs between carbon, with four valence electrons, and oxygen, with six:

$$:\ddot{O}: + \cdot\dot{C}\cdot + :\ddot{O}: \longrightarrow \ddot{O}::C::\ddot{O} \qquad (\text{or } \ddot{O}{=}C{=}\ddot{O})$$

As the diagram shows, each oxygen atom acquires an octet by sharing two electron pairs with carbon. In the case of CO_2, carbon acquires an octet by sharing two electron pairs with each of the two oxygen atoms; each double bond involves four electrons.

A **triple bond** corresponds to the sharing of three pairs of electrons, such as in the N_2 molecule:

$$:\dot{N}\cdot + \cdot\dot{N}: \longrightarrow :N:::N: \qquad (\text{or } :N{\equiv}N:)$$

Because each nitrogen atom has five valence electrons, three electron pairs must be shared to achieve the octet configuration.

The properties of N_2 are in complete accord with its Lewis structure. Nitrogen is a diatomic gas with exceptionally low reactivity that results from the very stable nitrogen–nitrogen bond. The nitrogen atoms are separated by only 1.10 Å. The short separation distance between the two N atoms is a result of the triple bond between the atoms. From studies of the structures of many different substances in which nitrogen atoms share one or two electron pairs, we have learned that the average distance between bonded nitrogen atoms varies with the number of shared electron pairs:

N—N	N=N	N≡N
1.47 Å	1.24 Å	1.10 Å

As a general rule, the length of the bond between two atoms decreases as the number of shared electron pairs increases. We will explore this point in greater detail in Section 8.8.

Give It Some Thought

The C—O bond length in carbon monoxide, CO, is 1.13 Å, whereas the C—O bond length in CO_2 is 1.24 Å. Without drawing a Lewis structure, do you think that CO contains a single, double, or triple bond?

8.4 Bond Polarity and Electronegativity

When two identical atoms bond, as in Cl_2 or H_2, the electron pairs must be shared equally. When two atoms from opposite sides of the periodic table bond, such as NaCl, there is relatively little sharing of electrons, which means that NaCl is best described as an ionic compound composed of Na^+ and Cl^- ions. The 3*s* electron of the Na atom is, in effect, transferred completely to chlorine. The bonds that are found in most substances fall somewhere between these extremes.

Bond polarity is a measure of how equally or unequally the electrons in any covalent bond are shared. A **nonpolar covalent bond** is one in which the electrons are shared equally, as in Cl_2 and N_2. In a **polar covalent bond**, one of the atoms exerts a greater attraction for the bonding electrons than the other. If the difference in relative ability to attract electrons is large enough, an ionic bond is formed.

Electronegativity

We use a quantity called electronegativity to estimate whether a given bond is nonpolar covalent, polar covalent, or ionic.

Electronegativity is defined as the ability of an atom *in a molecule* to attract electrons to itself.

The greater an atom's electronegativity, the greater its ability to attract electrons to itself. The electronegativity of an atom in a molecule is related to the atom's ionization energy and electron affinity, which are properties of isolated atoms. An atom with a very negative electron affinity and a high ionization energy both attracts electrons from other atoms and resists having its electrons attracted away; therefore, it is highly electronegative.

Electronegativity values can be based on a variety of properties, not just ionization energy and electron affinity. The American chemist Linus Pauling (1901–1994) developed the first and most widely used electronegativity scale, which is based on thermochemical data. As **Figure 8.8** shows, there is generally an increase in electronegativity from left to right across a period—that is, from the most metallic to the most nonmetallic elements. With some exceptions (especially in the transition metals), electronegativity decreases with increasing atomic number in a group. This is what we expect because we know that ionization energies decrease with increasing atomic number in a group and electron affinities do not change very much.

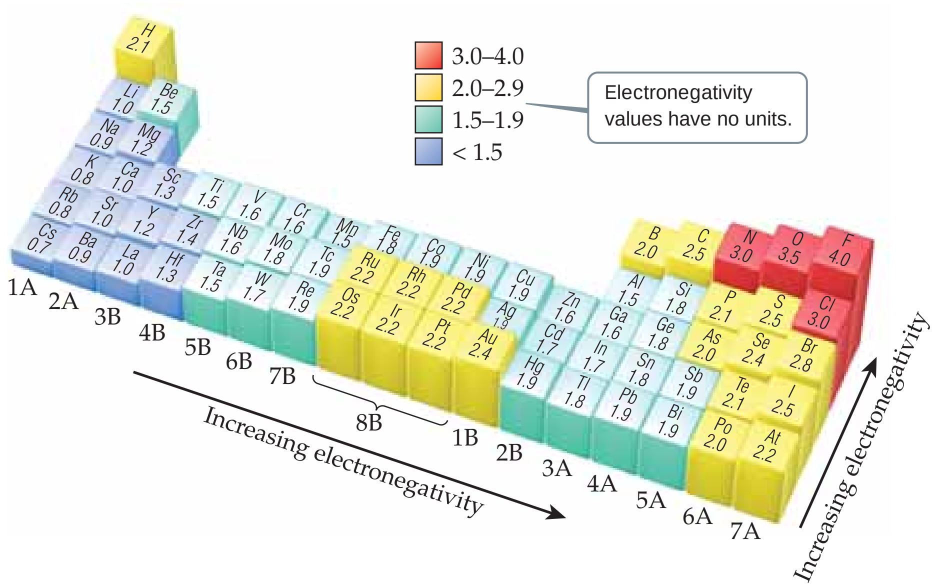
You do not need to memorize electronegativity values. Instead, you should know the periodic trends so that you can predict which of two elements is more electronegative.

Give It Some Thought

How does the *electronegativity* of an element differ from its *electron affinity*?

Go Figure

For the group 6A elements, what is the trend in electronegativity with increasing atomic number?



▲ **Figure 8.8** **Electronegativity values based on Pauling's thermochemical data.**

Electronegativity and Bond Polarity

We can use the difference in electronegativity between two atoms to gauge the polarity of the bond the atoms form. Consider these three fluorine-containing compounds:

	F_2	HF	LiF
Electronegativity difference	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
Type of bond	Nonpolar covalent	Polar covalent	Ionic

In F_2 the electrons are shared equally between the fluorine atoms and, thus, the covalent bond is *nonpolar*. A nonpolar covalent bond results when the electronegativities of the bonded atoms are equal.

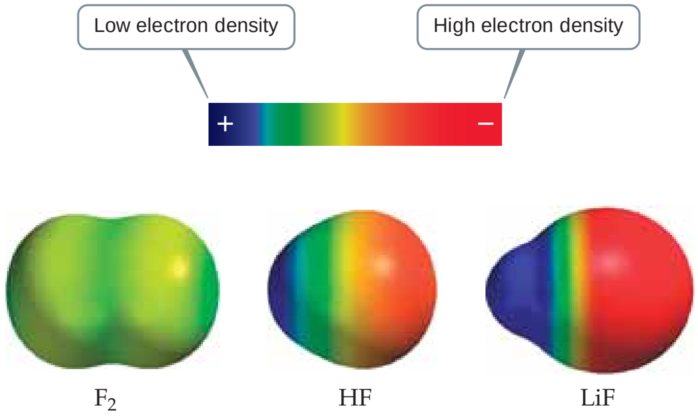
In HF the fluorine atom has a greater electronegativity than the hydrogen atom, with the result that the electrons are shared unequally—the bond is *polar*. In general, a polar covalent bond results when the atoms differ in electronegativity. In HF the more electronegative fluorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the fluorine atom. We can represent this charge distribution as

$$\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{F}}$$

The $\delta+$ and $\delta-$ (read "delta plus" and "delta minus") symbolize the partial positive and negative charges, respectively. In a polar bond, these numbers are less than the full charges of the ions.

In LiF the electronegativity difference is very large, meaning that the electron density is shifted far toward F. The resulting bond is therefore most accurately described as *ionic*. Thus, if we considered the bond in LiF to be fully ionic, we could say $\delta+$ for Li is $1+$ and $\delta-$ for F is $1-$. If two atoms differ in electronegativity by more than 2.0, many chemists would consider their bond to be an ionic bond.

The shift of electron density toward the more electronegative atom in a bond can be seen from the results of calculations of electron-density distributions. For the three species in our example, the calculated electron-density distributions are shown



◀ **Figure 8.9 Electron-density distribution.** This computer-generated rendering shows the calculated electron-density distribution on the surface of the F_2, HF, and LiF molecules.

in **Figure 8.9**. You can see that in F_2 the distribution is symmetrical, in HF the electron density is clearly shifted toward fluorine, and in LiF the shift is even greater. These examples illustrate, therefore, that *the greater the difference in electronegativity between two atoms, the more polar their bond.*

Sample Exercise 8.4

Bond Polarity

In each case, which bond is more polar? (**a**) B—Cl or C—Cl, (**b**) P—F or P—Cl. Indicate in each case which atom has the partial negative charge.

SOLUTION

Analyze We are asked to determine relative bond polarities, given nothing but the atoms involved in the bonds.

Plan Because we are not asked for quantitative answers, we can use the periodic table and our knowledge of electronegativity trends to answer the question.

Solve

(**a**) The chlorine atom is common to both bonds. Therefore, we just need to compare the electronegativities of B and C. Because boron is to the left of carbon in the periodic table, we predict that boron has the lower electronegativity. Chlorine, being on the right side of the table, has high electronegativity. The more polar bond will be the one between the atoms with the biggest differences in electronegativity. Consequently, the B—Cl bond is more polar; the chlorine atom carries the partial negative charge because it has a higher electronegativity.

(**b**) In this example, phosphorus is common to both bonds, and so we just need to compare the electronegativities of F and Cl. Because fluorine is above chlorine in the periodic table, it should be more electronegative and will form the more polar bond with P. The higher electronegativity of fluorine means that it will carry the partial negative charge.

Check

(**a**) Using Figure 8.8: The difference in the electronegativities of chlorine and boron is $3.0 - 2.0 = 1.0$; the difference between the electronegativities of chlorine and carbon is $3.0 - 2.5 = 0.5$. Hence, the B—Cl bond is more polar, as we had predicted.

(**b**) Using Figure 8.8: The difference in the electronegativities of chlorine and phosphorus is $3.0 - 2.1 = 0.9$; the difference between the electronegativities of fluorine and phosphorus is $4.0 - 2.1 = 1.9$. Hence, the P—F bond is more polar, as we had predicted.

▶ Practice Exercise 1

Which of the following bonds is the most polar?
(**a**) H—F (**b**) H—I (**c**) Se—F (**d**) N—P (**e**) Ga—Cl

▶ Practice Exercise 2

Which of the following bonds is most polar: S—Cl, S—Br, Se—Cl, or Se—Br?

Dipole Moments

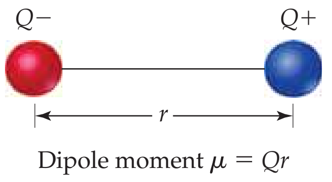
The difference in electronegativity between H and F leads to a polar covalent bond in the HF molecule. As a consequence, there is a concentration of negative charge on the more electronegative F atom, leaving the less electronegative H atom at the positive end of the molecule. A molecule such as HF, in which the centers of positive and negative charge do not coincide, is a **polar molecule**. Thus, we describe both bonds and entire molecules as being polar and nonpolar.

We can indicate the polarity of the HF molecule in two ways:

$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}} \quad \textit{or} \quad \overset{+\!\!\longrightarrow}{\mathrm{H}-\mathrm{F}}$$

Go Figure

If the charged particles are moved closer together, does μ increase, decrease, or stay the same?



▲ **Figure 8.10 Dipole and dipole moment.** When charges of equal magnitude and opposite sign $Q+$ and $Q-$ are separated by a distance r, a dipole is produced.

In the notation on the right, the arrow denotes the shift in electron density toward the fluorine atom. The crossed end of the arrow can be thought of as a plus sign designating the positive end of the molecule.

Polarity helps determine many properties we observe at the macroscopic level in the laboratory and in everyday life. Polar molecules align themselves with respect to one another, with the negative end of one molecule and the positive end of another attracting each other. Polar molecules are likewise attracted to ions. The negative end of a polar molecule is attracted to a positive ion, and the positive end is attracted to a negative ion. These interactions account for many properties of liquids, solids, and solutions, as you will see in Chapters 11, 12, and 13. Charge separation within molecules plays an important role in energy conversion processes such as photosynthesis and in solar cells.

How can we quantify the polarity of a molecule? Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. The quantitative measure of the magnitude of a dipole is called its **dipole moment**, denoted with the Greek letter mu, μ. If two equal and opposite charges $Q+$ and $Q-$ are separated by a distance r, as in **Figure 8.10**, the magnitude of the dipole moment is the product of Q and r:

$$\mu = Qr \qquad [8.10]$$

This expression tells us that the dipole moment increases as the magnitude of Q increases and as r increases. The larger the dipole moment, the more polar the bond. For a nonpolar molecule, such as F_2, the dipole moment is zero because there is no charge separation.

Give It Some Thought

Chlorine monofluoride, ClF, and iodine monofluoride, IF, are *interhalogen* compounds—compounds that contain bonds between different halogen elements. Which of these molecules has the larger dipole moment?

Dipole moments are experimentally measurable and are usually reported in *debyes* (D), a unit that equals 3.34×10^{-30} coulomb-meters (C-m). For molecules, we usually measure charge in units of the electronic charge e, 1.60×10^{-19} C, and distance in angstroms. This means we need to convert units whenever we want to report a dipole moment in debyes. Suppose that two charges 1+ and 1− (in units of e) are separated by 1.00 Å. The dipole moment produced is

Throughout the text, strikethroughs are used to show how units cancel when the solution is properly set up — **reinforcing dimensional analysis skills.**

$$\mu = Qr = (1.60 \times 10^{-19}\cancel{\text{C}})(1.00\cancel{\text{Å}})\left(\frac{10^{-10}\,\cancel{\text{m}}}{1\,\cancel{\text{Å}}}\right)\left(\frac{1\text{ D}}{3.34 \times 10^{-30}\,\cancel{\text{C-m}}}\right) = 4.79\text{ D}$$

Measurement of the dipole moments can provide us with valuable information about the charge distributions in molecules, as illustrated in Sample Exercise 8.5.

Sample Exercise 8.5

Dipole Moments of Diatomic Molecules

The bond length in the HCl molecule is 1.27 Å. (**a**) Calculate the dipole moment, in debyes, that results if the charges on the H and Cl atoms were 1+ and 1− respectively. (**b**) The experimentally measured dipole moment of HCl(g) is 1.08 D. What magnitude of charge, in units of e, on the H and Cl atoms leads to this dipole moment?

SOLUTION

Analyze and Plan We are asked in part (a) to calculate the dipole moment of HCl that would result if there were a full charge transferred from H to Cl. We can use Equation 8.10 to obtain this result. In part (b), we are given the actual dipole moment for the molecule and will use that value to calculate the actual partial charges on the H and Cl atoms.

Solve

(**a**) The charge on each atom is the electronic charge, $e = 1.60 \times 10^{-19}$ C. The separation is 1.27 Å. The dipole moment is therefore:

$$\mu = Qr = (1.60 \times 10^{-19}\,\cancel{C})(1.27\,\cancel{\mathring{A}})\left(\frac{10^{-10}\,\cancel{m}}{1\,\cancel{\mathring{A}}}\right)\left(\frac{1\,D}{3.34 \times 10^{-30}\,\cancel{C\text{-}m}}\right) = 6.08\,D$$

(**b**) We know the value of μ, 1.08 D, and the value of r, 1.27 Å. We want to calculate the value of Q:

$$Q = \frac{\mu}{r} = \frac{(1.08\,\cancel{D})\left(\dfrac{3.34 \times 10^{-30}\,C\text{-}\cancel{m}}{1\,\cancel{D}}\right)}{(1.27\,\cancel{\mathring{A}})\left(\dfrac{10^{-10}\,\cancel{m}}{1\,\cancel{\mathring{A}}}\right)} = 2.84 \times 10^{-20}\,C$$

We can readily convert this charge to units of e:

$$\text{Charge in } e = (2.84 \times 10^{-20}\,\cancel{C})\left(\frac{1e}{1.60 \times 10^{-19}\,\cancel{C}}\right) = 0.178e$$

Thus, the experimental dipole moment indicates that the charge separation in the HCl molecule is:

$$\overset{0.178+}{\mathrm{H}}\text{—}\overset{0.178-}{\mathrm{Cl}}$$

Because the experimental dipole moment is less than that calculated in part (a), the charges on the atoms are much less than a full electronic charge. We could have anticipated this because the H—Cl bond is polar covalent rather than ionic.

▶ Practice Exercise 1

What is the dipole moment for HF (bond length 0.917 Å), assuming that the bond is completely ionic?
(**a**) 0.917 D (**b**) 1.91 D (**c**) 2.75 D (**d**) 4.39 D (**e**) 7.37 D

▶ Practice Exercise 2

The dipole moment of chlorine monofluoride, ClF(g), is 0.88 D. The bond length of the molecule is 1.63 Å. (**a**) Which atom is expected to have the partial negative charge? (**b**) What is the charge on that atom in units of e?

Table 8.2 presents the bond lengths and dipole moments of the hydrogen halides. Notice that as we proceed from HF to HI, the electronegativity difference decreases and the bond length increases. The first effect decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI, even though the bond length is increasing. Calculations identical to those used in Sample Exercise 8.5 show that the charges on the atoms decrease from 0.41+ and 0.41− in HF to 0.057+ and 0.057− in HI. We can visualize the varying degree of electronic charge shift in these substances from computer-generated renderings based on calculations of electron distribution, as shown in **Figure 8.11**. For these molecules, the change in the electronegativity difference has a greater effect on the dipole moment than does the change in bond length.

Practice Exercises
Each Sample Exercise has two related Practice Exercises, Practice Exercise 1 and Practice Exercise 2. PE1 is always a multiple choice question that can be assigned in MasteringChemistry. These problems contain specific wrong answer feedback to help students think critically and make learning gains while problem solving. PE2 is similar to PE1 but usually requires a math-based solution to get the correct answer.

Give It Some Thought

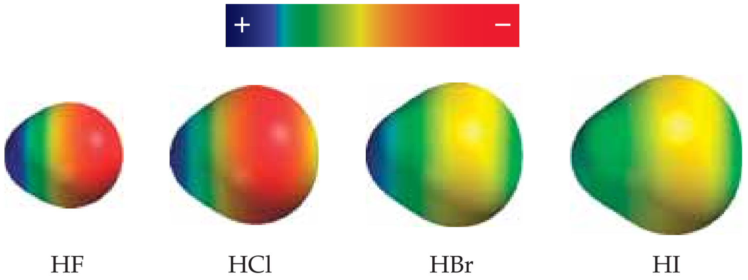
The bond between carbon and hydrogen is one of the most important types of bonds in chemistry. The length of an H—C bond is approximately 1.1 Å. Based on this distance and differences in electronegativity, do you expect the dipole moment of an individual H—C bond to be larger or smaller than that of an H—I bond?

TABLE 8.2 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

Go Figure

As you go from HF to HI, does the H—X bond become more or less polar?



▲ **Figure 8.11** **Charge separation in the hydrogen halides.** In HF, the strongly electronegative F pulls much of the electron density away from H. In HI, the I, being much less electronegative than F, does not attract the shared electrons as strongly, and, consequently, there is far less polarization of the bond.

Before leaving this section, let's return to the LiF molecule in Figure 8.9. Under standard conditions, LiF exists as an ionic solid with an arrangement of atoms analogous to the sodium chloride structure shown in Figure 8.4. However, it is possible to generate LiF *molecules* by vaporizing the ionic solid at high temperature. The molecules have a dipole moment of 6.28 D and a bond distance of 1.53 Å. From these values we can calculate the charge on lithium and fluorine to be 0.857+ and 0.857−, respectively. This bond is extremely polar, and the presence of such large charges strongly favors the formation of an extended ionic lattice in which each lithium ion is surrounded by fluoride ions and vice versa. But even here, the experimentally determined charges on the ions are still not 1+ and 1−. This tells us that even in ionic compounds, there is still some covalent contribution to the bonding.

Comparing Ionic and Covalent Bonding

To understand the interactions responsible for chemical bonding, it is advantageous to treat ionic and covalent bonding separately. That is the approach taken in this chapter, as well as in most other undergraduate-level chemistry texts. In reality, however, there is a continuum between the extremes of ionic and covalent bonding. This lack of a well-defined separation between the two types of bonding may seem unsettling or confusing at first.

The simple models of ionic and covalent bonding presented in this chapter go a long way toward understanding and predicting the structures and properties of chemical compounds. When covalent bonding is dominant, we expect compounds to exist as molecules,* having all the properties we associate with molecular substances, such as relatively low melting and boiling points and nonelectrolyte behavior when dissolved in water. When ionic bonding is dominant, we expect the compounds to be brittle, high-melting solids with extended lattice structures, exhibiting strong electrolyte behavior when dissolved in water.

Naturally, there are exceptions to these general characterizations, some of which we examine later in the book. Nonetheless, the ability to quickly categorize the predominant bonding interactions in a substance as covalent or ionic imparts considerable insight into the properties of that substance. The question then becomes the best way to recognize which type of bonding dominates.

The simplest approach is to assume that the interaction between a metal and a nonmetal is ionic and that between two nonmetals is covalent. While this classification scheme is reasonably predictive, there are far too many exceptions to use it blindly. For example, tin is a metal and chlorine is a nonmetal, but $SnCl_4$ is a molecular substance that exists as a colorless liquid at room temperature. It freezes at −33 °C and boils at 114 °C. The characteristics of $SnCl_4$ are not those typical of an ionic substance. Is there a more predictable way of determining what type of bonding is prevalent in a compound? A more sophisticated approach is to use the difference in electronegativity as the main criterion for determining whether ionic or covalent bonding will be dominant. This

---

* There are some exceptions to this statement, such as network solids, including diamond, silicon, and germanium, where an extended structure is formed even though the bonding is clearly covalent. These substances are discussed in Section 12.7.

approach correctly predicts the bonding in $SnCl_4$ to be polar covalent based on an electronegativity difference of 1.2 and at the same time correctly predicts the bonding in NaCl to be predominantly ionic based on an electronegativity difference of 2.1.

Evaluating bonding based on electronegativity difference is a useful system, but it has one shortcoming. The electronegativity values given in Figure 8.8 do not take into account changes in bonding that accompany changes in the oxidation state of the metal. For example, Figure 8.8 gives the electronegativity difference between manganese and oxygen as $3.5 - 1.5 = 2.0$, which falls in the range where the bonding is normally considered ionic (the electronegativity difference for NaCl is $3.0 - 0.9 = 2.1$). Therefore, it is not surprising to learn that manganese(II) oxide, MnO, is a green solid that melts at 1842 °C and has the same crystal structure as NaCl.

However, the bonding between manganese and oxygen is not always ionic. Manganese(VII) oxide, Mn_2O_7, is a green liquid that freezes at 5.9 °C, an indication that covalent rather than ionic bonding dominates. The change in the oxidation state of manganese is responsible for the change in bonding. In general, as the oxidation state of a metal increases, so does the degree of covalent bonding. When the oxidation state of the metal is highly positive (roughly speaking, +4 or larger), we can expect significant covalency in the bonds it forms with nonmetals. Thus, metals in high oxidation states form molecular substances, such as Mn_2O_7, or polyatomic ions, such as MnO_4^- and CrO_4^{2-}, rather than ionic compounds.

Give It Some Thought

You have a yellow solid that melts at 41 °C and boils at 131 °C and a green solid that melts at 2320 °C. If you are told that one of them is Cr_2O_3 and the other is OsO_4, which one do you expect to be the yellow solid?

8.5 | Drawing Lewis Structures

Lewis structures can help us understand the bonding in many compounds and are frequently used when discussing the properties of molecules. For this reason, drawing Lewis structures is an important skill that you should practice.

New! *How to ...* features in select chapters emphasize important skills and outline how to implement them. Students will find the features are easy to locate and easy to follow.

How to Draw Lewis Structures

1. **Sum the valence electrons from all atoms, taking into account overall charge.** Use the periodic table to help you determine the number of valence electrons in each atom. For an anion, add one electron to the total for each negative charge. For a cation, subtract one electron from the total for each positive charge. Do not worry about keeping track of which electrons come from which atoms. Only the total number is important.
2. **Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond (*a line, representing* two *electrons*).** Chemical formulas are often written in the order in which the atoms are connected in the molecule or ion. The formula HCN, for example, tells you that the carbon atom is bonded to the H and to the N. In many polyatomic molecules and ions, the central atom is usually written first, as in CO_3^{2-} and SF_4. Remember that the central atom is generally less electronegative than the atoms surrounding it. In other cases, you may need more information before you can draw the Lewis structure.
3. **Complete the octets around all the atoms bonded to the central atom.** Keep in mind that a hydrogen atom has only a single pair of electrons around it.
4. **Place any remaining electrons on the central atom,** even if doing so results in more than an octet of electrons around the atom.
5. **If there are not enough electrons to give the central atom an octet, try multiple bonds.** Use one or more of the unshared pairs of electrons on the atoms bonded to the central atom to form double or triple bonds.

The following examples of this procedure will help you put it into practice.

Sample Exercise 8.6

Drawing a Lewis Structure

Draw the Lewis structure for phosphorus trichloride, PCl_3.

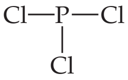
SOLUTION

Analyze and Plan We are asked to draw a Lewis structure from a molecular formula. Our plan is to follow the five-step procedure just described.

Solve First, we sum the valence electrons. Phosphorus (group 5A) has five valence electrons, and each chlorine (group 7A) has seven. The total number of valence electrons is therefore

$$5 + (3 \times 7) = 26$$

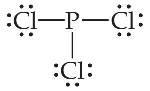
Second, we arrange the atoms to show which atom is connected to which, and we draw a single bond between them. There are various ways the atoms might be arranged. It helps to know, though, that in binary compounds the first element in the chemical formula is generally surrounded by the remaining atoms. So we proceed to draw a skeleton structure in which a single bond connects the P atom to each Cl atom:



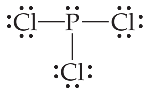
$$\begin{array}{c} Cl-P-Cl \\ | \\ Cl \end{array}$$

(It is not crucial that the Cl atoms be to the left of, right of, and below the P atom—any structure that shows each of the three Cl atoms bonded to P will work.)

Third, we add Lewis electron dots to complete the octets on the atoms bonded to the central atom. Completing the octets around each Cl atom accounts for 24 electrons (remember, each line in our structure represents *two* electrons):



Fourth, recalling that our total number of electrons is 26, we place the remaining two electrons on the central atom, P, which completes its octet:



This structure gives each atom an octet, so we stop at this point. (In checking for octets, remember to count a single bond as two electrons.)

Practice Exercise 1

Which of these molecules has a Lewis structure with a central atom having no nonbonding electron pairs?
(a) CO_2 **(b)** H_2S **(c)** PF_3 **(d)** SiF_4 **(e)** more than one of a, b, c, d

Practice Exercise 2

(a) How many valence electrons should appear in the Lewis structure for CH_2Cl_2?
(b) Draw the Lewis structure.

Sample Exercise 8.7

Lewis Structure with a Multiple Bond

Draw the Lewis structure for HCN.

SOLUTION

Hydrogen has one valence electron, carbon (group 4A) has four, and nitrogen (group 5A) has five. The total number of valence electrons is, therefore, $1 + 4 + 5 = 10$. In principle, there are different ways in which we might choose to arrange the atoms. Because hydrogen can accommodate only one electron pair, it always has only one single bond associated with it. Therefore, $C-H-N$ is an impossible arrangement. The remaining two possibilities are $H-C-N$ and $H-N-C$. The first is the arrangement found experimentally. You might have guessed this because the formula is written with the atoms in this order, and carbon is less electronegative than nitrogen. Thus, we begin with the skeleton structure

$$H-C-N$$

The two bonds account for four electrons. The H atom can have only two electrons associated with it, and so we will not add any more electrons to it. If we place the remaining six electrons around N to give it an octet, we do not achieve an octet on C:

$$H-C-\underset{\cdot\cdot}{\ddot{N}}:$$

We therefore try a double bond between C and N, using one of the unshared pairs we placed on N. Again we end up with fewer than eight electrons on C, and so we next try a triple bond. This structure gives an octet around both C and N:

The octet rule is satisfied for the C and N atoms, and the H atom has two electrons around it. This is a correct Lewis structure.

Practice Exercise 1

Draw the Lewis structure(s) for the molecule with the chemical formula C_2H_3N, where the N is connected to only one other atom. How many double bonds are there in the correct Lewis structure?
(a) zero **(b)** one **(c)** two **(d)** three **(e)** four

Practice Exercise 2

Draw the Lewis structure for **(a)** NO^+ ion, **(b)** C_2H_4.

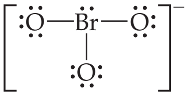
Sample Exercise 8.8

Lewis Structure for a Polyatomic Ion

Draw the Lewis structure for the BrO_3^- ion.

SOLUTION

Bromine (group 7A) has seven valence electrons, and oxygen (group 6A) has six. We must add one more electron to our sum to account for the 1− charge of the ion. The total number of valence electrons is, therefore, $7 + (3 \times 6) + 1 = 26$. For oxyanions—$SO_4^{2-}$, NO_3^-, CO_3^{2-}, and so forth—the oxygen atoms surround the central nonmetal atom. After arranging the O atoms around the Br atom, drawing single bonds, and distributing the unshared electron pairs, we have



Notice that the Lewis structure for an ion is written in brackets and the charge is shown outside the brackets at the upper right.

Practice Exercise 1

How many nonbonding electron pairs are there in the Lewis structure of the peroxide ion, O_2^{2-}?
(a) 7 **(b)** 6 **(c)** 5 **(d)** 4 **(e)** 3

Practice Exercise 2

Draw the Lewis structure for **(a)** ClO_2^-, **(b)** PO_4^{3-}.

Formal Charge and Alternative Lewis Structures

When we draw a Lewis structure, we are describing how the electrons are distributed in a molecule or polyatomic ion. In some instances, we can draw two or more valid Lewis structures for a molecule that all obey the octet rule. All of these structures can be thought of as contributing to the *actual* arrangement of the electrons in the molecule, but not all of them will contribute to the same extent. How do we decide which one of several Lewis structures is the most important? One approach is to do some “bookkeeping” of the valence electrons to determine the *formal charge* of each atom in each Lewis structure. The **formal charge** of any atom in a molecule is the charge the atom would have if each bonding electron pair in the molecule were shared equally between its two atoms.

How to Calculate the Formal Charges of Atoms in Lewis Structures

1. *All* unshared (nonbonding) electrons are assigned to the atom on which they are found.
2. For any bond—single, double, or triple—*half* of the bonding electrons are assigned to each atom in the bond.
3. The formal charge of each atom is calculated by subtracting the number of electrons assigned to the atom from the number of valence electrons in the neutral atom:

$$\textbf{Formal charge} = \text{valence electrons} - \tfrac{1}{2}(\text{bonding electrons}) - \text{nonbonding electrons} \qquad [8.11]$$

Let’s practice by calculating the formal charges for the atoms in the cyanide ion, CN^-, which has the Lewis structure

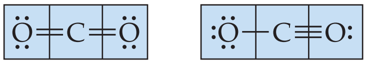
$$[:C\equiv N:]^-$$

The neutral C atom has four valence electrons. There are six electrons in the cyanide triple bond and two nonbonding electrons on C. We calculate the formal charge on C as $4 - \frac{1}{2}(6) - 2 = -1$. For N, the valence electron count is five; there are six electrons in the cyanide triple bond, and two nonbonding electrons on the N. The formal charge on N is $5 - \frac{1}{2}(6) - 2 = 0$. We can draw the whole ion with its formal charges as

$$[:\overset{-1}{C}\equiv\overset{0}{N}:]^-$$

Notice that the sum of the formal charges equals the overall charge on the ion, 1−. The formal charges on a neutral molecule must add to zero, whereas those on an ion add to give the charge on the ion.

If we can draw several Lewis structures for a molecule, the concept of formal charge can help us decide which is the most important, which we shall call the *dominant* Lewis structure. One Lewis structure for CO_2, for instance, has two double bonds. However, we can also satisfy the octet rule by drawing a Lewis structure having one single bond and one triple bond. Calculating formal charges in these structures, we have


$\ddot{\underset{\cdot\cdot}{O}}=C=\ddot{\underset{\cdot\cdot}{O}}$ $\quad :\ddot{\underset{\cdot\cdot}{O}}-C\equiv O:$

	$\ddot{\underset{\cdot\cdot}{O}}$	$=C=$	$\ddot{\underset{\cdot\cdot}{O}}$	$:\ddot{\underset{\cdot\cdot}{O}}$	$-C\equiv$	$O:$
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

Note that in both cases the formal charges add up to zero, as they must because CO_2 is a neutral molecule. So, which is the dominant structure? As a general rule, when more than one Lewis structure is possible, we will use the following guidelines to choose the dominant one:

How to Identify the Dominant Lewis Structure

1. The dominant Lewis structure is generally the one in which the atoms bear formal charges closest to zero.
2. A Lewis structure in which any negative charges reside on the more electronegative atoms is generally more dominant than one that has negative charges on the less electronegative atoms.

Thus, the first Lewis structure of CO_2 is the dominant one because the atoms carry no formal charges and so satisfy the first guideline. The other Lewis structure shown (and the similar one that has a triple bond to the left O and a single bond to the right O) contribute to the actual structure to a much smaller extent.

Although the concept of formal charge helps us to arrange alternative Lewis structures in order of importance, it is important to remember that *formal charges do not represent real charges on atoms*. These charges are just a bookkeeping convention. The actual charge distributions in molecules and ions are determined not by formal charges but by a number of other factors, including electronegativity differences between atoms.

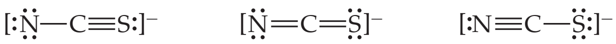
Give It Some Thought

Suppose a Lewis structure for a neutral fluorine-containing molecule results in a formal charge of +1 on the fluorine atom. What conclusion would you draw?

Sample Exercise 8.9

Lewis Structures and Formal Charges

Three possible Lewis structures for the thiocyanate ion, NCS^-, are

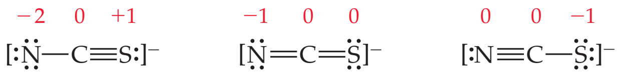

$[:\ddot{\underset{\cdot\cdot}{N}}-C\equiv S:]^-$ $\quad [\ddot{\underset{\cdot\cdot}{N}}=C=\ddot{\underset{\cdot\cdot}{S}}]^-$ $\quad [:N\equiv C-\ddot{\underset{\cdot\cdot}{S}}:]^-$

(**a**) Determine the formal charges in each structure.

(**b**) Based on the formal charges, which Lewis structure is the dominant one?

SOLUTION

(**a**) Neutral N, C, and S atoms have five, four, and six valence electrons, respectively. We can determine the formal charges in the three structures by using the rules we just discussed:


$\overset{-2}{[:\ddot{\underset{\cdot\cdot}{N}}}-\overset{0}{C}\equiv\overset{+1}{S}:]^-$ $\quad \overset{-1}{[\ddot{\underset{\cdot\cdot}{N}}}=\overset{0}{C}=\overset{0}{\ddot{\underset{\cdot\cdot}{S}}}]^-$ $\quad \overset{0}{[:N}\equiv\overset{0}{C}-\overset{-1}{\ddot{\underset{\cdot\cdot}{S}}}:]^-$

As they must, the formal charges in all three structures sum to 1−, the overall charge of the ion.

(**b**) The dominant Lewis structure generally produces formal charges of the smallest magnitude (guideline 1). That eliminates the left structure as the dominant one. Further, as discussed in Section 8.4, N is more electronegative than C or S. Therefore, we expect any negative formal charge to reside on the N atom (guideline 2). For these two reasons, the middle Lewis structure is the dominant one for NCS^-.

▶ Practice Exercise 1

The sulfate ion, SO_4^{2-}, can be drawn in many ways. If you minimize formal charge on the sulfur, how many $S{=}O$ double bonds should you draw in the Lewis structure?
(a) 0 **(b)** 1 **(c)** 2 **(d)** 3 **(e)** 4

▶ Practice Exercise 2

The cyanate ion, NCO^-, has three possible Lewis structures. **(a)** Draw these three structures and assign formal charges in each. **(b)** Which Lewis structure is dominant?

A CLOSER LOOK Oxidation Numbers, Formal Charges, and Actual Partial Charges

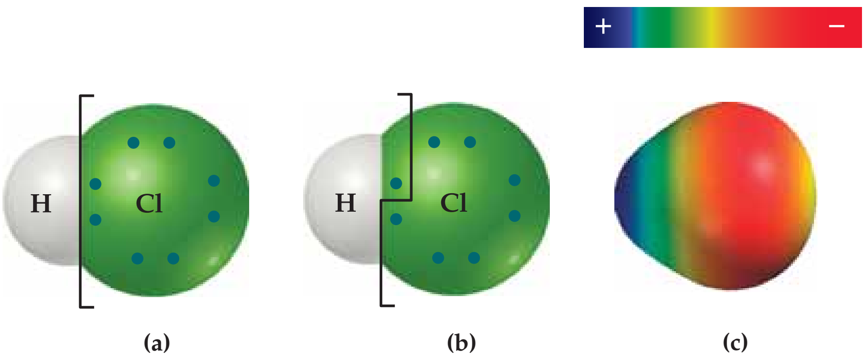
In Chapter 4 we introduced the rules for assigning *oxidation numbers* to atoms. The concept of electronegativity is the basis of these numbers. An atom's oxidation number is the charge the atom would have if its bonds were completely ionic. That is, in determining oxidation number, all shared electrons are counted with the more electronegative atom. For example, consider the Lewis structure of HCl in **Figure 8.12**(**a**). To assign oxidation numbers, both electrons in the covalent bond between the atoms are assigned to the more electronegative Cl atom. This procedure gives Cl eight valence electrons, one more than in the neutral atom. Thus, its oxidation number is −1. Hydrogen has no valence electrons when they are counted this way, giving it an oxidation number of +1.

In assigning formal charges to the atoms in HCl [Figure 8.12(b)], we ignore electronegativity; the electrons in bonds are assigned equally to the two bonded atoms. In this case Cl has seven assigned electrons, the same as that of the neutral Cl atom, and H has one assigned electron. Thus, the formal charges of both Cl and H in this compound are 0.

Neither oxidation number nor formal charge gives an accurate depiction of the actual charges on atoms because oxidation numbers overstate the role of electronegativity and formal charges ignore it. It seems reasonable that electrons in covalent bonds should be apportioned according to the relative electronegativities of the bonded atoms. Figure 8.8 (page 310) shows that Cl has an electronegativity of 3.0, while the electronegativity value of H is 2.1. The more electronegative Cl atom might therefore be expected to have roughly $3.0/(3.0 + 2.1) = 0.59$ of the electrical charge in the bonding pair, whereas the H atom would have $2.1/(3.0 + 2.1) = 0.41$ of the charge. Because the bond consists of two electrons, the Cl atom's share is $0.59 \times 2e = 1.18e$, or $0.18e$ more than the neutral Cl atom. This gives rise to a partial negative charge of 0.18− on Cl and therefore a partial positive charge of 0.18+ on H. (Notice again that we place the plus and minus signs *before* the magnitude in writing oxidation numbers and formal charges but *after* the magnitude in writing actual charges.)

The dipole moment of HCl gives an experimental measure of the partial charge on each atom. In Sample Exercise 8.5 we saw that the dipole moment of HCl corresponds to a partial charge of 0.178+ on H and 0.178− on Cl, in remarkably good agreement with our simple approximation based on electronegativities. Although our approximation method provides ballpark numbers for the magnitude of charge on atoms, the relationship between electronegativities and charge separation is generally more complicated. As we have already seen, computer programs employing quantum-mechanical principles have been developed to obtain more accurate estimates of the partial charges on atoms, even in complex molecules. A computer-graphical representation of the calculated charge distribution in HCl is shown in Figure 8.12(c).

Related Exercises: 8.8, 8.49–8.52, 8.86, 8.87, 8.90, 8.91



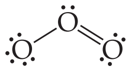
▲ **Figure 8.12** **(a) Oxidation number, (b) formal charge, and (c) electron-density distribution for the HCl molecule.**

Updated Features The four feature types in 14e — **A Closer Look, Chemistry and Life, Chemistry Put to Work, and Strategies For Success** — offer a more detailed exploration of important topics. Select features were replaced or updated to explore topics from recent events and newer technologies. Also, a list of Related Exercises at the end of each feature allows students to check their understanding.

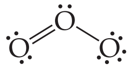
8.6 | Resonance Structures

We sometimes encounter molecules and ions in which the experimentally determined arrangement of atoms is not adequately described by a single dominant Lewis structure. Consider ozone, O_3, which is a bent molecule with two equal O—O bond lengths

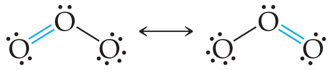
(**Figure 8.13**). Because each oxygen atom contributes 6 valence electrons, the ozone molecule has 18 valence electrons. This means the Lewis structure must have one O—O single bond and one O═O double bond to attain an octet about each atom:



However, this single structure cannot by itself be dominant because it requires that one O—O bond be different from the other, contrary to the observed structure—we would expect the O═O double bond to be shorter than the O—O single bond. In drawing the Lewis structure, however, we could just as easily have put the O═O bond on the left:



There is no reason for one of these Lewis structures to be dominant because they are equally valid representations of the molecule. The placement of the atoms in these two alternative but completely equivalent Lewis structures is the same, but the placement of the electrons is different; we call Lewis structures of this sort **resonance structures**. To describe the structure of ozone properly, we write both resonance structures and use a double-headed arrow to indicate that the real molecule is described by an average of the two:



To understand why certain molecules require more than one resonance structure, we can draw an analogy to mixing paint (**Figure 8.14**). Blue and yellow are both primary colors of paint pigment. An equal blend of blue and yellow pigments produces green pigment. We cannot describe green paint in terms of a single primary color, yet it still has its own identity. Green paint does not oscillate between its two primary colors: It is not blue part of the time and yellow the rest of the time. Similarly, molecules such as ozone cannot be described as oscillating between the two individual Lewis structures shown previously—there are two equivalent dominant Lewis structures that contribute equally to the actual structure of the molecule.

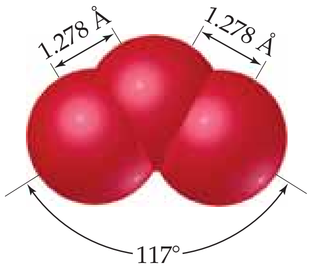
The actual arrangement of the electrons in molecules such as O_3 must be considered as a blend of two (or more) Lewis structures. By analogy to the green paint, the molecule has its own identity separate from the individual resonance structures. For example, the ozone molecule always has two equivalent O—O bonds whose lengths are intermediate between the lengths of an oxygen–oxygen single bond and an oxygen–oxygen double bond. Another way of looking at it is to say that the rules for drawing Lewis structures do not allow us to have a single dominant structure for the ozone molecule. For example, there are no rules for drawing half-bonds. We can get around this limitation by drawing two equivalent Lewis structures that, when averaged, amount to something very much like what is observed experimentally.

Give It Some Thought

The O—O bonds in ozone can be described as "one and a half bonds." Does this suggest that the bond lengths in ozone are longer or shorter than those in the O_2 molecule?

Go Figure

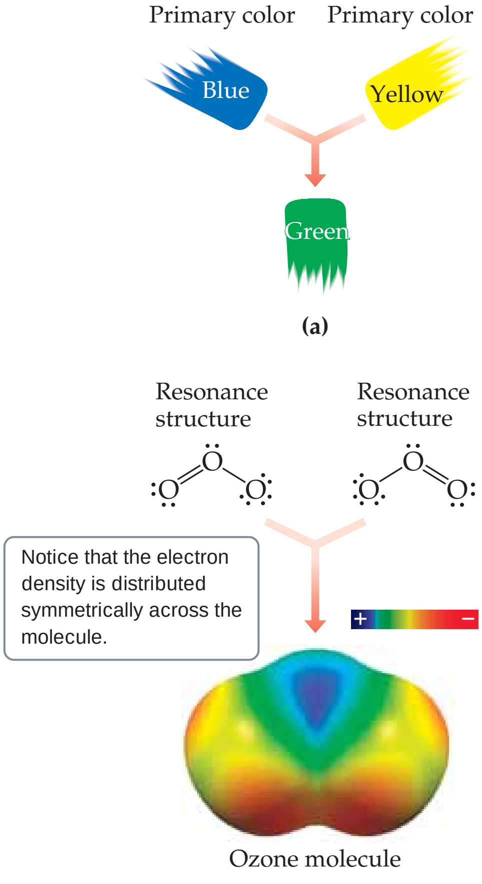
What feature of this structure suggests that the two outer O atoms are in some way equivalent to each other?



▲ **Figure 8.13** **Molecular structure of ozone.**

Go Figure

Is the electron density consistent with equal contributions from the two resonance structures for O_3? Explain.



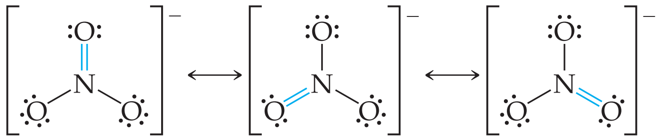
(a)

Notice that the electron density is distributed symmetrically across the molecule.

(b)

▲ **Figure 8.14** **Resonance.** Describing a molecule as a blend of different resonance structures is similar to describing a paint color as a blend of primary colors. (**a**) Green paint is a blend of blue and yellow. We cannot describe green as a single primary color. (**b**) The ozone molecule is a blend of two resonance structures. We cannot describe the ozone molecule in terms of a single Lewis structure.

As an additional example of resonance structures, consider the nitrate ion, NO_3^-, for which three equivalent Lewis structures can be drawn:



Notice that the arrangement of atoms is the same in each structure—only the placement of electrons differs. In writing resonance structures, the same atoms must be bonded to each other in all structures, so that the only differences are in the arrangements of electrons. All three NO_3^- Lewis structures are equally dominant and taken together adequately describe the ion, in which all three N—O bond lengths are the same.

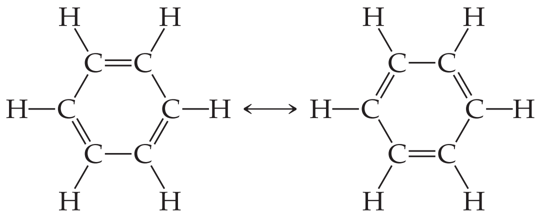
Give It Some Thought

Predict whether the N—O bonds in NO_3^- are stronger or weaker than the N—O bond in NO^+.

For some molecules or ions, all possible Lewis structures may not be equivalent; in other words, one or more resonance structures are more dominant than others. We will encounter examples of this as we proceed.

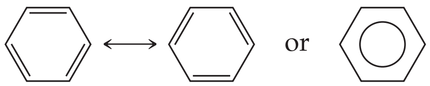
Resonance in Benzene

Resonance is an important concept in describing the bonding in organic molecules, particularly *aromatic* organic molecules, a category that includes the hydrocarbon *benzene,* C_6H_6. The six C atoms are bonded in a hexagonal ring, and one H atom is bonded to each C atom. We can write two equivalent dominant Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance:



Note that the double bonds are in different places in the two structures. Each of these resonance structures shows three carbon–carbon single bonds and three carbon–carbon double bonds. However, experimental data show that all six C—C bonds are of equal length, 1.40 Å, intermediate between the typical bond lengths for a C—C single bond (1.54 Å) and a C=C double bond (1.34 Å). Each of the C—C bonds in benzene can be thought of as a blend of a single bond and a double bond (**Figure 8.15**).

Benzene is commonly represented by omitting the hydrogen atoms and showing only the carbon–carbon framework with the vertices unlabeled. In this convention, the resonance in the molecule is represented either by two structures separated by a double-headed arrow or by a shorthand notation in which we draw a hexagon with a circle inside:



The shorthand notation reminds us that benzene is a blend of two resonance structures—it emphasizes that the C=C double bonds cannot be assigned to specific edges of the hexagon. Chemists use both representations of benzene interchangeably.

The bonding arrangement in benzene confers special stability to the molecule. As a result, millions of organic compounds contain the six-membered ring characteristic of

Go Figure

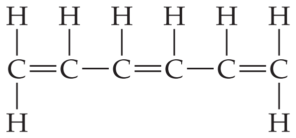
What is the significance of the dashed bonds in this ball-and-stick model?

▲ **Figure 8.15 Benzene, an "aromatic" organic compound.**
The benzene molecule is a regular hexagon of carbon atoms with a hydrogen atom bonded to each one. The dashed lines represent the blending of two equivalent resonance structures, leading to C—C bonds that are intermediate between single and double bonds.

benzene. Many of these compounds are important in biochemistry, in pharmaceuticals, and in the production of modern materials.

Give It Some Thought

Each Lewis structure of benzene has three C═C double bonds. Another hydrocarbon containing three C═C double bonds is *hexatriene*, C_6H_8. A Lewis structure of hexatriene is



Experiments show that three of the C—C bonds in hexatriene are shorter than the other two. Does this data suggest that hexatriene exhibits resonance structures?

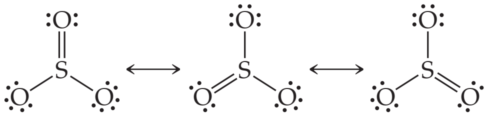
Sample Exercise 8.10

Resonance Structures

Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-}?

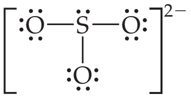
SOLUTION

The sulfur atom has six valence electrons, as does oxygen. Thus, SO_3 contains 24 valence electrons. In writing the Lewis structure, we see that three equivalent resonance structures can be drawn:



As with NO_3^- the actual structure of SO_3 is an equal blend of all three. Thus, each S—O bond length should be about one-third of the way between the length of a single bond and the length of a double bond. That is, S—O should be shorter than single bonds but not as short as double bonds.

The SO_3^{2-} ion has 26 electrons, which leads to a dominant Lewis structure in which all the S—O bonds are single:



Our analysis of the Lewis structures thus far leads us to conclude that SO_3 should have the shorter S—O bonds and SO_3^{2-} the longer ones. This conclusion is correct: The experimentally measured S—O bond lengths are 1.42 Å in SO_3 and 1.51 Å in SO_3^{2-}.

Practice Exercise 1

Which of these statements about resonance is true?

(a) When you draw resonance structures, it is permissible to alter the way atoms are connected.

(b) The nitrate ion has one long N—O bond and two short N—O bonds.

(c) "Resonance" refers to the idea that molecules are resonating rapidly between different bonding patterns.

(d) The cyanide ion has only one dominant resonance structure.

(e) All of the above are true.

Practice Exercise 2

Draw two equivalent resonance structures for the formate ion, HCO_2^-.

8.7 Exceptions to the Octet Rule

The octet rule is so simple and useful in introducing the basic concepts of bonding that you might assume it is always obeyed. In Section 8.2, however, we noted its limitation in dealing with ionic compounds of the transition metals. The rule also fails in many situations involving covalent bonding. These exceptions to the octet rule are of three main types:

Molecules and polyatomic ions containing an odd number of electrons

Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons

1. Molecules and polyatomic ions in which an atom has more than an octet of valence electrons

Odd Number of Electrons

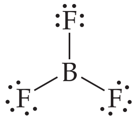
In the vast majority of molecules and polyatomic ions, the total number of valence electrons is even, and complete pairing of electrons occurs. However, in a few molecules and polyatomic ions, such as ClO_2, NO, NO_2, and O_2^-, the number of valence electrons is odd. Complete pairing of these electrons is impossible, and an octet around each atom cannot be achieved. For example, NO contains 5 + 6 = 11 valence electrons. The two most important Lewis structures for this molecule are

Give It Some Thought

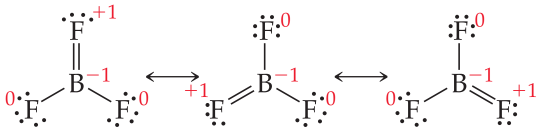
Which of the Lewis structures for NO is dominant based on analysis of the formal charges?

Less Than an Octet of Valence Electrons

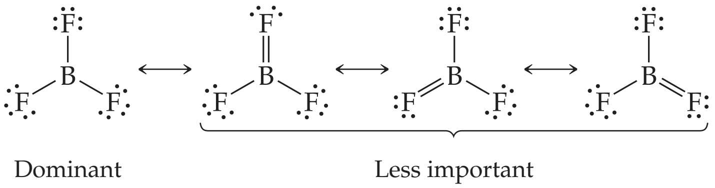
A second type of exception occurs when there are fewer than eight valence electrons around an atom in a molecule or polyatomic ion. This situation is also relatively rare (with the exception of hydrogen and helium as we have already discussed), and is most often encountered in compounds of boron and beryllium. As an example, let's consider boron trifluoride, BF_3. If we follow the first steps of our procedure for drawing Lewis structures, we obtain the structure



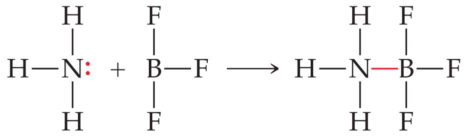
which has only six electrons around the boron atom. The formal charge is zero on both B and F, and we could complete the octet around boron by forming a double bond (recall that if there are not enough electrons to give the central atom an octet, a multiple bond may be the answer). In so doing, we see that there are three equivalent resonance structures (the formal charges are shown in red):



Each of these structures forces a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine. In fact, the formal charges tell us that this is an unfavorable situation. In each structure, the F atom involved in the B═F double bond has a formal charge of +1, while the less electronegative B atom has a formal charge of −1. Thus, the resonance structures containing a B═F double bond are less important than the one in which there are fewer than an octet of valence electrons around boron:



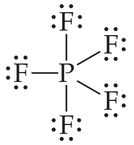
We usually represent BF_3 solely by the dominant resonance structure, in which there are only six valence electrons around boron. The chemical behavior of BF_3 is consistent with this representation. In particular, BF_3 reacts energetically with molecules having an unshared pair of electrons that can be used to form a bond with boron, as, for example, in the reaction

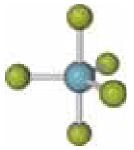


In the stable compound NH_3BF_3, boron has an octet of valence electrons.

More Than an Octet of Valence Electrons

The third and largest class of exceptions consists of molecules or polyatomic ions in which there are more than eight electrons in the valence shell of an atom. When we draw the Lewis structure for PF_5, for example, we are forced to place ten electrons around the central phosphorus atom:





Molecules and ions with more than an octet of electrons around the central atom are often called *hypervalent*. Other examples of hypervalent species are SF_4, AsF_6^-, and ICl_4^-. The corresponding molecules with a second-period atom as the central atom, such as NCl_5 and OF_4, do *not* exist.

Hypervalent molecules are formed only for central atoms from period 3 and below in the periodic table. The principal reason for their formation is the relatively larger size of the central atom. For example, a P atom is large enough that five F (or even five Cl) atoms can be bonded to it without being too crowded. By contrast, an N atom is too small to accommodate five atoms bonded to it. Because size is a factor, hypervalent molecules occur most often when the central atom is bonded to the smallest and most electronegative atoms—F, Cl, and O.

The notion that a valence shell can contain more than eight electrons is also consistent with the presence of unfilled *nd* orbitals in atoms from period 3 and below. ∞ (Section 6.8) By comparison, in elements of the second period, only the 2*s* and 2*p* valence orbitals are available for bonding. However, theoretical work on the bonding in molecules such as PF_5 and SF_6 suggests that the presence of unfilled 3*d* orbitals in P and S has a relatively minor impact on the formation of hypervalent molecules. Most chemists now believe that the larger size of the atoms from periods 3 through 6 is more important to explain hypervalency than is the presence of unfilled *d* orbitals.

Sample Exercise 8.11

Lewis Structure for an Ion with More Than an Octet of Electrons

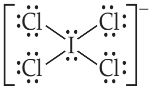
Draw the Lewis structure for ICl_4^-.

SOLUTION

Iodine (group 7A) has seven valence electrons. Each chlorine atom (group 7A) also has seven. An extra electron is added to account for the 1− charge of the ion. Therefore, the total number of valence electrons is $7 + (4 \times 7) + 1 = 36$.

The I atom is the central atom in the ion. Putting eight electrons around each Cl atom (including a pair of electrons between I and each Cl to represent the single bond between these atoms) requires $8 \times 4 = 32$ electrons.

We are thus left with $36 - 32 = 4$ electrons to be placed on the larger iodine:



Iodine has 12 valence electrons around it, four more than needed for an octet.

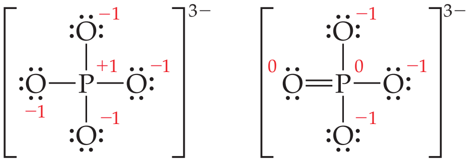
Practice Exercise 1

In which of these molecules or ions is there only one lone pair of electrons on the central sulfur atom?
(**a**) SF_4 (**b**) SF_6 (**c**) SOF_4 (**d**) SF_2 (**e**) SO_4^{2-}

Practice Exercise 2

(**a**) Which of the following atoms is never found with more than an octet of valence electrons around it? S, C, P, Br, I.
(**b**) Draw the Lewis structure for XeF_2.

Finally, there are Lewis structures where you might have to choose between satisfying the octet rule and obtaining the most favorable formal charges by using more than an octet of electrons. For example, consider these Lewis structures for the phosphate ion, PO_4^{3-}:



The formal charges on the atoms are shown in red. In the left structure, the P atom obeys the octet rule. In the right structure, however, the P atom has five electron pairs, leading to smaller formal charges on the atoms. (You should be able to see that there are three additional resonance structures for the Lewis structure on the right.)

Chemists are still debating which of these two structures is dominant for PO_4^{3-}. Recent theoretical calculations based on quantum mechanics suggest to some researchers that the left structure is the dominant one. Other researchers claim that the bond lengths in the ion are more consistent with the right structure being dominant. This disagreement is a convenient reminder that, in general, multiple Lewis structures can contribute to the actual electron distribution in an atom or molecule.

8.8 Strengths and Lengths of Covalent Bonds

The stability of a molecule is related to the strengths of its covalent bonds. We saw in Chapter 5 that we can measure the average bond enthalpy of many single bonds (Table 5.4). Table 5.4 is repeated here as **Table 8.3**. As you might expect, Table 8.3 shows that multiple bonds are generally stronger than single bonds.

TABLE 8.3 Average Bond Enthalpies (kJ/mol)

Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						
Multiple Bonds							
C=C	614	N=N	418	O=O	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

Just as we can define an average bond enthalpy, we can also define an average bond length for a number of common bonds (**Table 8.4**). Of particular interest is the relationship, in any atom pair, among bond enthalpy, bond length, and number of bonds between the atoms. For example, we can use data in Tables 8.3 and 8.4 to compare the bond lengths and bond enthalpies of carbon–carbon single, double, and triple bonds:

C—C	C═C	C≡C
1.54 Å	1.34 Å	1.20 Å
348 kJ/mol	614 kJ/mol	839 kJ/mol

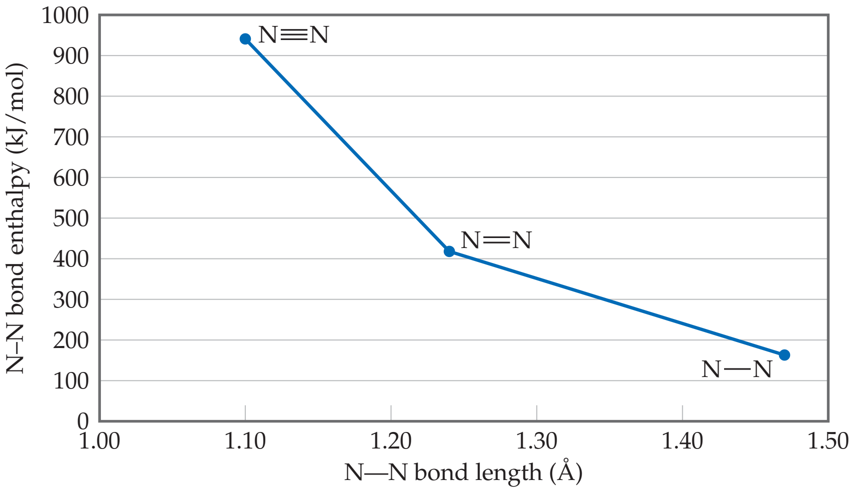
TABLE 8.4 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C═C	1.34	N═N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C═N	1.38	N═O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O═O	1.21
C═O	1.23		
C≡O	1.13		

As the number of bonds between the carbon atoms increases, the bond length decreases and the bond enthalpy increases. That is, the carbon atoms are held more closely and more tightly together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger*. This trend is illustrated in **Figure 8.16** for N—N single, double, and triple bonds.

Go Figure

Predict the N—N bond enthalpy for an N—N bond that has resonance forms that include equal contributions from single and double N—N bonds.



▲ **Figure 8.16** **Bond strength versus bond length for N—N bonds.**

Sample Integrative Exercise

Putting Concepts Together

Integrative Examples and Integrative Exercises
Each chapter concludes with an Integrative Example. Integrative Examples and Integrative Exercises (which appear in the end of chapter material) combine newly learned concepts with skills learned in previous chapters.

Phosgene, a substance used in poisonous gas warfare during World War I, is so named because it was first prepared by the action of sunlight on a mixture of carbon monoxide and chlorine gases. Its name comes from the Greek words *phos* (light) and *genes* (born of). Phosgene has the following elemental composition: 12.14% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol. (**a**) Determine the molecular formula of this compound. (**b**) Draw three Lewis structures for the molecule that satisfy the octet rule for each atom. (The Cl and O atoms bond to C.) (**c**) Using formal charges, determine which Lewis structure is the dominant one. (**d**) Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from $CO(g)$ and $Cl_2(g)$.

2-Column Problem-Solving Format
Select Sample Exercises feature a 2-column format that walks students through the problem, providing guidance on the left and the related step of the solution on the right.

SOLUTION

(**a**) The empirical formula of phosgene can be determined from its elemental composition. (Section 3.5) Assuming 100 g of the compound and calculating the number of moles of C, O, and Cl in this sample, we have:

$$(12.14\ \cancel{\text{g C}})\left(\frac{1\ \text{mol C}}{12.01\ \cancel{\text{g C}}}\right) = 1.011\ \text{mol C}$$

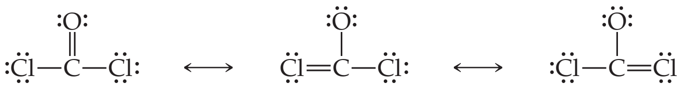
$$(16.17\ \cancel{\text{g O}})\left(\frac{1\ \text{mol O}}{16.00\ \cancel{\text{g O}}}\right) = 1.011\ \text{mol O}$$

$$(71.69\ \cancel{\text{g Cl}})\left(\frac{1\ \text{mol Cl}}{35.45\ \cancel{\text{g Cl}}}\right) = 2.022\ \text{mol Cl}$$

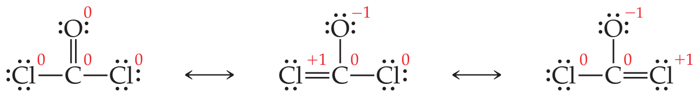
The ratio of the number of moles of each element, obtained by dividing each number of moles by the smallest quantity, indicates that there is one C and one O for each two Cl in the empirical formula, $COCl_2$.

The molar mass of the empirical formula is $12.01 + 16.00 + 2(35.45) = 98.91$ g/mol, the same as the molar mass of the molecule. Thus, $COCl_2$ is the molecular formula.

(**b**) Carbon has four valence electrons, oxygen has six, and chlorine has seven, giving $4 + 6 + 2(7) = 24$ electrons for the Lewis structures. Drawing a Lewis structure with all single bonds does not give the central carbon atom an octet. Using multiple bonds, we find that three structures satisfy the octet rule:



(**c**) Calculating the formal charges on each atom gives:



The first structure is expected to be the dominant one because it has the lowest formal charges on each atom. Indeed, the molecule is usually represented by this single Lewis structure.

(**d**) Writing the chemical equation in terms of the Lewis structures of the molecules, we have:

Thus, the reaction involves breaking a C≡O bond and a Cl—Cl bond and forming a C=O bond and two C—Cl bonds. Using bond enthalpies from Table 8.3, we have:

$$\begin{aligned}\Delta H &= [D(\text{C}\equiv\text{O}) + D(\text{Cl}-\text{Cl})] - [D(\text{C}=\text{O}) + 2D(\text{C}-\text{Cl})] \\ &= [1072\ \text{kJ} + 242\ \text{kJ}] - [799\ \text{kJ} + 2(328\ \text{kJ})] = -141\ \text{kJ}\end{aligned}$$

Notice that the reaction is exothermic. Nevertheless, energy is needed from sunlight or another source for the reaction to begin, as is the case for the combustion of $H_2(g)$ and $O_2(g)$ to form $H_2O(g)$.

Chapter Summary and Key Terms

CHEMICAL BONDS, LEWIS SYMBOLS, AND THE OCTET RULE (INTRODUCTION AND SECTION 8.1) In this chapter, we have focused on the interactions that lead to the formation of **chemical bonds**. We classify these bonds into three broad groups: **ionic bonds**, which result from the electrostatic forces that exist between ions of opposite charge; **covalent bonds**, which result from the sharing of electrons by two atoms; and **metallic bonds**, which result from a delocalized sharing of electrons in metals. The formation of bonds involves interactions of the outermost electrons of atoms, their valence electrons. The valence electrons of an atom can be represented by electron-dot symbols, called **Lewis symbols**. The tendencies of atoms to gain, lose, or share their valence electrons often follow the **octet rule**, which says that the atoms in molecules or ions (usually) have eight valence electrons.

IONIC BONDING (SECTION 8.2) Ionic bonding results from the transfer of electrons from one atom to another, leading to the formation of a three-dimensional lattice of charged particles. The stabilities of ionic substances result from the strong electrostatic attractions between an ion and the surrounding ions of opposite charge. The magnitude of these interactions is measured by the **lattice energy**, which is the energy needed to separate an ionic lattice into gaseous ions. Lattice energy increases with increasing charge on the ions and with decreasing distance between the ions. The **Born–Haber cycle** is a useful thermochemical cycle in which we use Hess's law to calculate the lattice energy as the sum of several steps in the formation of an ionic compound.

COVALENT BONDING (SECTION 8.3) A covalent bond results from the sharing of valence electrons between atoms. We can represent the electron distribution in molecules by means of **Lewis structures**, which indicate how many valence electrons are involved in forming bonds and how many remain as **nonbonding electron pairs** (or **lone pairs**). The octet rule helps determine how many bonds will be formed between two atoms. The sharing of one pair of electrons produces a **single bond**; the sharing of two or three pairs of electrons between two atoms produces **double** or **triple bonds**, respectively. Double and triple bonds are examples of multiple bonding between atoms. The bond length decreases as the number of bonds between the atoms increases.

BOND POLARITY AND ELECTRONEGATIVITY (SECTION 8.4) In covalent bonds, the electrons may not necessarily be shared equally between two atoms. **Bond polarity** helps describe unequal sharing of electrons in a bond. In a **nonpolar covalent bond**, the electrons in the bond are shared equally by the two atoms; in a **polar covalent bond**, one of the atoms exerts a greater attraction for the electrons than the other.

Electronegativity is a numerical measure of the ability of an atom to compete with other atoms for the electrons shared between them. Fluorine is the most electronegative element, meaning it has the greatest ability to attract electrons from other atoms. Electronegativity values range from 0.7 for Cs to 4.0 for F. Electronegativity generally increases from left to right in a row of the periodic table and decreases going down a column. The difference in the electronegativities of bonded atoms can be used to determine the polarity of a bond. The greater the electronegativity difference, the more polar the bond.

A **polar molecule** is one whose centers of positive and negative charge do not coincide. Thus, a polar molecule has a positive side and a negative side. This separation of charge produces a **dipole**, the magnitude of which is given by the **dipole moment**, which is measured in debyes (D). Dipole moments increase with increasing amount of charge separated and increasing distance of separation. Any diatomic molecule X—Y in which X and Y have different electronegativities is a polar molecule.

Most bonding interactions lie between the extremes of covalent and ionic bonding. While it is generally true that the bonding between a metal and a nonmetal is predominantly ionic, exceptions to this guideline are not uncommon when the difference in electronegativity of the atoms is relatively small or when the oxidation state of the metal becomes large.

DRAWING LEWIS STRUCTURES AND RESONANCE STRUCTURES (SECTIONS 8.5 AND 8.6) If we know which atoms are connected to one another, we can draw Lewis structures for molecules and ions by a simple procedure. Once we do so, we can determine the **formal charge** of each atom in a Lewis structure, which is the charge that the atom would have if all atoms had the same electronegativity. In general, the dominant Lewis structure will have low formal charges, with any negative formal charges residing on more electronegative atoms.

Sometimes a single dominant Lewis structure is inadequate to represent a particular molecule (or ion). In such situations, we describe the molecule by using two or more **resonance structures** for the molecule. The molecule is envisioned as a blend of these multiple resonance structures. Resonance structures are important in describing the bonding in molecules such as ozone, O_3, and the organic molecule benzene, C_6H_6.

EXCEPTIONS TO THE OCTET RULE (SECTION 8.7) The octet rule is not obeyed in all cases. Exceptions occur when (**a**) a molecule has an odd number of electrons, (**b**) it is not possible to complete an octet around an atom without forcing an unfavorable distribution of electrons, or (**c**) a large atom is surrounded by a sufficiently large number of small electronegative atoms that it has more than an octet of electrons around it. Lewis structures with more than an octet of electrons are observed for atoms in the third row and beyond in the periodic table.

STRENGTHS AND LENGTHS OF COVALENT BONDS (SECTION 8.8) The average strengths and lengths of many common covalent bonds can be measured. Average bond enthalpies for multiple bonds are generally larger than those of single bonds. The average bond length between two atoms decreases as the number of bonds between the atoms increases, consistent with the bond being stronger as the number of bonds increases.

New! Each Learning Outcomes section is now correlated to a set of related end-of-chapter exercises that allow students to check their mastery of the material.

Learning Outcomes After studying this chapter, you should be able to:

- Write Lewis symbols for atoms and ions. (Section 8.1) *Related Exercises: 8.13, 8.14, 8.19, 8.20*
- Define lattice energy and be able to arrange compounds in order of increasing lattice energy based on the charges and sizes of the ions involved. (Section 8.2) *Related Exercises: 8.21–8.24*
- Use atomic electron configurations and the octet rule to draw Lewis structures for molecules. (Section 8.3) *Related Exercises: 8.35, 8.36, 8.47, 8.48*
- Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds. (Section 8.4) *Related Exercises: 8.37–8.40*
- Calculate charge separation in diatomic molecules based on the experimentally measured dipole moment and bond length. (Section 8.4) *Related Exercises: 8.43, 8.44*
- Calculate formal charges from Lewis structures and use those formal charges to identify the dominant Lewis structure for a molecule or ion. (Section 8.5) *Related Exercises: 8.49–8.52*
- Recognize molecules where resonance structures are needed to describe the bonding and draw the dominant resonance structures. (Section 8.6) *Related Exercises: 8.53–8.56*
- Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed. (Section 8.7) *Related Exercises: 8.63, 8.64*
- Predict the relationship between bond type (single, double, and triple), bond strength (or enthalpy), and bond length. (Section 8.8) *Related Exercises: 8.71–8.74*

New! Enhanced EOC Problems
Hundreds of enhanced EOC problems now feature wrong answer feedback in MasteringChemistry.

Key Equations

- $E_{\text{el}} = \frac{\kappa Q_1 Q_2}{d}$ [8.4] The potential energy of two interacting charges
- $\mu = Qr$ [8.10] The dipole moment of two charges of equal magnitude but opposite sign, separated by a distance r
- Formal charge $=$ valence electrons $-$ $\frac{1}{2}$(bonding electrons) $-$ nonbonding electrons [8.11] The definition of formal charge

Reviewed and Revised Questions and Problems
The author team analyzed student user data from MasteringChemistry to inform their review of all in-chapter questions and end-of-chapter problems. This allowed the authors to identify "problem" problems and to revise them as needed to improve clarity or focus. The result is an even a more diverse and polished set of problems.

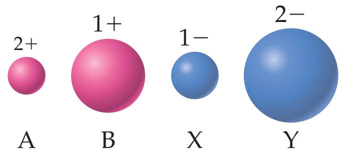
Exercises

Visualizing Concepts

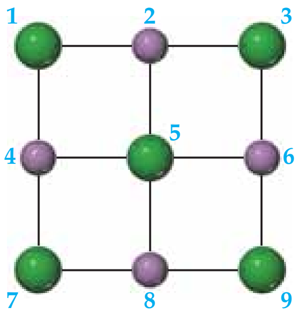
8.1 For each of these Lewis symbols, indicate the group in the periodic table in which the element X belongs: [Section 8.1]

(**a**) $\cdot\dot{\underset{\cdot}{\mathrm{X}}}\cdot$ (**b**) $\cdot\mathrm{X}\cdot$ (**c**) $:\dot{\underset{\cdot}{\mathrm{X}}}\cdot$

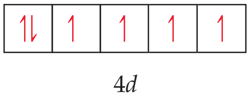
8.2 Illustrated are four ions — A, B, X, and Y— showing their relative ionic radii. The ions shown in red carry positive charges: a 2+ charge for A and a 1+ charge for B. Ions shown in blue carry negative charges: a 1− charge for X and a 2− charge for Y. (**a**) Which combinations of these ions produce ionic compounds where there is a 1:1 ratio of cations and anions? (**b**) Among the combinations in part (a), which leads to the ionic compound having the largest lattice energy? [Section 8.2]



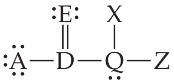
8.3 A portion of a two-dimensional "slab" of NaCl(s) is shown here (see Figure 8.2) in which the ions are numbered. (**a**) Which colored balls must represent sodium ions? (**b**) Which colored balls must represent chloride ions? (**c**) Consider ion 5. How many attractive electrostatic interactions are shown for it? (**d**) Consider ion 5. How many repulsive interactions are shown for it? (**e**) Is the sum of the attractive interactions in part (c) larger or smaller than the sum of the repulsive interactions in part (d)? (**f**) If this pattern of ions was extended indefinitely in two dimensions, would the lattice energy be positive or negative? [Section 8.2]



8.4 The orbital diagram that follows shows the valence electrons for a 2+ ion of an element. (**a**) What is the element? (**b**) What is the electron configuration of an atom of this element? [Section 8.2]



8.5 In the Lewis structure shown here, A, D, E, Q, X, and Z represent elements in the first two rows of the periodic table. Identify all six elements so that the formal charges of all atoms are zero. [Section 8.3]



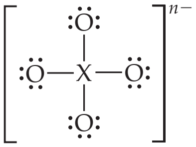
8.6 Incomplete Lewis structures for the nitrous acid molecule, HNO_2, and the nitrite ion, NO_2^-, are shown here. (**a**) Complete each Lewis structure by adding electron pairs as needed. (**b**) Is the formal charge on N the same or different in these two species? (**c**) Would either HNO_2 or NO_2^- be expected to exhibit resonance? (**d**) Would you expect the N═O bond in HNO_2 to be longer, shorter, or the same length as the N—O bonds in NO_2^-? [Sections 8.5 and 8.6]

$$H{-}O{-}N{=}O \qquad O{-}N{=}O$$

8.7 The partial Lewis structure that follows is for a hydrocarbon molecule. In the full Lewis structure, each carbon atom satisfies the octet rule, and there are no unshared electron pairs in the molecule. The carbon—carbon bonds are labeled 1, 2, and 3. (**a**) How many hydrogen atoms are in the molecule? (**b**) Rank the carbon–carbon bonds in order of increasing bond length. (**c**) Which carbon—carbon bond is the strongest one? [Sections 8.3 and 8.8]

$$C\overset{1}{=}C\overset{2}{-}C\overset{3}{\equiv}C$$

8.8 Consider the Lewis structure for the polyatomic oxyanion shown here, where X is an element from the third period (Na − Ar). By changing the overall charge, *n*, from 1− to 2− to 3− we get three different polyatomic ions. For each of these ions (**a**) identify the central atom, X; (**b**) determine the formal charge of the central atom, X; (**c**) draw a Lewis structure that makes the formal charge on the central atom equal to zero. [Sections 8.5, 8.6, and 8.7]



Lewis Symbols (Section 8.1)

8.9 (**a**) True or false: An element's number of valence electrons is the same as its atomic number. (**b**) How many valence electrons does a nitrogen atom possess? (**c**) An atom has the electron configuration $1s^22s^22p^63s^23p^2$. How many valence electrons does the atom have?

8.10 (**a**) True or false: The hydrogen atom is most stable when it has a full octet of electrons. (**b**) How many electrons must a sulfur atom gain to achieve an octet in its valence shell? (**c**) If an atom has the electron configuration $1s^22s^22p^3$, how many electrons must it gain to achieve an octet?

8.11 Consider the element silicon, Si. (**a**) Write its electron configuration. (**b**) How many valence electrons does a silicon atom have? (**c**) Which subshells hold the valence electrons?

8.12 (**a**) Write the electron configuration for the element titanium, Ti. How many valence electrons does this atom possess? (**b**) Hafnium, Hf, is also found in group 4B. Write the electron configuration for Hf. (**c**) Ti and Hf behave as though they possess the same number of valence electrons. Which of the subshells in the electron configuration of Hf behave as valence orbitals? Which behave as core orbitals?

8.13 Write the Lewis symbol for atoms of each of the following elements: (**a**) Al, (**b**) Br, (**c**) Ar, (**d**) Sr.

8.14 What is the Lewis symbol for each of the following atoms or ions? (**a**) K, (**b**) As, (**c**) Sn^{2+}, (**d**) N^{3-}.

Ionic Bonding (Section 8.2)

8.15 (**a**) Using Lewis symbols, diagram the reaction between magnesium and oxygen atoms to give the ionic substance MgO. (**b**) How many electrons are transferred? (**c**) Which atom loses electrons in the reaction?

8.16 (**a**) Use Lewis symbols to represent the reaction that occurs between Ca and F atoms. (**b**) What is the chemical formula of the most likely product? (**c**) How many electrons are transferred? (**d**) Which atom loses electrons in the reaction?

8.17 Predict the chemical formula of the ionic compound formed between the following pairs of elements: (**a**) Al and F, (**b**) K and S, (**c**) Y and O, (**d**) Mg and N.

8.18 Which ionic compound is expected to form from combining the following pairs of elements? (**a**) barium and fluorine, (**b**) cesium and chlorine, (**c**) lithium and nitrogen, (**d**) aluminum and oxygen.

8.19 Write the electron configuration for each of the following ions, and determine which ones possess noble-gas configurations: (**a**) Sr^{2+}, (**b**) Ti^{2+}, (**c**) Se^{2-}, (**d**) Ni^{2+}, (**e**) Br^-, (**f**) Mn^{3+}.

8.20 Write electron configurations for the following ions, and determine which have noble-gas configurations: (**a**) Cd^{2+}, (**b**) P^{3-}, (**c**) Zr^{4+}, (**d**) Ru^{3+}, (**e**) As^{3-}, (**f**) Ag^+.

8.21 (**a**) Is lattice energy usually endothermic or exothermic? (**b**) Write the chemical equation that represents the process of lattice energy for the case of NaCl. (**c**) Would you expect salts like NaCl, which have singly charged ions, to have larger or smaller lattice energies compared to salts like CaO which are composed of doubly-charged ions?

8.22 NaCl and KF have the same crystal structure. The only difference between the two is the distance that separates cations and anions. (**a**) The lattice energies of NaCl and KF are given in Table 8.1. Based on the lattice energies, would you expect the Na—Cl or the K—F distance to be longer? (**b**) Use the ionic radii given in Figure 7.8 to estimate the Na—Cl and K—F distances.

8.23 The substances NaF and CaO are isoelectronic (have the same number of valence electrons). (**a**) What are the charges on each of the cations in each compound? (**b**) What are the charges of each of the anions in each compound? (**c**) Without looking up lattice energies, which compound is predicted to have the larger lattice energy? (**d**) Using the lattice energies in Table 8.1, predict the lattice energy of ScN.

8.24 (**a**) Does the lattice energy of an ionic solid increase or decrease (i) as the charges of the ions increase, (ii) as the sizes of the ions increase? (**b**) Arrange the following substances not listed in Table 8.1 according to their expected lattice energies, listing them from lowest lattice energy to the highest: MgS, KI, GaN, LiBr.

8.25 Consider the ionic compounds KF, NaCl, NaBr, and LiCl. (**a**) Use ionic radii (Figure 7.8) to estimate the cation–anion distance for each compound. (**b**) Based on your answer to part (a), arrange these four compounds in order of decreasing lattice energy. (**c**) Check your predictions in part (b) with the experimental values of lattice energy from Table 8.1. Are the predictions from ionic radii correct?

8.26 Which of the following trends in lattice energy is due to differences in ionic radii? (**a**) NaCl > RbBr > CsBr, (**b**) BaO > KF, (**c**) SrO > $SrCl_2$.

8.27 Energy is required to remove two electrons from Ca to form Ca^{2+}, and energy is required to add two electrons to O to form O^{2-}. Yet CaO is stable relative to the free elements. Which statement is the best explanation? (**a**) The lattice energy of CaO is large enough to overcome these processes. (**b**) CaO is a covalent compound, and these processes are irrelevant. (**c**) CaO has a higher molar mass than either Ca or O. (**d**) The enthalpy of formation of CaO is small. (**e**) CaO is stable to atmospheric conditions.

8.28 List the individual steps used in constructing a Born–Haber cycle for the formation of BaI_2 from the elements. Which of the steps would you expect to be exothermic?

8.29 Use data from Appendix C, Figure 7.10, and Figure 7.12 to calculate the lattice energy of RbCl.

8.30 (**a**) Based on the lattice energies of $MgCl_2$ and $SrCl_2$ given in Table 8.1, what is the range of values that you would expect for the lattice energy of $CaCl_2$? (**b**) Using data from Appendix C, Figure 7.11, Figure 7.13, and the value of the second ionization energy for Ca, 1145 kJ/mol, calculate the lattice energy of $CaCl_2$.

Covalent Bonding, Electronegativity, and Bond Polarity (Sections 8.3 and 8.4)

8.31 (**a**) State whether or not the bonding in each substance is likely to be covalent: (i) iron, (ii) sodium chloride, (iii) water, (iv) oxygen, (v) argon. (**b**) A substance XY, formed from two different elements, boils at −33 °C. Is XY likely to be a covalent or an ionic substance?

8.32 Which of these elements are unlikely to form covalent bonds? S, H, K, Ar, Si.

8.33 Using Lewis symbols and Lewis structures, diagram the formation of $SiCl_4$ from Si and Cl atoms, showing valence-shell electrons. (**a**) How many valence electrons does Si have initially? (**b**) How many valence electrons does each Cl have initially? (**c**) How many valence electrons surround the Si in the $SiCl_4$ molecule? (**d**) How many valence electrons surround each Cl in the $SiCl_4$ molecule? (**e**) How many bonding pairs of electrons are in the $SiCl_4$ molecule?

8.34 Use Lewis symbols and Lewis structures to diagram the formation of PF_3 from P and F atoms, showing valence-shell electrons. (**a**) How many valence electrons does P have initially? (**b**) How many valence electrons does each F have initially? (**c**) How many valence electrons surround the P in the PF_3 molecule? (**d**) How many valence electrons surround each F in the PF_3 molecule? (**e**) How many bonding pairs of electrons are in the PF_3 molecule?

8.35 (**a**) Construct a Lewis structure for O_2 in which each atom achieves an octet of electrons. (**b**) How many bonding electrons are in the structure? (**c**) Would you expect the O—O bond in O_2 to be shorter or longer than the O—O bond in compounds that contain an O—O single bond? Explain.

8.36 (**a**) Construct a Lewis structure for hydrogen peroxide, H_2O_2, in which each atom achieves an octet of electrons. (**b**) How many bonding electrons are between the two oxygen atoms? (**c**) Do you expect the O—O bond in H_2O_2 to be longer or shorter than the O—O bond in O_2? Explain.

8.37 Which of the following statements about electronegativity is false? (**a**) Electronegativity is the ability of an atom in a molecule to attract electron density toward itself. (**b**) Electronegativity is the same thing as electron affinity. (**c**) The numerical values for electronegativity have no units. (**d**) Fluorine is the most electronegative element. (**e**) Cesium is the least electronegative element.

8.38 (**a**) What is the trend in electronegativity going from left to right in a row of the periodic table? (**b**) How do electronegativity values generally vary going down a column in the periodic table? (**c**) True or false: The most easily ionizable elements are the most electronegative.

8.39 Using only the periodic table as your guide, select the most electronegative atom in each of the following sets: (**a**) Na, Mg, K, Ca; (**b**) P, S, As, Se; (**c**) Be, B, C, Si; (**d**) Zn, Ge, Ga, As.

8.40 By referring only to the periodic table, select (**a**) the most electronegative element in group 6A; (**b**) the least electronegative element in the group Al, Si, P; (**c**) the most electronegative element in the group Ga, P, Cl, Na; (**d**) the element in the group K, C, Zn, F that is most likely to form an ionic compound with Ba.

8.41 Which of the following bonds are polar? (**a**) B—F, (**b**) Cl—Cl, (**c**) Se—O, (**d**) H—I. Which is the more electronegative atom in each polar bond?

8.42 Arrange the bonds in each of the following sets in order of increasing polarity: (**a**) C—F, O—F, Be—F; (**b**) O—Cl, S—Br, C—P; (**c**) C—S, B—F, N—O.

8.43 (**a**) From the data in Table 8.2, calculate the effective charges on the H and Br atoms of the HBr molecule in units of the electronic charge, *e*. (**b**) If you were to put HBr under very high pressure, so its bond length decreased significantly, would its dipole moment increase, decrease, or stay the same, if you assume that the effective charges on the atoms do not change?

8.44 The iodine monobromide molecule, IBr, has a bond length of 2.49 Å and a dipole moment of 1.21 D. (**a**) Which atom of the molecule is expected to have a negative charge? (**b**) Calculate the effective charges on the I and Br atoms in IBr in units of the electronic charge, *e*.

8.45 In the following pairs of binary compounds, determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: (**a**) SiF_4 and LaF_3, (**b**) $FeCl_2$ and $ReCl_6$, (**c**) $PbCl_4$ and RbCl.

8.46 In the following pairs of binary compounds, determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: (**a**) $TiCl_4$ and CaF_2, (**b**) ClF_3 and VF_3, (**c**) $SbCl_5$ and AlF_3.

Lewis Structures; Resonance Structures (Sections 8.5 and 8.6)

8.47 Draw Lewis structures for the following: (**a**) SiH_4, (**b**) CO, (**c**) SF_2, (**d**) H_2SO_4 (H is bonded to O), (**e**) ClO_2^-, (**f**) NH_2OH.

8.48 Write Lewis structures for the following: (**a**) H_2CO (both H atoms are bonded to C), (**b**) H_2O_2, (**c**) C_2F_6 (contains a C—C bond), (**d**) AsO_3^{3-}, (**e**) H_2SO_3 (H is bonded to O), (**f**) NH_2Cl.

8.49 Which one of these statements about formal charge is true? (**a**) Formal charge is the same as oxidation number. (**b**) To draw the best Lewis structure, you should minimize formal charge. (**c**) Formal charge takes into account the different electronegativities of the atoms in a molecule. (**d**) Formal charge is most useful for ionic compounds. (**e**) Formal charge is used in calculating the dipole moment of a diatomic molecule.

8.50 (**a**) Draw the dominant Lewis structure for the phosphorus trifluoride molecule, PF_3. (**b**) Determine the oxidation numbers of the P and F atoms. (**c**) Determine the formal charges of the P and F atoms.

8.51 Write Lewis structures that obey the octet rule for each of the following, and assign oxidation numbers and formal charges to each atom: (**a**) OCS, (**b**) $SOCl_2$ (S is the central atom), (**c**) BrO_3^-, (**d**) $HClO_2$ (H is bonded to O).

8.52 For each of the following molecules or ions of sulfur and oxygen, write a single Lewis structure that obeys the octet rule, and calculate the oxidation numbers and formal charges on all the atoms: (**a**) SO_2, (**b**) SO_3, (**c**) SO_3^{2-}. (**d**) Arrange these molecules/ions in order of increasing S—O bond length.

8.53 (**a**) Draw the best Lewis structure(s) for the nitrite ion, NO_2^-. (**b**) With what allotrope of oxygen is it isoelectronic? (**c**) What would you predict for the lengths of the bonds in NO_2^- relative to N—O single bonds and double bonds?

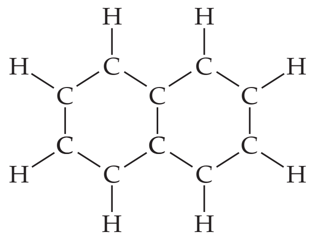
8.54 Consider the formate ion, HCO_2^-, which is the anion formed when formic acid loses an H^+ ion. The H and the two O atoms are bonded to the central C atom. (**a**) Draw the best Lewis structure(s) for this ion. (**b**) Are resonance structures needed to describe the structure? (**c**) Would you predict that the C—O bond lengths in the formate ion would be longer or shorter relative to those in CO_2?

8.55 Predict the ordering, from shortest to longest, of the bond lengths in CO, CO_2, and CO_3^{2-}.

8.56 Based on Lewis structures, predict the ordering, from shortest to longest, of N—O bond lengths in NO^+, NO_2^-, and NO_3^-.

8.57 True or false: (**a**) The C—C bonds in benzene are all the same length and correspond to typical single C—C bond lengths. (**b**) The C—C bond in acetylene, HCCH, is longer than the average C—C bond length in benzene.

[8.58] Mothballs are composed of naphthalene, $C_{10}H_8$, a molecule that consists of two six-membered rings of carbon fused along an edge, as shown in this incomplete Lewis structure:



(**a**) Draw all of the resonance structures of naphthalene. How many are there? (**b**) Do you expect the C—C bond lengths in the molecule to be similar to those of C—C single bonds, C=C double bonds, or intermediate between C—C single and C=C double bonds? (**c**) Not all of the C—C bond lengths in naphthalene are equivalent. Based on your resonance structures, how many C—C bonds in the molecule do you expect to be shorter than the others?

Exceptions to the Octet Rule (Section 8.7)

8.59 (**a**) Which of these compounds is an exception to the octet rule: carbon dioxide, water, ammonia, phosphorus trifluoride, or arsenic pentafluoride? (**b**) Which of these compounds or ions is an exception to the octet rule: borohydride (BH_4^-), borazine ($B_3N_3H_6$, which is analogous to benzene with alternating B and N in the ring), or boron trichloride?

8.60 Fill in the blank with the appropriate numbers for both electrons and bonds (considering that single bonds are counted as one, double bonds as two, and triple bonds as three).

(**a**) Fluorine has ______ valence electrons and makes ______ bond(s) in compounds.

(**b**) Oxygen has ______ valence electrons and makes ______ bond(s) in compounds.

(**c**) Nitrogen has ______ valence electrons and makes ______ bond(s) in compounds.

(**d**) Carbon has ______ valence electrons and makes ______ bond(s) in compounds.

8.61 Draw the dominant Lewis structures for these chlorine–oxygen molecules/ions: ClO, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-. Which of these do not obey the octet rule?

8.62 For Group 3A–7A in the third row of the periodic table and beyond, the octet rule is often not obeyed. A friend of yours says this is because these heavier elements are more likely to make double or triple bonds. Another friend of yours says that this is because the heavier elements are larger and can make bonds to more than four atoms at a time. Which friend is more correct?

8.63 Draw the Lewis structures for each of the following ions or molecules. Identify those in which the octet rule is not obeyed; state which atom in each compound does not follow the octet rule; and state, for those atoms, how many electrons surround these atoms: (**a**) PH_3, (**b**) AlH_3, (**c**) N_3^-, (**d**) CH_2Cl_2, (**e**) SnF_6^{2-}.

8.64 Draw the Lewis structures for each of the following molecules or ions. Identify instances where the octet rule is not obeyed; state which atom in each compound does not follow the octet rule; and state how many electrons surround these atoms: (**a**) NO, (**b**) BF_3, (**c**) ICl_2^-, (**d**) $OPBr_3$ (the P is the central atom), (**e**) XeF_4.

8.65 In the vapor phase, $BeCl_2$ exists as a discrete molecule. (**a**) Draw the Lewis structure of this molecule, using only single bonds. Does this Lewis structure satisfy the octet rule? (**b**) What other resonance structures are possible that satisfy the octet rule? (**c**) On the basis of the formal charges, which Lewis structure is expected to be dominant for $BeCl_2$?

8.66 (**a**) Describe the molecule xenon trioxide, XeO_3, using four possible Lewis structures, one each with zero, one, two, or three Xe—O double bonds. (**b**) Do any of these resonance structures satisfy the octet rule for every atom in the molecule? (**c**) Do any of the four Lewis structures have multiple resonance structures? If so, how many resonance structures do you find? (**d**) Which of the Lewis structures in part (a) yields the most favorable formal charges for the molecule?

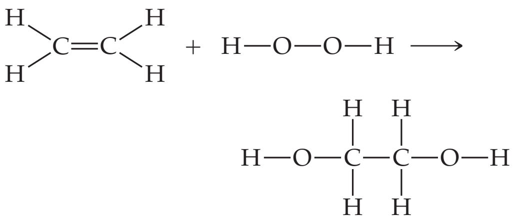
8.67 There are many Lewis structures you could draw for sulfuric acid, H_2SO_4 (each H is bonded to an O). (**a**) What Lewis structure(s) would you draw to satisfy the octet rule? (**b**) What Lewis structure(s) would you draw to minimize formal charge?

8.68 Some chemists believe that satisfaction of the octet rule should be the top criterion for choosing the dominant Lewis structure of a molecule or ion. Other chemists believe that achieving the best formal charges should be the top criterion. Consider the dihydrogen phosphate ion, $H_2PO_4^-$, in which the H atoms are bonded to O atoms. (**a**) What is the predicted dominant Lewis structure if satisfying the octet rule is the top criterion? (**b**) What is the predicted dominant Lewis structure if achieving the best formal charges is the top criterion?

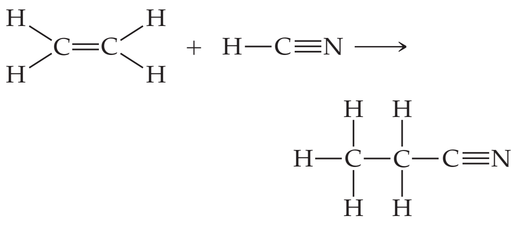
Strengths and Lengths of Covalent Bonds (Section 8.8)

8.69 Using Table 8.3, estimate ΔH for each of the following gas-phase reactions (note that lone pairs on atoms are not shown):

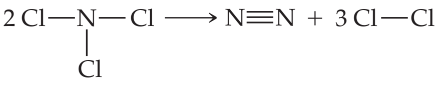
(**a**)



(**b**)



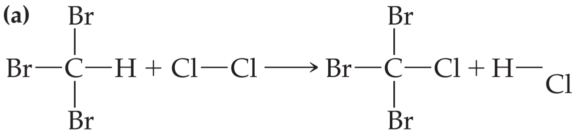
(**c**)



$$2\,\mathrm{Cl{-}\underset{Cl}{N}{-}Cl} \longrightarrow \mathrm{N{\equiv}N} + 3\,\mathrm{Cl{-}Cl}$$

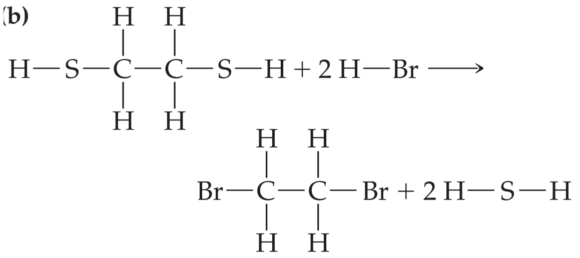
8.70 Using Table 8.3, estimate ΔH for the following gas-phase reactions:

(**a**)



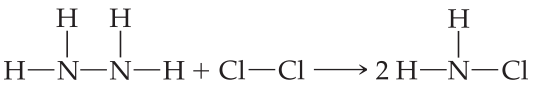
$$\mathrm{Br{-}\overset{Br}{\underset{Br}{C}}{-}H + Cl{-}Cl \longrightarrow Br{-}\overset{Br}{\underset{Br}{C}}{-}Cl + H{-}Cl}$$

(**b**)



$$\mathrm{H{-}S{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}S{-}H} + 2\,\mathrm{H{-}Br} \longrightarrow \mathrm{Br{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Br} + 2\,\mathrm{H{-}S{-}H}$$

(**c**)



$$\mathrm{H{-}\overset{H}{N}{-}\overset{H}{N}{-}H + Cl{-}Cl} \longrightarrow 2\,\mathrm{H{-}\overset{H}{N}{-}Cl}$$

8.71 State whether each of these statements is true or false. (**a**) The longer the bond, the larger the bond enthalpy. (**b**) C—C bonds are stronger than C—H bonds. (**c**) A typical single bond length is in the 5–10 Å range. (**d**) If you break a chemical bond, energy is released. (**e**) Energy is stored in chemical bonds.

8.72 State whether each of these statements is true or false. (**a**) A carbon–carbon triple bond is shorter than a carbon–carbon single bond. (**b**) There are six bonding electrons in the O_2 molecule. (**c**) The C—O bond in carbon monoxide is longer than the C—O bond in carbon dioxide. (**d**) The O—O bond in ozone is shorter than the O—O bond in O_2. (**e**) The more electronegative the atom, the more bonds it makes to other atoms.

8.73 We can define average bond enthalpies and bond lengths for ionic bonds, just like we have for covalent bonds. Which ionic bond is predicted to be stronger, Na—Cl or Ca—O?

8.74 We can define average bond enthalpies and bond lengths for ionic bonds, just like we have for covalent bonds. Which ionic bond is predicted to have the smaller bond enthalpy, Li—F or Cs—F?

8.75 A *carbene* is a compound that has a carbon bonded to two atoms and a lone pair remaining on the carbon. Many carbenes are very reactive. (**a**) Draw the Lewis structure for the simplest carbene, H_2C. (**b**) Predict the length of the carbon–carbon bond you would expect if two H_2C molecules reacted with each other by a combination reaction.

8.76 Draw the Lewis structure for NO^+. Is the nitrogen–oxygen bond in NO^+ longer, shorter, or the same length as the nitrogen–oxygen bond in NO? Explain.

Additional Exercises

8.77 A new compound is made that has a C—C bond length of 1.15 Å. Is this bond likely to be a single, double, or triple C—C bond?

8.78 A new compound is made that has an N—N bond length of 1.26 Å. Is this bond likely to be a single, double, or triple N—N bond?

8.79 Consider the lattice energies of the following Group 2A compounds: BeH_2, 3205 kJ/mol; MgH_2, 2791 kJ/mol; CaH_2, 2410 kJ/mol; SrH_2, 2250 kJ/mol; BaH_2, 2121 kJ/mol. (**a**) What is the oxidation number of H in these compounds? (**b**) Assuming that all of these compounds have the same three-dimensional arrangement of ions in the solid, which of these compounds has the shortest cation–anion distance? (**c**) Consider BeH_2. Does it require 3205 kJ of energy to break one mole of the solid into its ions, or does breaking up one mole of solid into its ions release 3205 kJ of energy? (**d**) The lattice energy of ZnH_2 is 2870 kJ/mol. Considering the trend in lattice enthalpies in the Group 2A compounds, predict which Group 2A element is most similar in ionic radius to the Zn^{2+} ion.

8.80 Based on data in Table 8.1, estimate (within 30 kJ/mol) the lattice energy for (**a**) LiBr, (**b**) CsBr, (**c**) $CaCl_2$.

8.81 An ionic substance of formula MX has a lattice energy of 6×10^3 kJ/mol. Is the charge on the ion M likely to be 1+, 2+, or 3+? Explain.

[8.82] The ionic compound CaO crystallizes with the same structure as sodium chloride (Figure 8.3). (**a**) In this structure, how many O^{2-} are in contact with each Ca^{2+} ion (*Hint:* Remember the pattern of ions shown in Figure 8.3 repeats over and over again in all three directions.) (**b**) Would energy be consumed or released if a crystal of CaO was converted to a collection of widely separated Ca—O ion pairs? (**c**) From the ionic radii given in Figure 7.8, calculate the potential energy of a single Ca—O ion pair that is just touching (the magnitude of electronic charge is given on the inside back cover). (**d**) Calculate the energy of a mole of such pairs. How does this compare to the lattice energy of CaO? (**e**) What factor do you think accounts for most of the discrepancy between the energies in part (d)—the bonding in CaO is more covalent than ionic, or the electrostatic interactions in a crystal lattice are more complicated than those in a single ion pair?

8.83 Construct a Born–Haber cycle for the formation of the hypothetical compound $NaCl_2$, where the sodium ion has a 2+ charge (the second ionization energy for sodium is given in Table 7.2). (**a**) How large would the lattice energy need to be for the formation of $NaCl_2$ to be exothermic? (**b**) If we were to estimate the lattice energy of $NaCl_2$ to be roughly equal to that of $MgCl_2$ (2326 kJ/mol from Table 8.1), what value would you obtain for the standard enthalpy of formation, ΔH_f°, of $NaCl_2$?

8.84 A classmate of yours is convinced that he knows everything about electronegativity. (**a**) In the case of atoms X and Y having different electronegativities, he says, the diatomic molecule X—Y must be polar. Is your classmate correct? (**b**) Your classmate says that the farther the two atoms are apart in a bond, the larger the dipole moment will be. Is your classmate correct?

8.85 Consider the collection of nonmetallic elements O, P, Te, I, and B. (**a**) Which two would form the most polar single bond? (**b**) Which two would form the longest single bond? (**c**) Which two would be likely to form a compound of formula XY_2? (**d**) Which combinations of elements would likely yield a compound of empirical formula X_2Y_3?

8.86 The substance chlorine monoxide, ClO(*g*), is important in atmospheric processes that lead to depletion of the ozone layer. The ClO molecule has an experimental dipole moment of 1.24 D, and the Cl—O bond length is 1.60 Å. (**a**) Determine the magnitude of the charges on the Cl and O atoms in units of the electronic charge, *e*. (**b**) Based on the electronegativities of the elements, which atom would you expect to have a partial negative charge in the ClO molecule? (**c**) Using formal charges as a guide, propose the dominant Lewis structure for the molecule. (**d**) The anion ClO^- exists. What is the formal charge on the Cl for the best Lewis structure for ClO^-?

[8.87] (**a**) Using the electronegativities of Br and Cl, estimate the partial charges on the atoms in the Br—Cl molecule. (**b**) Using these partial charges and the atomic radii given in Figure 7.8, estimate the dipole moment of the molecule. (**c**) The measured dipole moment of BrCl is 0.57 D. If you assume the bond length in BrCl is the sum of the atomic radii, what are the partial charges on the atoms in BrCl using the experimental dipole moment?

8.88 A major challenge in implementing the "hydrogen economy" is finding a safe, lightweight, and compact way of storing hydrogen for use as a fuel. The hydrides of light metals are attractive for hydrogen storage because they can store a high weight percentage of hydrogen in a small volume. For example, $NaAlH_4$ can release 5.6% of its mass as H_2 upon decomposing to NaH(*s*), Al(*s*), and $H_2(g)$. $NaAlH_4$ possesses both covalent bonds, which hold polyatomic anions together, and ionic bonds. (**a**) Write a balanced equation for the decomposition of $NaAlH_4$. (**b**) Which element in $NaAlH_4$ is the most electronegative? Which one is the least electronegative? (**c**) Based on electronegativity differences, predict the identity of the polyatomic anion. Draw a Lewis structure for this ion. (**d**) What is the formal charge on hydrogen in the polyatomic ion?

8.89 Although I_3^- is a known ion, F_3^- is not. (**a**) Draw the Lewis structure for I_3^- (it is linear, not a triangle). (**b**) One of your classmates says that F_3^- does not exist because F is too electronegative to make bonds with another atom. Give an example that proves your classmate is wrong. (**c**) Another classmate says F_3^- does not exist because it would violate the octet rule. Is this classmate possibly correct? (**d**) Yet another classmate says F_3^- does not exist because F is too small to make bonds to more than one atom. Is this classmate possibly correct?

8.90 Calculate the formal charge on the indicated atom in each of the following molecules or ions: (**a**) the central oxygen atom in O_3, (**b**) phosphorus in PF_6^-, (**c**) nitrogen in NO_2, (**d**) iodine in ICl_3, (**e**) chlorine in $HClO_4$ (hydrogen is bonded to O).

8.91 The hypochlorite ion, ClO^-, is the active ingredient in bleach. The perchlorate ion, ClO_4^-, is a main component of rocket propellants. Draw Lewis structures for both ions.

(**a**) What is the formal charge of Cl in the hypochlorite ion? (**b**) What is the formal charge of Cl in the perchlorate ion, assuming the Cl—O bonds are all single bonds? (**c**) What is the oxidation number of Cl in the hypochlorite ion? (**d**) What is the oxidation number of Cl in the perchlorate ion, assuming the Cl—O bonds are all single bonds? (**e**) In a redox reaction, which ion would you expect to be more easily reduced?

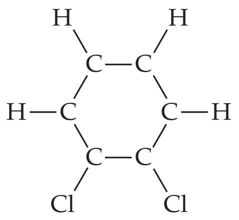
8.92 The following three Lewis structures can be drawn for N_2O:

$$:N\equiv N-\underset{..}{\ddot{O}}: \longleftrightarrow :\underset{..}{\ddot{N}}-N\equiv O: \longleftrightarrow :\ddot{N}=N=\ddot{O}:$$

(**a**) Using formal charges, which of these three resonance forms is likely to be the most important? (**b**) The N—N bond length in N_2O is 1.12 Å, slightly longer than a typical N≡N bond; and the N—O bond length is 1.19 Å, slightly shorter than a typical N=O bond (see Table 8.4). Based on these data, which resonance structure best represents N_2O?

[8.93] (**a**) Triazine, $C_3H_3N_3$, is like benzene except that in triazine every other C—H group is replaced by a nitrogen atom. Draw the Lewis structure(s) for the triazine molecule. (**b**) Estimate the carbon–nitrogen bond distances in the ring.

[8.94] *Ortho*-Dichlorobenzene, $C_6H_4Cl_2$, is obtained when two of the adjacent hydrogen atoms in benzene are replaced with Cl atoms. A skeleton of the molecule is shown here. (**a**) Complete a Lewis structure for the molecule using bonds and electron pairs as needed. (**b**) Are there any resonance structures for the molecule? If so, sketch them. (**c**) Are the resonance structures in (a) and (b) equivalent to one another as they are in benzene?



Integrative Exercises

8.95 Consider the hypothetical molecule B—A=B. Are the following statements true or false? (**a**) This molecule cannot exist. (**b**) If resonance was important, the molecule would have identical A–B bond lengths.

8.96 An important reaction for the conversion of natural gas to other useful hydrocarbons is the conversion of methane to ethane.

$$2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

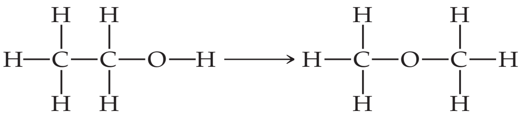
In practice, this reaction is carried out in the presence of oxygen, which converts the hydrogen produced into water.

$$2\,CH_4(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_6(g) + H_2O(g)$$

Use Table 8.3 to estimate Δ*H* for these two reactions. Why is the conversion of methane to ethane more favorable when oxygen is used?

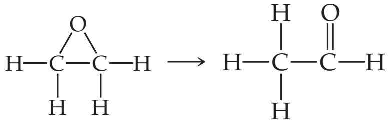
8.97 Two compounds are isomers if they have the same chemical formula but different arrangements of atoms. Use Table 8.3 to estimate Δ*H* for each of the following gas-phase isomerization reactions and indicate which isomer has the lower enthalpy.

(**a**)



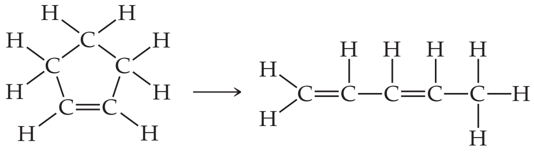
Ethanol Dimethyl ether

(**b**)



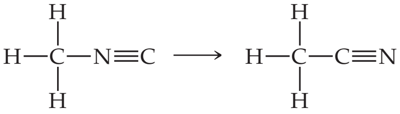
Ethylene oxide Acetaldehyde

(**c**)



Cyclopentene Pentadiene

(**d**)



Methyl isocyanide Acetonitrile

8.98 The Ti^{2+} ion is isoelectronic with the Ca atom. (**a**) Write the electron configurations of Ti^{2+} and Ca. (**b**) Calculate the number of unpaired electrons for Ca and for Ti^{2+}. (**c**) What charge would Ti have to be isoelectronic with Ca^{2+}?

8.99 (**a**) Draw the Lewis structure for hydrogen peroxide, H_2O_2. (**b**) What is the weakest bond in hydrogen peroxide? (**c**) Hydrogen peroxide is sold commercially as an aqueous solution in brown bottles to protect it from light. Calculate the longest wavelength of light that has sufficient energy to break the weakest bond in hydrogen peroxide.

8.100 The electron affinity of oxygen is -141 kJ/mol, corresponding to the reaction

$$\mathrm{O}(g) + e^{-} \longrightarrow \mathrm{O}^{-}(g)$$

The lattice energy of $K_2O(s)$ is 2238 kJ/mol. Use these data along with data in Appendix C and Figure 7.10 to calculate the "second electron affinity" of oxygen, corresponding to the reaction

$$\mathrm{O}^{-}(g) + e^{-} \longrightarrow \mathrm{O}^{2-}(g)$$

8.101 You and a partner are asked to complete a lab entitled "Oxides of Ruthenium" that is scheduled to extend over two lab periods. The first lab, which is to be completed by your partner, is devoted to carrying out compositional analysis. In the second lab, you are to determine melting points. Upon going to lab you find two unlabeled vials, one containing a soft yellow substance and the other a black powder. You also find the following notes in your partner's notebook—*Compound 1*: 76.0% Ru and 24.0% O (by mass), *Compound 2*: 61.2% Ru and 38.8% O (by mass). (**a**) What is the empirical formula for Compound 1? (**b**) What is the empirical formula for Compound 2? Upon determining the melting points of these two compounds, you find that the yellow compound melts at 25 °C, while the black powder does not melt up to the maximum temperature of your apparatus, 1200 °C. (**c**) What is the identity of the yellow compound? (**d**) What is the identity of the black compound? (**e**) Which compound is molecular? (**f**) Which compound is ionic?

8.102 One scale for electronegativity is based on the concept that the electronegativity of any atom is proportional to the ionization energy of the atom minus its electron affinity: electronegativity $= k(I - EA)$, where k is a proportionality constant. (**a**) How does this definition explain why the electronegativity of F is greater than that of Cl, even though Cl has the greater electron affinity? (**b**) Why are both ionization energy and electron affinity relevant to the notion of electronegativity? (**c**) By using data in Chapter 7, determine the value of k that would lead to an electronegativity of 4.0 for F under this definition. (**d**) Use your result from part (c) to determine the electronegativities of Cl and O using this scale. (**e**) Another scale for electronegativity defines electronegativity as the average of an atom's first ionization energy and its electron affinity. Using this scale, calculate the electronegativities for the halogens, and scale them so that fluorine has an electronegativity of 4.0. On this scale, what is Br's electronegativity?

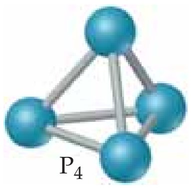
8.103 The compound chloral hydrate, known in detective stories as knockout drops, is composed of 14.52% C, 1.83% H, 64.30% Cl, and 13.35% O by mass, and has a molar mass of 165.4 g/mol. (**a**) What is the empirical formula of this substance? (**b**) What is the molecular formula of this substance? (**c**) Draw the Lewis structure of the molecule, assuming that the Cl atoms bond to a single C atom and that there are a C—C bond and two C—O bonds in the compound.

8.104 Barium azide is 62.04% Ba and 37.96% N. Each azide ion has a net charge of 1−. (**a**) Determine the chemical formula of the azide ion. (**b**) Write three resonance structures for the azide ion. (**c**) Which structure is most important? (**d**) Predict the bond lengths in the ion.

8.105 Acetylene (C_2H_2) and nitrogen (N_2) both contain a triple bond, but they differ greatly in their chemical properties. (**a**) Write the Lewis structures for the two substances. (**b**) By referring to Appendix C, look up the enthalpies of formation of acetylene and nitrogen. Which compound is more stable? (**c**) Write balanced chemical equations for the complete oxidation of N_2 to form $N_2O_5(g)$ and of acetylene to form $CO_2(g)$ and $H_2O(g)$. (**d**) Calculate the enthalpy of oxidation per mole for N_2 and for C_2H_2 (the enthalpy of formation of $N_2O_5(g)$ is 11.30 kJ/mol). (**e**) Both N_2 and C_2H_2 possess triple bonds with quite high bond enthalpies (Table 8.3). Calculate the enthalpy of hydrogenation per mole for both compounds: acetylene plus H_2 to make methane, CH_4; nitrogen plus H_2 to make ammonia, NH_3.

8.106 Under special conditions, sulfur reacts with anhydrous liquid ammonia to form a binary compound of sulfur and nitrogen. The compound is found to consist of 69.6% S and 30.4% N. Measurements of its molecular mass yield a value of 184.3 g/mol. The compound occasionally detonates on being struck or when heated rapidly. The sulfur and nitrogen atoms of the molecule are joined in a ring. All the bonds in the ring are of the same length. (**a**) Calculate the empirical and molecular formulas for the substance. (**b**) Write Lewis structures for the molecule, based on the information you are given. (*Hint:* You should find a relatively small number of dominant Lewis structures.) (**c**) Predict the bond distances between the atoms in the ring. (*Note*: The S—S distance in the S_8 ring is 2.05 Å.) (**d**) The enthalpy of formation of the compound is estimated to be 480 kJ/mol^{-1}. ΔH_f° of S(g) is 222.8 kJ/mol. Estimate the average bond enthalpy in the compound.

8.107 A common form of elemental phosphorus is the tetrahedral P_4 molecule, where all four phosphorus atoms are equivalent:



P_4

At room temperature phosphorus is a solid. (**a**) Are there any lone pairs of electrons in the P_4 molecule? (**b**) How many P—P bonds are there in the molecule? (**c**) Draw a Lewis structure for a linear P_4 molecule that satisfies the octet rule. Does this molecule have resonance structures? (**d**) On the basis of formal charges, which is more stable, the linear molecule or the tetrahedral molecule?

8.108 Formic acid has the chemical formula HCOOH. It is a colorless liquid that has a density of 1.220 g/mL. (**a**) The carbon atom in formic acid is bound to one H and both O's. Draw the Lewis structure for formic acid, showing resonance if present. (**b**) Formic acid can react with NaOH in aqueous solution to produce the formate ion, $HCOO^-$. Write the balanced chemical equation for this reaction. (**c**) Draw the Lewis structure of the formate ion, showing resonance if present. (**d**) How many milliliters of a 0.100 M solution of NaOH would it take to completely react with 0.785 mL of formic acid?

8.109 Ammonia reacts with boron trifluoride to form a stable compound, as we saw in Section 8.7. (**a**) Draw the Lewis structure of the ammonia–boron trifluoride reaction product. (**b**) The B—N bond is obviously more polar than the

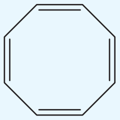
C—C bond. Draw the charge distribution you expect on the B—N bond within the molecule (using the delta plus and delta minus symbols mentioned in Section 8.4). (**c**) Boron trichloride also reacts with ammonia in a similar way to the trifluoride. Predict whether the B—N bond in the trichloride reaction product would be more or less polar than the B—N bond in the trifluoride product, and justify your reasoning.

8.110 Ammonium chloride, NH_4Cl, is a very soluble salt in water. (**a**) Draw the Lewis structures of the ammonium and chloride ions. (**b**) Is there an N—Cl bond in solid ammonium chloride? (**c**) If you dissolve 14 g of ammonium chloride in 500.0 mL of water, what is the molar concentration of the solution? (**d**) How many grams of silver nitrate do you need to add to the solution in part (c) to precipitate all of the chloride as silver chloride?

Design an Experiment

You have learned that the resonance of benzene, C_6H_6, gives the compound special stability.

(**a**) By using data in Appendix C, compare the heat of combustion of 1.0 mol $C_6H_6(g)$ to the heat of combustion of 3.0 mol acetylene, $C_2H_2(g)$. Which has the greater fuel value, 1.0 mol $C_6H_6(g)$ or 3.0 mol $C_2H_2(g)$? Are your calculations consistent with benzene being especially stable? (**b**) Repeat part (a), with the appropriate molecules, for toluene ($C_6H_5CH_3$), a derivative of benzene that has a —CH_3 group in place of one H. (**c**) Another reaction you can use to compare molecules is *hydrogenation*, the reaction of a carbon–carbon double bond with H_2 to make a C—C single bond and two C—H single bonds. The experimental heat of hydrogenation of benzene to make cyclohexane (C_6H_{12}, a six-membered ring with 6 C—C single bonds and 12 C—H bonds) is 208 kJ/mol. The experimental heat of hydrogenation of cyclohexene (C_6H_{10}, a six-membered ring with one C═C double bond, 5 C—C single bonds, and 10 C—H bonds) to make cyclohexane is 120 kJ/mol. Show how these data can provide you with an estimate of the *resonance stabilization energy* of benzene. (**d**) Are the bond lengths or angles in benzene, compared to other hydrocarbons, sufficient to decide if benzene exhibits resonance and is especially stable? Discuss. (**e**) Consider cyclooctatetraene, C_8H_8, which has the octagonal structure shown below.



Cyclooctatetraene

What experiments or calculations could you perform to determine whether cyclooctatetraene exhibits resonance?

Design An Experiment provides a departure from the usual kinds of end-of-chapter exercises with an inquiry-based, open-ended approach that tries to stimulate the student to "think like a scientist." Designed to foster critical thinking, each exercise presents the student with a scenario in which various unknowns require investigation. The student is called upon to ponder how experiments might be set up to provide answers to particular questions about observations.