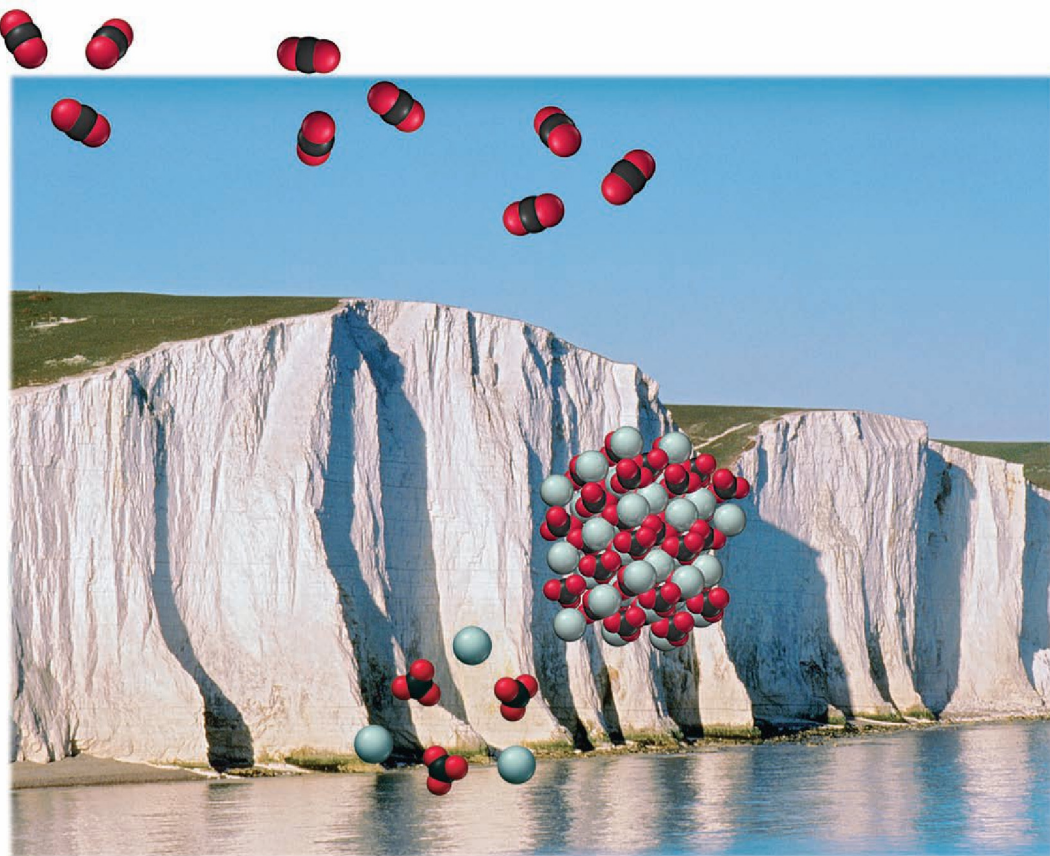


CHAPTER
8

BASIC CONCEPTS OF CHEMICAL BONDING



THE WHITE CLIFFS OF DOVER in southeastern England are made up largely of chalk, a porous form of limestone. The mineral calcite, with a composition of CaCO_3 , is the predominant chemical substance in both chalk and limestone. Much of Earth's calcite is produced by marine organisms, which combine Ca^{2+} and CO_3^{2-} ions to form shells of CaCO_3 . The presence of CO_3^{2-} ions in oceans can be traced to dissolved CO_2 from the atmosphere.

8.1 Chemical Bonds, Lewis Symbols, and the Octet Rule

We can broadly characterize chemical bonds into three types: *ionic*, *covalent*, and *metallic*. In evaluating bonding, *Lewis symbols* provide a useful shorthand notation for keeping track of the valence electrons in atoms and ions.

8.2 Ionic Bonding

We will observe that in ionic substances the atoms are held together by the electrostatic attractions between ions of opposite charge. We will study the energetics of formation of ionic substances and describe the *lattice energy* of these substances.

8.3 Covalent Bonding

We also recognize that the atoms in molecular substances are held together by the sharing of one or more electron pairs between atoms. In general the electrons are shared in such a way that each atom attains an *octet* of electrons.

8.4 Bond Polarity and Electronegativity

We define *electronegativity* as the ability of an atom in a compound to attract electrons to itself. In general, electron pairs will be shared unequally between atoms of differing electronegativity, leading to *polar covalent bonds*.

8.5 Drawing Lewis Structures

We will see that *Lewis structures* are a simple yet powerful way of predicting the covalent bonding

patterns within molecules. In addition to the octet rule, we will see that the concept of *formal charge* can be used to identify the most favorable Lewis structure.

8.6 Resonance Structures

We observe that in some cases more than one equivalent Lewis structure can be drawn for a molecule or polyatomic ion. The actual structure in such cases is a blend of two or more contributing Lewis structures, called *resonance structures*.

8.7 Exceptions to the Octet Rule

We recognize that the octet rule is more of a guideline than an inviolate rule. Exceptions to the octet rule include molecules with an odd number of electrons; molecules where large differences in electronegativity prevent an atom from completing its octet; and, most commonly, molecules where an element from the third period or lower attains more than an octet of electrons.

8.8 Strengths of Covalent Bonds

We observe that bond strengths vary with the number of shared electron pairs as well as other factors. We can use *average bond enthalpy* values to estimate the enthalpies of reactions in cases where thermodynamic data such as heats of formation are unavailable.

CALCIUM CARBONATE, CaCO_3 , IS ONE OF THE MOST INTERESTING AND VERSATILE COMPOUNDS on the planet. It accounts for roughly 4% of Earth's crust and is the major component of rocks such as limestone and marble. The white cliffs of Dover in southeastern England are one of the most

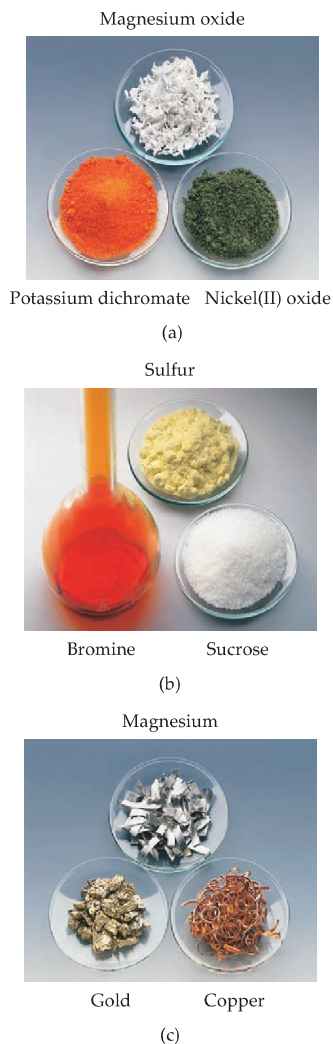
famous natural formations of CaCO_3 . The cliffs consist almost entirely of a porous form of limestone called chalk.

Unlike most inorganic substances, CaCO_3 is widely used by living organisms and is found in objects such as seashells, coral, eggshells, and pearls. Calcium carbonate plays a role in the complex chemistry associated with the greenhouse effect because it is formed in the oceans through the reaction between calcium ions and dissolved carbon dioxide. When limestone is heated to elevated temperatures, CaCO_3 decomposes into solid CaO (the important industrial chemical called quicklime) and gaseous CO_2 . Calcium carbonate undergoes the reactions that it does because the atoms in CaCO_3 are held

together by a combination of two different types of bonds. The carbon and oxygen atoms that make up the carbonate ion share valence electrons, resulting in the formation of *covalent bonds*. The oppositely charged Ca^{2+} and CO_3^{2-} ions are held together by electrostatic attractions, which are called *ionic bonds*.

The properties of substances are determined in large part by the *chemical bonds* that hold their atoms together. What determines the type of bonding in each 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 structures of the atoms involved, which we discussed in Chapters 6 and 7. In this chapter and the next, we will examine the relationship between the electronic structures of atoms and the chemical bonds they form. We will also see how the properties of ionic and covalent substances arise from the distributions of electronic charge within atoms, ions, and molecules.

▼ **Figure 8.1 Chemical bonds.**
Examples of substances in which (a) ionic, (b) covalent, and (c) metallic bonds are found.



8.1 CHEMICAL BONDS, LEWIS SYMBOLS, AND THE OCTET RULE

Whenever two atoms or ions are strongly attached to each other, we say there is a **chemical bond** between them. There are three general types of chemical bonds: ionic, covalent, and metallic. Figure 8.1 ◀ shows examples of substances in which we find each of these types of attractive forces.

The term **ionic bond** refers to electrostatic forces that exist between ions of opposite charge. Ions may be formed from atoms by the transfer of one or more electrons from one atom to another. 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). Ionic bonding will be discussed in Section 8.2.

A **covalent bond** results from the sharing of electrons between two atoms. The most familiar examples of covalent bonding are seen in the interactions of nonmetallic elements with one another. We devote much of this chapter and the next to describing and understanding covalent bonds.

Metallic bonds are found in metals, such as copper, iron, and aluminum. Each atom in a metal is bonded to several neighboring atoms. The bonding electrons are relatively free to move throughout the three-dimensional structure of the metal. Metallic bonds give rise to such typical metallic properties as high electrical conductivity and luster. We will examine these bonds in Chapter 23.

Lewis Symbols

The electrons involved in chemical bonding are the *valence electrons*, which, for most atoms, are those residing in the outermost occupied shell of an atom. ◀◀ (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 in the course of bond formation, using what are now known as *Lewis electron-dot symbols*, or merely Lewis symbols.

The **Lewis symbol** for an element consists of the chemical symbol for the element plus a dot for each valence electron. Sulfur, for example, has the electron configuration $[\text{Ne}]3s^23p^4$; its Lewis symbol therefore shows six valence electrons:



The dots are placed on the four sides of the atomic symbol: the top, the bottom, and the left and right sides. Each side can accommodate up to two electrons. All four sides of the symbol are equivalent, which means that the choice of which sides accommodate the fifth and sixth electrons is arbitrary.

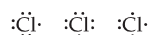
TABLE 8.1 Lewis Symbols

| Element | Electron Configuration | Lewis Symbol | Element | Electron Configuration | Lewis Symbol |
|---------|-------------------------------------|--------------|---------|-------------------------------------|--------------|
| Li | [He]2s ¹ | Li· | Na | [Ne]3s ¹ | Na· |
| Be | [He]2s ² | ·Be· | Mg | [Ne]3s ² | ·Mg· |
| B | [He]2s ² 2p ¹ | ·B· | Al | [Ne]3s ² 3p ¹ | ·Al· |
| C | [He]2s ² 2p ² | ·C· | Si | [Ne]3s ² 3p ² | ·Si· |
| N | [He]2s ² 2p ³ | ·N· | P | [Ne]3s ² 3p ³ | ·P· |
| O | [He]2s ² 2p ⁴ | ·O· | S | [Ne]3s ² 3p ⁴ | ·S· |
| F | [He]2s ² 2p ⁵ | ·F· | Cl | [Ne]3s ² 3p ⁵ | ·Cl· |
| Ne | [He]2s ² 2p ⁶ | ·Ne· | Ar | [Ne]3s ² 3p ⁶ | ·Ar· |

The electron configurations and Lewis symbols for the representative elements of the second and third rows of the periodic table are shown in Table 8.1 ▲. Notice that the number of valence electrons in any representative element is the same as the group number of the element. For example, the Lewis symbols for oxygen and sulfur, members of group 6A, both show six dots.

GIVE IT SOME THOUGHT

Are all three of the following Lewis symbols for Cl correct?



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 noble gases (except He) have eight valence electrons, many atoms undergoing reactions also 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 terms of Lewis symbols, an octet can be thought of as four pairs of valence electrons arranged around the atom, as in the Lewis symbol for Ne in Table 8.1. There are many exceptions to the octet rule, but it provides a useful framework for introducing many important concepts of bonding.

8.2 IONIC BONDING

When sodium metal, Na(*s*), is brought into contact with chlorine gas, Cl₂(*g*), a violent reaction ensues (Figure 8.2 ▼). The product of this very exothermic reaction is sodium chloride, NaCl(*s*):

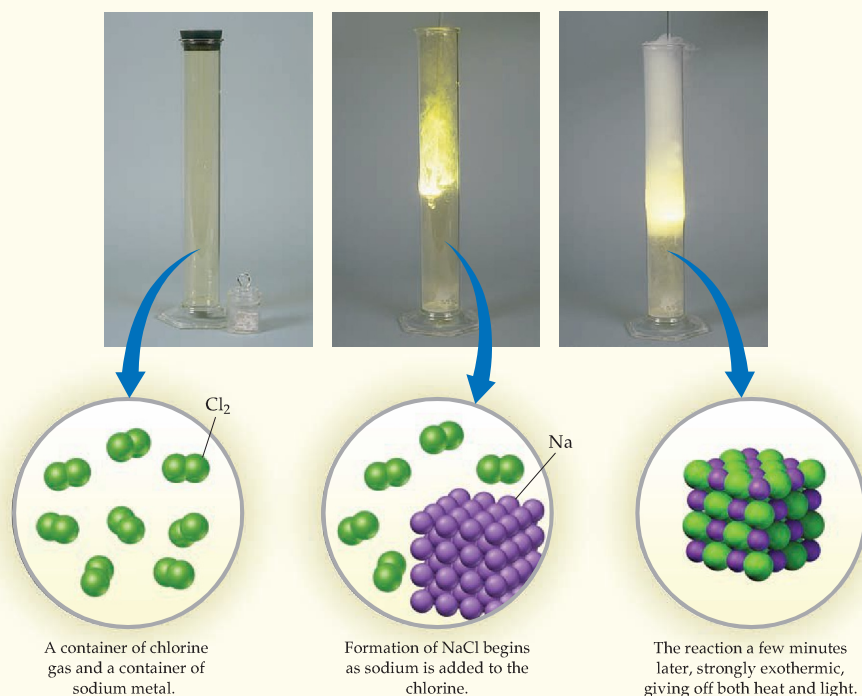


Sodium chloride is composed of Na⁺ and Cl[−] ions, which are arranged in a regular three-dimensional array, as shown in Figure 8.3 ▼.

The formation of Na⁺ from Na and Cl[−] from Cl₂ indicates that an electron has been lost by a sodium atom and gained by a chlorine atom—we can envision an *electron transfer* from the Na atom to the Cl atom. Two of the atomic properties we discussed in Chapter 7 give us an indication of how readily electron transfer

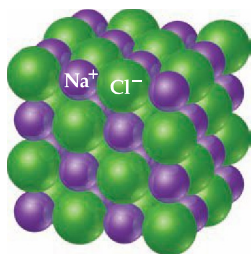
FORMATION OF SODIUM CHLORIDE

When metals and nonmetals react, electrons are transferred from the metal atoms to the nonmetal atoms, forming ions. The principal reason that ionic compounds are stable is the attraction between ions of unlike charge, which draws them together, releasing energy and causing the ions to form a solid array or lattice.

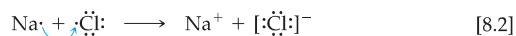


▲ Figure 8.2 Formation of sodium chloride.

occurs: the ionization energy, which indicates how easily an electron can be removed from an atom, and the 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 of the atoms readily gives up an electron (low ionization energy) and the other 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 Cl₂ molecule), we can represent this reaction as follows:



▲ Figure 8.3 The crystal structure of sodium chloride. In this three-dimensional array of ions, each Na⁺ ion is surrounded by six Cl⁻ ions, and each Cl⁻ ion is surrounded by six Na⁺ ions.



The arrow indicates the transfer of an electron from the Na atom to the Cl atom. Each ion has an octet of electrons, the octet on Na⁺ being the 2s²2p⁶ electrons that lie below the single 3s valence electron of the Na atom. We have put a bracket around the chloride ion to emphasize that all eight electrons are located on the Cl⁻ ion.

GIVE IT SOME THOUGHT

Describe the electron transfers that occur in the formation of calcium oxide from elemental calcium and oxygen.

Energetics of Ionic Bond Formation

As seen in Figure 8.2, the reaction of sodium with chlorine is *very* exothermic. In fact, Equation 8.1 is the reaction for the formation of NaCl(s) from its elements, so that the enthalpy change for the reaction is ΔH_f° for NaCl(s). In Appendix C we see that the heat of formation of other ionic substances is also quite negative. What factors make the formation of ionic compounds so exothermic?

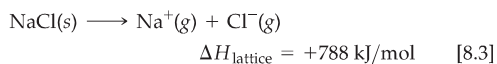
In Equation 8.2 we represented the formation of NaCl as the transfer of an electron from Na to Cl. Recall from our discussion of ionization energies, however, that the loss of electrons from an atom is always an endothermic process. ∞ (Section 7.4) Removing an electron from Na(g) to form Na⁺(g), for instance, requires 496 kJ/mol. Conversely, when a nonmetal gains an electron, the process is generally exothermic, as seen from the negative electron affinities of the elements. ∞ (Section 7.5) Adding an electron to Cl(g), for example, releases 349 kJ/mol. If the transfer of an electron from one atom to another were the only factor in forming an ionic bond, the overall process would not be exothermic. For example, removing an electron from Na(g) and adding it to Cl(g) is 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 are not interacting with one another, which is quite different from the situation in ionic solids.

GIVE IT SOME THOUGHT

Consider the ionization energies of the alkali metals and the electron affinities of the halogens given in Chapter 7. Can you find any pair where the transfer of an electron from the alkali metal to the halogen would be an exothermic process?

The principal reason that ionic compounds are stable is the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array, or lattice, such as that shown for NaCl in Figure 8.3. A measure of just 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 a mole of a solid ionic compound into its gaseous ions*.

To get a picture of this process for NaCl, imagine that the structure shown in Figure 8.3 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:



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 8.2 \blacktriangleright lists the lattice energies of NaCl and other ionic compounds. All are large positive values, indicating that the ions are strongly attracted to one another in these solids. The energy released by the

TABLE 8.2 ■ Lattice Energies for Some Ionic Compounds

| Compound | Lattice Energy (kJ/mol) | Compound | Lattice Energy (kJ/mol) |
|----------|-------------------------|-------------------|-------------------------|
| LiF | 1030 | MgCl ₂ | 2326 |
| 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 | | |

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.

The magnitude of the lattice energy of a solid depends on the charges of the ions, their sizes, and their arrangement in the solid. We saw in Chapter 5 that the potential energy of two interacting charged particles is given by

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

In this equation Q_1 and Q_2 are the charges on the particles, d is the distance between their centers, and κ is a constant, $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$. [∞∞ \(Section 5.1\)](#) 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 magnitude of lattice energies depends predominantly on the ionic charges because ionic radii vary over only a limited range.

■ SAMPLE EXERCISE 8.1 | Magnitudes of Lattice Energies

Without consulting Table 8.2, arrange the following ionic compounds in order of increasing lattice energy: NaF, CsI, and CaO.

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 can then use Equation 8.4 qualitatively to determine the relative energies, knowing that the larger the ionic charges, the greater the energy and 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 of the charges, $Q_1 Q_2$, appears in the numerator of Equation 8.4, the lattice energy will increase dramatically when the charges of the ions 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 in NaF and CsI are the same. As a result, the difference in their lattice energies will depend on the difference in the distance between the centers of the ions in their 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 the Na^+ and F^- ions in NaF will be 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 $\text{CsI} < \text{NaF} < \text{CaO}$.

Check: Table 8.2 confirms our predicted order is correct.

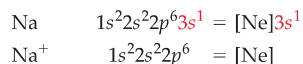
■ PRACTICE EXERCISE

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

Answer: ZrO_2

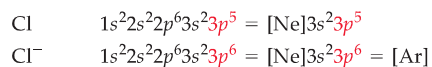
Electron Configurations of Ions of the *s*- and *p*-Block Elements

We began considering the electron configurations of ions in Section 7.4. In light of our examination of ionic bonding, we will continue with that discussion here. 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:



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



To form a Cl^{2-} ion, the second electron would have to be added to the next higher shell of the Cl atom, which is energetically very unfavorable. Therefore, we never observe Cl^{2-} ions in ionic compounds. Based on these concepts, we expect that ionic compounds of the representative metals from groups 1A, 2A, and 3A will contain cations with charges of $1+$, $2+$, and $3+$, respectively. Likewise, ionic compounds of the representative nonmetals of groups 5A, 6A, and 7A usually contain anions of charge $3-$, $2-$, and $1-$, respectively.

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 it will form a cation or an anion. We can then use its electron configuration to determine the ion that is likely to be formed.

Solve: (a) Strontium is a metal in group 2A and will therefore form a cation. Its electron configuration is $[\text{Kr}]5s^2$, and so we expect that the two valence electrons can be lost easily 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 ($[\text{Ne}]3s^2 3p^4$) 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

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

Answer: Mg^{2+} and N^{3-}

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 $[\text{Kr}]4d^{10}5s^1$ 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.

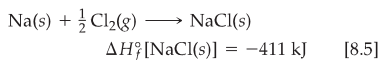
Recall from our discussion in Section 7.4 that when a positive ion is formed from an atom, electrons are always lost first from the subshell having the

A Closer Look

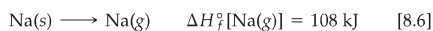
CALCULATION OF LATTICE ENERGIES: THE BORN-HABER CYCLE

Lattice energy is a useful concept because it relates directly to the stability of an ionic solid. Unfortunately, the lattice energy cannot be determined directly by experiment. It 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 put these steps together in a way that gives us 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.

In the Born-Haber cycle for NaCl, we consider the formation of NaCl(s) from the elements Na(s) and Cl₂(g) by two different routes, as shown in Figure 8.4. The enthalpy change for the direct route (red arrow) is the heat of formation of NaCl(s):



The indirect route consists of five steps, shown by the green arrows in Figure 8.4. First, we generate gaseous atoms of sodium by vaporizing sodium metal. Then we form gaseous atoms of chlorine by breaking the bonds in the Cl₂ molecules. The enthalpy changes for these processes are available to us as enthalpies of formation (Appendix C):

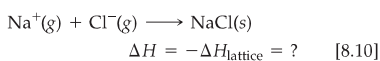


Both of these processes are endothermic; energy is required to generate gaseous sodium and chlorine atoms.

In the next two steps we remove the electron from Na(g) to form Na⁺(g) and then add the electron to Cl(g) to form Cl⁻(g). The enthalpy changes for these processes equal the first ionization energy of Na, I₁(Na), and the electron affinity of Cl, denoted E(Cl), respectively: ∞∞ (Sections 7.4, 7.5)



Finally, we combine the gaseous sodium and chloride ions to form solid sodium chloride. Because this process is just the reverse of the lattice energy (breaking a solid into gaseous ions), the enthalpy change is the negative of the lattice energy, the quantity that we want to determine:



The sum of the five steps in the indirect path (green arrows) gives us NaCl(s) from Na(s) and $\frac{1}{2}$ Cl₂(g). Thus, from Hess's law we know that the sum of the enthalpy changes for these five steps equals that for the direct path, indicated by the red arrow, Equation 8.5:

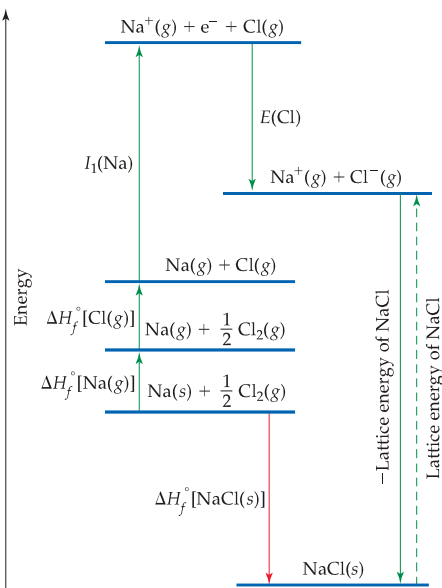
$$\Delta H_f^\circ[\text{NaCl(s)}] = \Delta H_f^\circ[\text{Na(g)}] + \Delta H_f^\circ[\text{Cl(g)}] \\ + I_1(\text{Na}) + E(\text{Cl}) - \Delta H_{\text{lattice}} \\ -411 \text{ kJ} = 108 \text{ kJ} + 122 \text{ kJ} + 496 \text{ kJ} - 349 \text{ kJ} - \Delta H_{\text{lattice}}$$

Solving for ΔH_{lattice}:

$$\Delta H_{\text{lattice}} = 108 \text{ kJ} + 122 \text{ kJ} + 496 \text{ kJ} - 349 \text{ kJ} + 411 \text{ kJ} \\ = 788 \text{ kJ}$$

Thus, the lattice energy of NaCl is 788 kJ/mol.

Related Exercises: 8.26, 8.27, and 8.28



▲ Figure 8.4 The Born-Haber cycle. This representation shows the energetic relationships in the formation of ionic solids from the elements. By Hess's law, the enthalpy of formation of NaCl(s) from elemental sodium and chlorine (Equation 8.5) is equal to the sum of the energies of several individual steps (Equations 8.6 through 8.10).

largest value of n . Thus, in forming ions, transition metals lose the valence-shell s electrons first, then as many d electrons as are required to reach the charge of the ion. Let's consider Fe, which has the electron configuration [Ar]3d⁶4s². In forming the Fe²⁺ ion, the two 4s electrons are lost, leading to an [Ar]3d⁶ configuration. Removal of an additional electron gives the Fe³⁺ ion, whose electron configuration is [Ar]3d⁵.

GIVE IT SOME THOUGHT

Which element forms a $2+$ ion that has the electron configuration $[\text{Kr}]4d^8$?

8.3 COVALENT BONDING

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 8.3.

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 paraffin.

For the very large class of substances that do not behave like ionic substances, we need a different model for the bonding between atoms. G. N. Lewis reasoned that atoms might acquire a noble-gas electron configuration by sharing electrons with other atoms. As we noted in Section 8.1, a chemical bond formed by sharing a pair of electrons is called 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, electrostatic interactions occur between them. 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 8.5. Because the H_2 molecule exists as a stable entity, the attractive forces must exceed the repulsive ones. Let's take a closer look at the attractive forces that hold this molecule together.

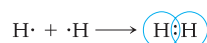
By using quantum mechanical methods analogous to those employed for atoms ∞ (Section 6.5), it is possible to calculate the distribution of electron density in molecules. Such a calculation for H_2 shows that the attractions between the nuclei and the electrons cause electron density to concentrate between the nuclei, as shown in Figure 8.5(b). As a result, the overall electrostatic interactions are attractive. Thus, the atoms in H_2 are held together principally because the two nuclei are electrostatically 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

If a H_2 molecule is ionized to form H_2^+ , it will change the bond strength. Based on the simple description of covalent bonding given above, would you expect the $\text{H}-\text{H}$ bond in H_2^+ to be weaker or stronger than the $\text{H}-\text{H}$ bond in H_2 ?

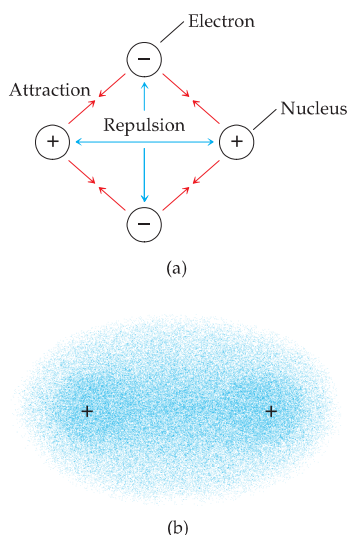
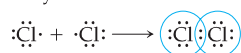
Lewis Structures

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



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

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



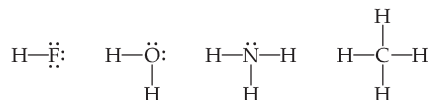
▲ Figure 8.5 The covalent bond in H_2 . (a) The attractions and repulsions among electrons and nuclei in the hydrogen molecule. (b) Electron distribution in the H_2 molecule. The concentration of electron density between the nuclei leads to a net attractive force that constitutes the covalent bond holding the molecule together.

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

The structures shown here for H_2 and Cl_2 are called **Lewis structures** (or Lewis electron-dot structures). In writing Lewis structures, we usually show each electron pair shared between atoms as a line and the unshared electron pairs as dots. Written this way, the Lewis structures for H_2 and Cl_2 are



For the 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 covalent bonds; and 4A elements, such as C, would form four covalent bonds. These predictions are borne out in many compounds. For example, consider the simple hydrogen compounds of the nonmetals of the second row of the periodic table:



Thus, the Lewis model succeeds in accounting for the compositions of many compounds of nonmetals, in which covalent bonding predominates.

SAMPLE EXERCISE 8.3 | Lewis Structure of a Compound

Given the Lewis symbols for the elements nitrogen and fluorine shown in Table 8.1, 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 in the compound. Nitrogen requires three additional electrons to complete its octet, whereas fluorine requires only 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 Lewis structure for the resulting compound, NF_3 , is



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

Compare the Lewis symbol for neon with the Lewis structure for methane, CH_4 . In what important way are the electron arrangements about neon and carbon alike? In what important respect are they different?

Answer: Both atoms have an octet of electrons about them. However, the electrons about neon are unshared electron pairs, whereas those about carbon are shared with four hydrogen atoms.

Multiple Bonds

The sharing of a pair of electrons 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, two lines are drawn, representing a **double bond**. In carbon dioxide, for example, bonding occurs between carbon, with four valence electrons, and oxygen, with six:



As the diagram shows, each oxygen acquires an octet of electrons by sharing two electron pairs with carbon. Carbon, on the other hand, acquires an octet of electrons by sharing two electron pairs in each of the two bonds it forms with oxygen.

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



Because each nitrogen atom possesses five electrons in its valence shell, 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. Study of the structure of N_2 reveals that the nitrogen atoms are separated by only 1.10 Å. The short N—N bond distance is a result of the triple bond between the atoms. From structure studies 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 distance between bonded atoms decreases as the number of shared electron pairs increases. The distance between the nuclei of the atoms involved in a bond is called the **bond length** for the bond. We first encountered bond lengths in Section 7.3 in our discussion of atomic radii, and we will discuss them further 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 carbon monoxide has a single, double, or triple bond between the C and O atoms?

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. In highly ionic compounds, on the other hand, such as NaCl, there is relatively little sharing of electrons, which means that NaCl is best described as composed of Na^+ and Cl^- ions. The 3s 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.

The concept of **bond polarity** helps describe the sharing of electrons between atoms. A **nonpolar covalent bond** is one in which the electrons are shared equally between two atoms, as in the Cl_2 and N_2 examples we just cited.

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.

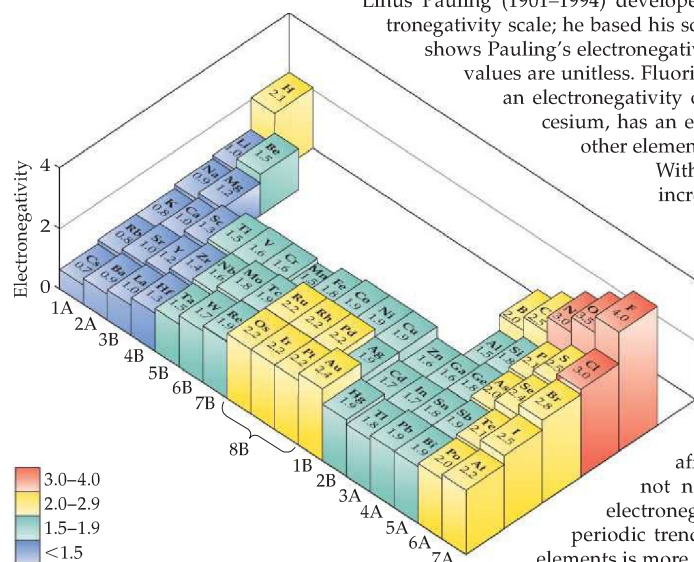
Electronegativity

We use a quantity called electronegativity to estimate whether a given bond will be 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 is its ability to attract electrons to itself. The electronegativity of an atom in a molecule is related to its ionization energy and electron affinity, which are properties of isolated atoms. The *ionization energy* measures how strongly a gaseous atom holds on to its electrons, ∞ (Section 7.4) while the *electron affinity* is a measure of how strongly an atom attracts additional electrons. ∞ (Section 7.5) An atom with a very negative electron affinity and high ionization energy will both attract electrons from other atoms and resist having its electrons attracted away; it will be highly electronegative.

Numerical estimates of electronegativity 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; he based his scale on thermochemical data. Figure 8.6 shows Pauling's electronegativity values for many of the elements. The values are unitless. Fluorine, the most electronegative element, has an electronegativity of 4.0. The least electronegative element, cesium, has an electronegativity of 0.7. The values for all other elements lie between these two extremes.

Within each period there is generally a steady increase in electronegativity from left to right; that is, from the most metallic to the most nonmetallic elements. With some exceptions (especially within the transition metals), electronegativity decreases with increasing atomic number in any one group. This is what we might expect because we know that ionization energies tend to decrease with increasing atomic number in a group and electron affinities do not change very much. You do not need to memorize numerical values for electronegativity. Instead, you should know the periodic trends so that you can predict which of two elements is more electronegative.

▼ **Figure 8.6** Electronegativities of the elements. Electronegativity generally increases from left to right across a period and decreases from top to bottom down a group.



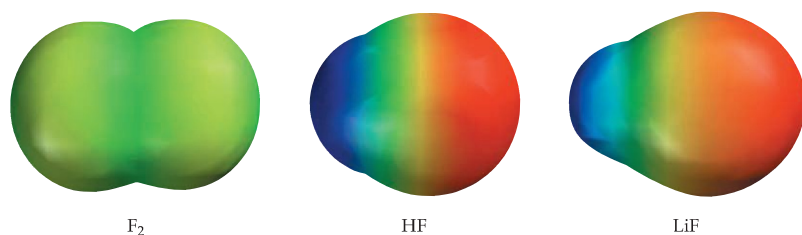
GIVE IT SOME THOUGHT

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

Electronegativity and Bond Polarity

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

| Compound | 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 |



▲ **Figure 8.7 Electron density distribution.** This computer-generated rendering shows the calculated electron-density distribution on the surface of the F_2 , HF, and LiF molecules. The regions of relatively low electron density (net positive charge) appear blue, those of relatively high electron density (net negative charge) appear red, and regions that are close to electrically neutral appear green.

In F_2 the electrons are shared equally between the fluorine atoms, and thus the covalent bond is *nonpolar*. In general, 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 sharing of electrons is unequal—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



The $\delta+$ and $\delta-$ (read “delta plus” and “delta minus”) symbolize the partial positive and negative charges, respectively.

In LiF the electronegativity difference is very large, meaning that the electron density is shifted far toward F. The resultant bond is therefore most accurately described as *ionic*. This shift of electron density toward the more electronegative atom can be seen in the results of calculations of electron density distributions. For the three species in our example, the calculated electron density distributions are shown in Figure 8.7▲. The regions of space that have relatively higher electron density are shown in red, and those with a relatively lower electron density are shown in blue. You can see that in F_2 the distribution is symmetrical, in HF it 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*.

GIVE IT SOME THOUGHT

Based on differences in electronegativity, how would you characterize the bonding in silicon nitride, Si_3N_4 ? Would you expect the bonds between Si and N to be nonpolar, polar covalent, or ionic?

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, the analysis reduces to a comparison of 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 a higher electronegativity. The more polar bond will be the one between the atoms having the lowest electronegativity (boron) and the highest electronegativity (chlorine). 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 the analysis reduces to a comparison of 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 8.6: The difference in the electronegativities of chlorine and boron is $3.0 - 2.0 = 1.0$; the difference between 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 8.6: The difference in the electronegativities of chlorine and phosphorus is $3.0 - 2.1 = 0.9$; the difference between fluorine and phosphorus is $4.0 - 2.1 = 1.9$. Hence the P—F bond is more polar, as we had predicted.

PRACTICE EXERCISE

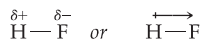
Which of the following bonds is most polar: S—Cl, S—Br, Se—Cl, or Se—Br?

Answer: Se—Cl

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 said to be 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:

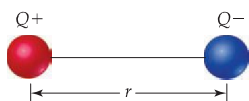


Recall from the preceding subsection that “ $\delta+$ ” and “ $\delta-$ ” indicate the partial positive and negative charges on the H and F atoms. In the notation on the right, the arrow denotes the shift in electron density toward the fluorine atom. The crossed end of the arrow can be thought of as a plus sign that designates the positive end of the molecule.

Polarity helps determine many of the properties of substances that 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.

How can we quantify the polarity of a molecule? Whenever a distance separates two electrical charges of equal magnitude but opposite sign, a **dipole** is established. The quantitative measure of the magnitude of a dipole is called its **dipole moment**, denoted μ . If a distance r separates two equal and opposite charges $Q+$ and $Q-$, the magnitude of the dipole moment is the product of Q and r (Figure 8.8 ◀):

$$\mu = Qr \quad [8.11]$$



▲ **Figure 8.8 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. The size of the dipole is given by the dipole moment, μ , which is the product of the charge separated and the distance of separation between the charge centers: $\mu = Qr$.

The dipole moment increases as the magnitude of charge that is separated increases and as the distance between the charges increases. For a nonpolar molecule, such as F_2 , the dipole moment is zero because there is no charge separation.

GIVE IT SOME THOUGHT

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

Dipole moments 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 units of angstroms. Suppose that two charges $1+$ and $1-$ (in units of e) are separated by a distance of 1.00 \AA . The dipole moment produced is

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

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 \AA . (a) Calculate the dipole moment, in debyes, that would result 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 would lead to this dipole moment?

SOLUTION

Analyze and Plan: We are asked in (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 8.11 to obtain this result. In (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, $e = 1.60 \times 10^{-19} \text{ C}$. The separation is 1.27 \AA . The dipole moment is therefore

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

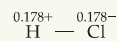
(b) We know the value of μ , 1.08 D and the value of r , 1.27 \AA . We want to calculate the value of Q :

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

We can readily convert this charge to units of e :

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

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



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

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

Answers: (a) F, (b) $0.11-$

TABLE 8.3 ■ 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 |

Table 8.3 ◀ 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 actual charges on the atoms decrease from $0.41+/0.41-$ in HF to $0.057+/0.057-$

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 8.9 ▼. For these molecules, the change in the electronegativity difference has a greater effect on the dipole moment than does the change in bond length.

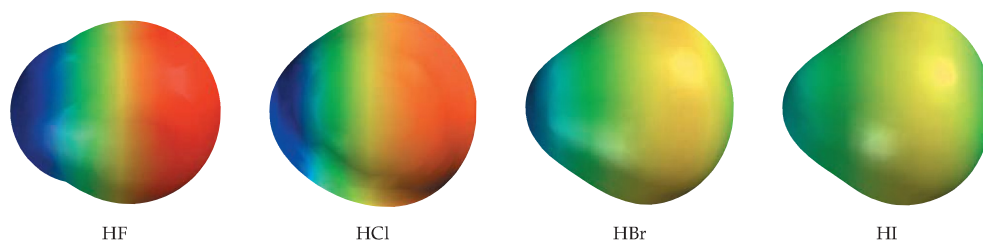
GIVE IT SOME THOUGHT

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

Before leaving this section let's return to the LiF molecule pictured in Figure 8.7. Under standard conditions LiF exists as an extended ionic solid with an arrangement of atoms analogous to the sodium chloride structure shown in Figure 8.3. However, it is possible to generate LiF molecules by vaporizing the 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 whereby each lithium ion is surrounded by fluoride ions and vice versa.

Differentiating 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 undergraduate-level chemistry texts. The partitioning of bonding into ionic and covalent extremes is considered when we name chemical substances. We saw in Section 2.8 that there are two general approaches



▲ **Figure 8.9** Charge separation in the hydrogen halides. Blue represents regions of lowest electron density, red regions of highest electron density. 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.

to naming binary compounds: one used for ionic compounds and the other for molecular ones. However, in reality 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.

Fortunately, the simple models of ionic and covalent bonding presented in this chapter go quite a long way toward understanding and predicting the structures and properties of chemical compounds. When covalent bonding is dominant, more often than not we expect compounds to exist as molecules*, with all of the properties we associate with molecular substances, such as relatively low melting and boiling points and non-electrolyte behavior when dissolved in water. Furthermore, we will see later that the polarity of covalent bonds has important consequence for the properties of substances. On the other hand, when ionic bonding is dominant, we expect the compounds to possess very different properties. Ionic compounds tend to be brittle, high-melting solids with extended lattice structures and they exhibit strong electrolyte behavior when dissolved in water.

There are of course exceptions to these general stereotypes, some of which we will 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 what is the best system for recognizing which type of bonding will be dominant?

The simplest approach one can take is to assume that the interaction between a metal and a nonmetal will be ionic, while the interaction between two nonmetals will be 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 . Clearly the bonding in this substance is better described as polar covalent than ionic. A more sophisticated approach, as outlined in the preceding discussion, is to use the difference in electronegativity as the main criterion for determining whether ionic or covalent bonding will be dominant. This 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 the bonding based on electronegativity difference is a useful system, but it has one shortcoming. Our electronegativity scale does not explicitly take into account changes in bonding that accompany changes in the oxidation state of the metal. For example, the electronegativity difference between manganese and oxygen is $3.5 - 1.5 = 2.0$, which falls in the range where the bonding is normally considered to be ionic (the electronegativity difference for NaCl was 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, it would be incorrect to assume that the bonding between manganese and oxygen is always ionic. Manganese (VII) oxide, which has the formula Mn_2O_7 , is a green liquid that freezes at 5.9°C , signaling that covalent rather than ionic bonding is dominant. The change in the oxidation state of manganese is responsible for the change in bonding type. As a general principle, whenever the oxidation state of the metal increases, it will lead to an increase in the degree of covalent character in the bonding. When the oxidation state of the metal becomes highly positive (roughly speaking $+4$ or larger), we should expect a significant degree of covalency in bonds it forms with nonmetals. In such instances you should not be surprised if a compound or polyatomic ion (such as MnO_4^- or CrO_4^{2-}) exhibits the general properties of molecular, rather than ionic compounds.

*There are some obvious exceptions to this rule, such as the network solids, including diamond, silicon, and germanium, where an extended structure is formed even though the bonding is clearly covalent. These examples are discussed in more detail in Section 11.8.

GIVE IT SOME THOUGHT

You encounter two substances: one is a yellow solid that melts at 41 °C and boils at 131 °C. The other is a green solid that melts at 2320 °C. If you are told that one of the compounds is Cr₂O₃ and the other is OsO₄, which one would 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. To do so, you should follow a regular procedure. First we will outline the procedure, and then we will go through several examples.

1. *Sum the valence electrons from all atoms.* (Use the periodic table as necessary 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 to show which atoms are attached to which, and connect them with a single bond* (a dash, 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 CO₃²⁻ and SF₄. 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.* Remember, however, that you use only a single pair of electrons around hydrogen.
4. *Place any leftover electrons on the central atom, even if doing so results in more than an octet of electrons around the atom.* In Section 8.7 we will discuss molecules that do not adhere to the octet rule.
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.

SAMPLE EXERCISE 8.6 | Drawing Lewis Structures

Draw the Lewis structure for phosphorus trichloride, PCl₃.

SOLUTION

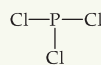
Analyze and Plan: We are asked to draw a Lewis structure from a molecular formula. Our plan is to follow the five-step procedure just described.

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

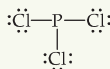
$$5 + (3 \times 7) = 26$$

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. In binary (two-element) compounds, however, the first element listed in the chemical formula is generally surrounded by the remaining atoms. Thus, we begin with a skeleton structure that shows a single bond between the phosphorus atom and each chlorine atom:

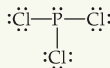


(It is not crucial to place the atoms in exactly this arrangement.)

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



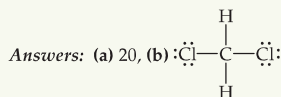
Fourth, we place the remaining two electrons on the central atom, completing the octet around it:



This structure gives each atom an octet, so we stop at this point. (Remember that in achieving an octet, the bonding electrons are counted for both atoms.)

■ PRACTICE EXERCISE

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

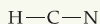


■ SAMPLE EXERCISE 8.7 | Lewis Structures with Multiple Bonds

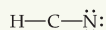
Draw the Lewis structure for HCN.

SOLUTION

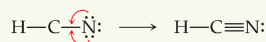
Hydrogen has one valence electron, carbon (group 4A) has four, and nitrogen (group 5A) has five. The total number of valence electrons is therefore $1 + 4 + 5 = 10$. In principle, there are different ways in which we might choose to arrange the atoms. Because hydrogen can accommodate only one electron pair, it always has only one single bond associated with it in any compound. 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 to be the atomic arrangement because (a) the formula is written with the atoms in this order, and (b) carbon is less electronegative than nitrogen. Thus, we begin with a skeleton structure that shows single bonds between hydrogen, carbon, and nitrogen:



These two bonds account for four electrons. If we then place the remaining six electrons around N to give it an octet, we do not achieve an octet on C:



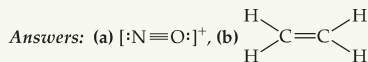
We therefore try a double bond between C and N, using one of the unshared pairs of electrons we placed on N. Again, there are fewer than eight electrons on C, and so we next try a triple bond. This structure gives an octet around both C and N:



We see that the octet rule is satisfied for the C and N atoms, and the H atom has two electrons around it. This appears to be a correct Lewis structure.

■ PRACTICE EXERCISE

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

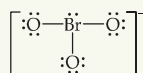


SAMPLE EXERCISE 8.8 | Lewis Structure for a Polyatomic Ion

Draw the Lewis structure for the BrO_3^- ion.

SOLUTION

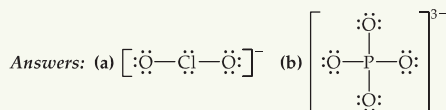
Bromine (group 7A) has seven valence electrons, and oxygen (group 6A) has six. We must now add one more electron to our sum to account for the $1-$ charge of the ion. The total number of valence electrons is therefore $7 + (3 \times 6) + 1 = 26$. For oxyanions— BrO_3^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , and so forth—the oxygen atoms surround the central nonmetal atoms. After following this format and then putting in the single bonds and distributing the unshared electron pairs, we have



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

PRACTICE EXERCISE

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

**Formal Charge**

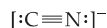
When we draw a Lewis structure, we are describing how the electrons are distributed in a molecule (or polyatomic ion). In some instances we can draw several different Lewis structures that all obey the octet rule. How do we decide which one is the most reasonable? One approach is to do some “bookkeeping” 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 all the atoms in the molecule had the same electronegativity (that is, if each bonding electron pair in the molecule were shared equally between its two atoms).

To calculate the formal charge on any atom in a Lewis structure, we assign the electrons to the atom as follows:

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.

The formal charge of each atom is then calculated by subtracting the number of electrons assigned to the atom from the number of valence electrons in the isolated atom.

Let's illustrate this procedure by calculating the formal charges on the C and N atoms in the cyanide ion, CN^- , which has the Lewis structure



For the C atom, there are 2 nonbonding electrons and 3 electrons from the 6 in the triple bond ($\frac{1}{2} \times 6 = 3$) for a total of 5. The number of valence electrons on a neutral C atom is 4. Thus, the formal charge on C is $4 - 5 = -1$. For N, there are 2 nonbonding electrons and 3 electrons from the triple bond. Because the number of valence electrons on a neutral N atom is 5, its formal charge is $5 - 5 = 0$. Thus, the formal charges on the atoms in the Lewis structure of CN^- are



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 overall charge on the ion.

The concept of formal charge can help us choose between alternative Lewis structures. We will consider the CO_2 molecule to see how this is done. As shown in Section 8.3, CO_2 is represented as having 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 the formal charge for each atom in these structures, we have

| | | |
|--------------------------------|--|--|
| | $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$ | $:\ddot{\text{O}}-\text{C}\equiv\text{O}:$ |
| 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 correct structure? As a general rule, when several Lewis structures are possible, we will use the following guidelines to choose the most correct one:

1. We generally choose the Lewis structure in which the atoms bear formal charges closest to zero.
2. We generally choose the Lewis structure in which any negative charges reside on the more electronegative atoms.

Thus, the first Lewis structure of CO_2 is preferred because the atoms carry no formal charges and so satisfy the first guideline.

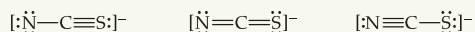
Although the concept of formal charge helps us choose between alternative Lewis structures, it is very important that you remember that *formal charges do not represent real charges on atoms*. These charges are just a bookkeeping convention. The actual charge distributions in molecules and ions are determined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

GIVE IT SOME THOUGHT

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

SAMPLE EXERCISE 8.9 Lewis Structures and Formal Charges

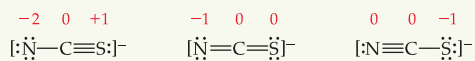
The following are three possible Lewis structures for the thiocyanate ion, NCS^- :



(a) Determine the formal charges of the atoms in each structure. (b) Which Lewis structure is the preferred one?

SOLUTION

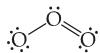
(a) Neutral N, C, and S atoms have five, four, and six valence electrons, respectively. We can determine the following formal charges in the three structures by using the rules we just discussed:



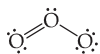
As they must, the formal charges in all three structures sum to $1-$, the overall charge of the ion.

8.6 RESONANCE STRUCTURES

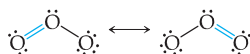
We sometimes encounter molecules and ions in which the experimentally determined arrangement of atoms is not adequately described by a single Lewis structure. Consider a molecule of ozone, O_3 , which is a bent molecule with two equal $\text{O}-\text{O}$ bond lengths (Figure 8.11 ▶). Because each oxygen atom contributes 6 valence electrons, the ozone molecule has 18 valence electrons. In writing the Lewis structure, we find that we must have one $\text{O}-\text{O}$ single bond and one $\text{O}=\text{O}$ double bond to attain an octet of electrons about each atom:



However, this structure cannot by itself be correct because it requires that one $\text{O}-\text{O}$ bond be different from the other, contrary to the observed structure—we would expect the $\text{O}=\text{O}$ double bond to be shorter than the $\text{O}-\text{O}$ single bond. ∞∞ (Section 8.3) In drawing the Lewis structure, however, we could just as easily have put the $\text{O}=\text{O}$ bond on the left:



The placement of the atoms in these two alternative but completely equivalent Lewis structures for ozone is the same, but the placement of the electrons is different. Lewis structures of this sort are called **resonance structures**. To describe the structure of ozone properly, we write both Lewis structures and use a double-headed arrow to indicate that the real molecule is described by an average of the two resonance structures:

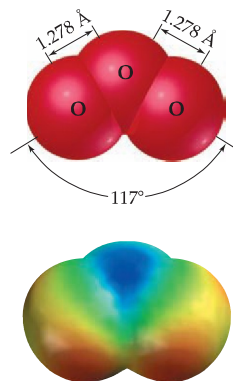


To understand why certain molecules require more than one resonance structure, we can draw an analogy to the mixing of paint (Figure 8.12 ▶). Blue and yellow are both primary colors of paint pigment. An equal blend of blue and yellow pigments produces green pigment. We cannot describe green paint in 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 above.

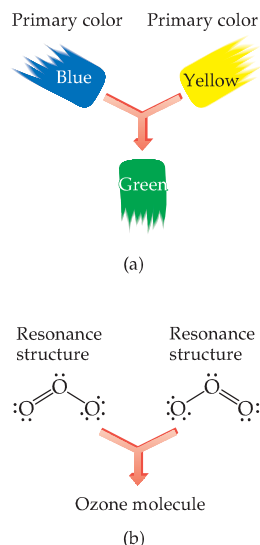
The true arrangement of the electrons in molecules such as O_3 must be considered as a blend of two (or more) Lewis structures. By analogy to the green paint, the molecule has its own identity separate from the individual resonance structures. For example, the ozone molecule always has two equivalent $\text{O}-\text{O}$ 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 structure that adequately represents 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 $\text{O}-\text{O}$ bonds in ozone are often described as “one-and-a-half” bonds. Is this description consistent with the idea of resonance?

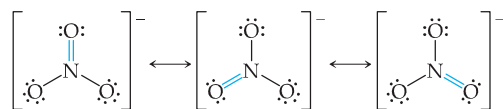


▲ **Figure 8.11 Ozone.** Molecular structure (top) and electron-distribution diagram (bottom) for the ozone molecule, O_3 .



▲ **Figure 8.12 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 Lewis structures taken together adequately describe the nitrate ion, in which all three N—O bond lengths are the same.

GIVE IT SOME THOUGHT

In the same sense that we describe the O—O bonds in O_3 as “one-and-a-half” bonds, how would you describe the N—O bonds in NO_3^- ?

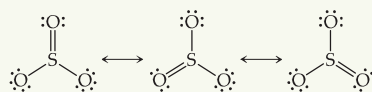
In some instances all the possible Lewis structures for a species may not be equivalent to one another. Instead, one or more may represent a more stable arrangement than other possibilities. We will encounter examples of this as we proceed.

SAMPLE EXERCISE 8.10 | Resonance Structures

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

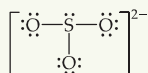
SOLUTION

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 was the case for NO_3^- , the actual structure of SO_3 is an equal blend of all three. Thus, each S—O bond distance should be about one-third of the way between that of a single and that of a double bond (see the Give It Some Thought exercise above). That is, they 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 Lewis structure in which all the S—O bonds are single bonds:

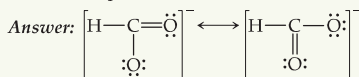


There are no other reasonable Lewis structures for this ion. It can be described quite well by a single Lewis structure rather than by multiple resonance structures.

Our analysis of the Lewis structures 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

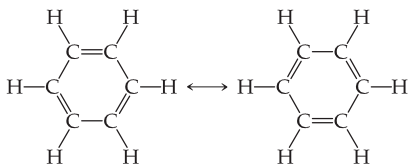
Draw two equivalent resonance structures for the formate ion, HCO_2^- .



Resonance in Benzene

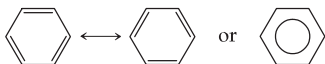
Resonance is an extremely important concept in describing the bonding in organic molecules, particularly in the ones called *aromatic* molecules. Aromatic organic molecules include the hydrocarbon called *benzene*, which has the molecular formula C_6H_6 (Figure 8.13 ►). The six C atoms of benzene are bonded in a hexagonal ring, and one H atom is bonded to each C atom.

We can write two equivalent Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance:



Each resonance structure shows three C—C single bonds and three C=C double bonds, but the double bonds are in different places in the two structures. The experimental structure of benzene shows 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).

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

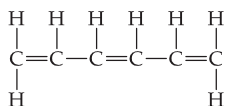


The shorthand notation on the right reminds us that benzene is a blend of two resonance structures—it emphasizes that the C=C double bonds cannot be assigned to specific edges of the hexagon. Chemists use both representations of benzene interchangeably.

The bonding arrangement in benzene confers special stability to the molecule. As a result, literally millions of organic compounds contain the six-membered rings characteristic of benzene. Many of these compounds are important in biochemistry, in pharmaceuticals, and in the production of modern materials. We will say more about the bonding in benzene in Chapter 9 and about its unusual stability in Chapter 25.

GIVE IT SOME THOUGHT

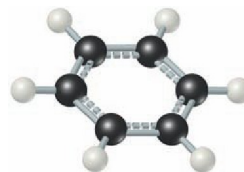
Each Lewis structure of benzene has three C=C double bonds. Another hydrocarbon containing three C=C double bonds is *hexatriene*, C_6H_8 . A Lewis structure of hexatriene is



Would you expect hexatriene to have multiple resonance structures like benzene? If not, why is this molecule different from benzene with respect to resonance?



(a)



(b)

▲ Figure 8.13 Benzene, an “aromatic” organic compound.

(a) Benzene is obtained from the distillation of fossil fuels. More than 4 billion pounds of benzene is produced annually in the United States. Because benzene is a carcinogen, its use is closely regulated. (b) The benzene molecule is a regular hexagon of carbon atoms with a hydrogen atom bonded to each one.

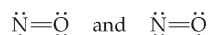
8.7 EXCEPTIONS TO THE OCTET RULE

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 octet rule also fails in many situations involving covalent bonding. These exceptions to the octet rule are of three main types:

1. Molecules and polyatomic ions containing an odd number of electrons
2. Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons
3. 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

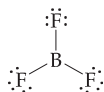


GIVE IT SOME THOUGHT

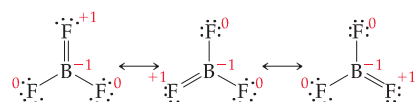
Which of the Lewis structures shown above for NO would be preferred based on analysis of the formal charges?

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), most often encountered in compounds of boron and beryllium. As an example, let's consider boron trifluoride, BF_3 . If we follow the first four steps of the procedure at the beginning of Section 8.5 for drawing Lewis structures, we obtain the structure

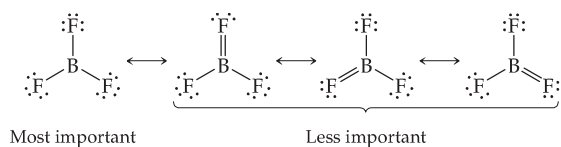


There are only six electrons around the boron atom. In this Lewis structure the formal charges on both the B and the F atoms are zero. We could complete the octet around boron by forming a double bond (step 5). In so doing, we see that there are three equivalent resonance structures (the formal charges on each atom are shown in red):

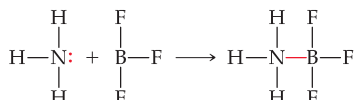


These Lewis structures force a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine. In fact, the formal charges tell us that this is an unfavorable situation.

In each of the Lewis structures, 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 Lewis structures in which there is a B=F double bond are less important than the one in which there are fewer than an octet of valence electrons around boron:



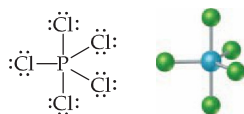
We usually represent BF_3 solely by the leftmost resonance structure, in which there are only six valence electrons around boron. The chemical behavior of BF_3 is consistent with this representation. In particular, BF_3 reacts very energetically with molecules having an unshared pair of electrons that can be used to form a bond with boron. For example, BF_3 reacts with ammonia, NH_3 , to form the compound NH_3BF_3 :



In this stable compound, boron has an octet of valence electrons. We will consider reactions of this type in more detail in Chapter 16 when we study Lewis acids and bases. [∞ \(Section 16.11\)](#)

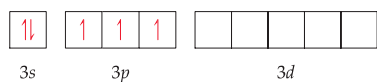
More than an Octet of Valence Electrons

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 PCl_5 , for example, we are forced to “expand” the valence shell and place ten electrons around the central phosphorus atom:



Other examples of molecules and ions with “expanded” valence shells 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. Let’s take a look at why expanded valence shells are observed only for elements in period 3 and beyond in the periodic table.

Elements of the second period have only the $2s$ and $2p$ valence orbitals available for bonding. Because these orbitals can hold a maximum of eight electrons, we never find more than an octet of electrons around elements from the second period. Elements from the third period and beyond, however, have ns , np , and unfilled nd orbitals that can be used in bonding. For example, the orbital diagram for the valence shell of a phosphorus atom is



Although third-period elements often satisfy the octet rule, as in PCl_3 , they also often exceed an octet by seeming to use their empty d orbitals to accommodate additional electrons.*

Size also plays an important role in determining whether an atom in a molecule or polyatomic ion can accommodate more than eight electrons in its valence shell. The larger the central atom is, the larger the number of atoms that can surround it. The number of molecules and ions with expanded valence shells therefore increases with increasing size of the central atom. The size of the surrounding atoms is also important. Expanded valence shells occur most often when the central atom is bonded to the smallest and most electronegative atoms, such as F, Cl, and O.

SAMPLE EXERCISE 8.11 | Lewis Structure for an Ion with an Expanded Valence Shell

Draw the Lewis structure for ICl_4^- .

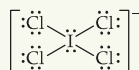
SOLUTION

Iodine (group 7A) has seven valence electrons. Each chlorine (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

$$7 + 4(7) + 1 = 36$$

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:



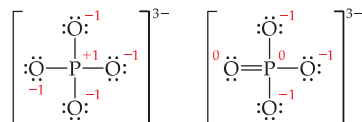
Iodine has 12 valence electrons around it, four more than needed for an octet.

PRACTICE EXERCISE

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

Answers: (a) C, (b)

At times you may see Lewis structures written with an expanded valence shell even though structures can be written with an octet. For example, consider the following Lewis structures for the phosphate ion, PO_4^{3-} :



The formal charges on the atoms are shown in red. In the Lewis structure shown on the left, the P atom obeys the octet rule. In the Lewis structure shown on the right, the P atom has an expanded valence shell of five electron pairs[†] leading to smaller formal charges on the atoms. Which Lewis structure is a better representation of the bonding in PO_4^{3-} ? Theoretical calculations based on quantum

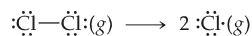
*Based on theoretical calculations, some chemists have questioned whether valence d orbitals are actually used in the bonding of molecules and ions with expanded valence shells. Nevertheless, the presence of valence d orbitals in period 3 and beyond provides the simplest explanation of this phenomenon, especially within the scope of a general chemistry textbook.

[†]The Lewis structure shown on the right has four equivalent resonance forms. Only one is shown for clarity.

mechanics suggest that the structure on the left is the best single Lewis structure for the phosphate ion. In general, when choosing between alternative Lewis structures, if it is possible to draw a Lewis structure where the octet rule is satisfied without using multiple bonds, that structure will be preferred.

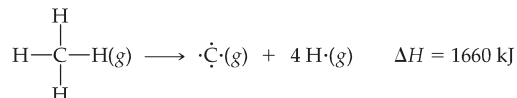
8.8 STRENGTHS OF COVALENT BONDS

The stability of a molecule is related to the strengths of the covalent bonds it contains. The strength of a covalent bond between two atoms is determined by the energy required to break that bond. It is easiest to relate bond strength to the enthalpy change in reactions in which bonds are broken. ∞ (Section 5.4) The **bond enthalpy** is the enthalpy change, ΔH , for the breaking of a particular bond in one mole of a gaseous substance. For example, the bond enthalpy for the bond between chlorine atoms in the Cl_2 molecule is the enthalpy change when 1 mol of Cl_2 is dissociated into chlorine atoms:



We use the designation $D(\text{bond type})$ to represent bond enthalpies.

It is relatively simple to assign bond enthalpies to bonds that are found in diatomic molecules, such as the $\text{Cl}-\text{Cl}$ bond in Cl_2 , $D(\text{Cl}-\text{Cl})$, or the $\text{H}-\text{Br}$ bond in HBr , $D(\text{H}-\text{Br})$. The bond enthalpy is just the energy required to break the diatomic molecule into its component atoms. Many important bonds, such as the $\text{C}-\text{H}$ bond, exist only in polyatomic molecules. For these types of bonds, we usually use *average* bond enthalpies. For example, the enthalpy change for the following process in which a methane molecule is decomposed to its five atoms (a process called *atomization*) can be used to define an average bond enthalpy for the $\text{C}-\text{H}$ bond, $D(\text{C}-\text{H})$:



Because there are four equivalent $\text{C}-\text{H}$ bonds in methane, the heat of atomization is equal to the sum of the bond enthalpies of the four $\text{C}-\text{H}$ bonds. Therefore, the average $\text{C}-\text{H}$ bond enthalpy for CH_4 is $D(\text{C}-\text{H}) = (1660/4) \text{ kJ/mol} = 415 \text{ kJ/mol}$.

The bond enthalpy for a given set of atoms, say $\text{C}-\text{H}$, depends on the rest of the molecule of which the atom pair is a part. However, the variation from one molecule to another is generally small, which supports the idea that bonding electron pairs are localized between atoms. If we consider $\text{C}-\text{H}$ bond enthalpies in many different compounds, we find that the average bond enthalpy is 413 kJ/mol , which compares closely with the 415 kJ/mol value calculated from CH_4 .

GIVE IT SOME THOUGHT

The hydrocarbon *ethane*, C_2H_6 , was first introduced in Section 2.9. How could you use the enthalpy of atomization of $\text{C}_2\text{H}_6(g)$ along with the value of $D(\text{C}-\text{H})$ to provide an estimate for $D(\text{C}-\text{C})$?

Table 8.4 \blacktriangledown lists several average bond enthalpies. *The bond enthalpy is always a positive quantity*; energy is always required to break chemical bonds. Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments. The greater the bond enthalpy is, the stronger the bond.

TABLE 8.4 ■ 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 ₂ | 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 | | | | | | |

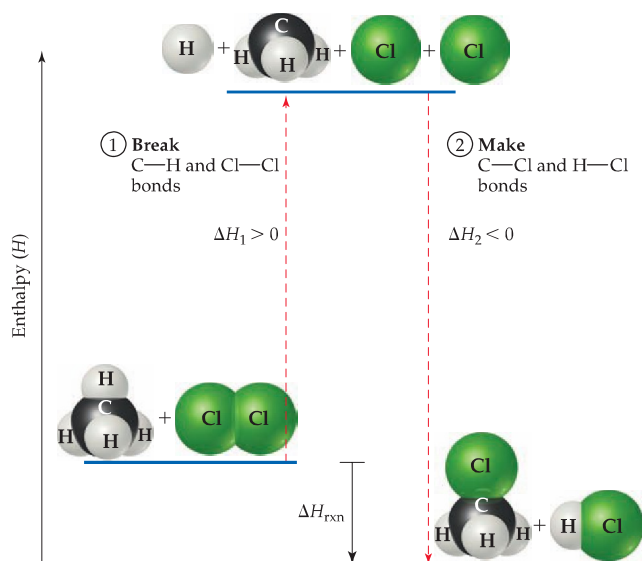
A molecule with strong chemical bonds generally has less tendency to undergo chemical change than does one with weak bonds. This relationship between strong bonding and chemical stability helps explain the chemical form in which many elements are found in nature. For example, Si—O bonds are among the strongest ones that silicon forms. It should not be surprising, therefore, that SiO₂ and other substances containing Si—O bonds (silicates) are so common; it is estimated that over 90% of Earth's crust is composed of SiO₂ and silicates.

Bond Enthalpies and the Enthalpies of Reactions

We can use average bond enthalpies to estimate the enthalpies of reactions in which bonds are broken and new bonds are formed. This procedure allows us to estimate quickly whether a given reaction will be endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$) even if we do not know ΔH_f° for all the chemical species involved.

Our strategy for estimating reaction enthalpies is a straightforward application of Hess's law. [∞∞ \(Section 5.6\)](#) We use the fact that breaking bonds is always an endothermic process, and bond formation is always exothermic. We therefore imagine that the reaction occurs in two steps: (1) We supply enough energy to break those bonds in the reactants that are not present in the products. In this step the enthalpy of the system is increased by the sum of the bond enthalpies of the bonds that are broken. (2) We form the bonds in the products that were not present in the reactants. This step releases energy and therefore lowers the enthalpy of the system by the sum of the bond enthalpies of the bonds that are formed. The enthalpy of the reaction, ΔH_{rxn} , is estimated as the sum of the bond enthalpies of the bonds broken minus the sum of the bond enthalpies of the bonds formed:

$$\Delta H_{\text{rxn}} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed}) \quad [8.12]$$



◀ **Figure 8.14 Using bond enthalpies to calculate ΔH_{rxn} .** Average bond enthalpies are used to estimate ΔH_{rxn} for the reaction in Equation 8.13. Breaking the C—H and Cl—Cl bonds produces a positive enthalpy change (ΔH_1), whereas making the C—Cl and H—Cl bonds causes a negative enthalpy change (ΔH_2). The values of ΔH_1 and ΔH_2 are estimated from the values in Table 8.4. From Hess's law, $\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2$.

Consider, for example, the gas-phase reaction between methane, CH_4 , and chlorine to produce methyl chloride, CH_3Cl , and hydrogen chloride, HCl :



Our two-step procedure is outlined in Figure 8.14. We note that in the course of this reaction the following bonds are broken and made:

Bonds broken: 1 mol C—H, 1 mol Cl—Cl

Bonds made: 1 mol C—Cl, 1 mol H—Cl

We first supply enough energy to break the C—H and Cl—Cl bonds, which will raise the enthalpy of the system. We then form the C—Cl and H—Cl bonds, which will release energy and lower the enthalpy of the system. By using Equation 8.12 and the data in Table 8.4, we estimate the enthalpy of the reaction as

$$\begin{aligned} \Delta H_{\text{rxn}} &= [D(\text{C}-\text{H}) + D(\text{Cl}-\text{Cl})] - [D(\text{C}-\text{Cl}) + D(\text{H}-\text{Cl})] \\ &= (413 \text{ kJ} + 242 \text{ kJ}) - (328 \text{ kJ} + 431 \text{ kJ}) = -104 \text{ kJ} \end{aligned}$$

The reaction is exothermic because the bonds in the products (especially the H—Cl bond) are stronger than the bonds in the reactants (especially the Cl—Cl bond).

We usually use bond enthalpies to estimate ΔH_{rxn} only if we do not have the needed ΔH_f° values readily at hand. For the above reaction, we cannot calculate ΔH_{rxn} from ΔH_f° values and Hess's law because the value of ΔH_f° for $\text{CH}_3\text{Cl}(\text{g})$ is not given in Appendix C. If we obtain the value of ΔH_f° for $\text{CH}_3\text{Cl}(\text{g})$ from another source (such as the *CRC Handbook of Chemistry and Physics*) and use Equation 5.31, we find that $\Delta H_{\text{rxn}} = -99.8 \text{ kJ}$ for the reaction in Equation 8.13. Thus, the use of average bond enthalpies provides a reasonably accurate estimate of the actual reaction enthalpy change.

It is important to remember that bond enthalpies are derived for *gaseous* molecules and that they are often *averaged* values. Nonetheless, average bond enthalpies are useful for estimating reaction enthalpies quickly, especially for gas-phase reactions.

Chemistry Put to Work EXPLOSIVES AND ALFRED NOBEL

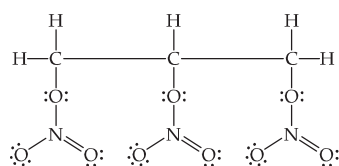
Enormous amounts of energy can be stored in chemical bonds. Perhaps the most graphic illustration of this fact is seen in certain molecular substances that are used as explosives. Our discussion of bond enthalpies allows us to examine more closely some of the properties of such explosive substances.

An explosive must have the following characteristics: (1) It must decompose very exothermically; (2) the products of its decomposition must be gaseous, so that a tremendous gas pressure accompanies the decomposition; (3) its decomposition must occur very rapidly; and (4) it must be stable enough so that it can be detonated predictably. The combination of the first three effects leads to the violent evolution of heat and gases.

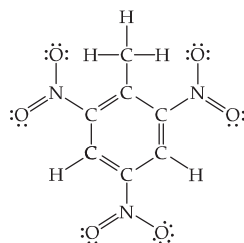
To give the most exothermic reaction, an explosive should have weak chemical bonds and should decompose into molecules with very strong bonds. Looking at bond enthalpies (Table 8.4), the $\text{N}\equiv\text{N}$, $\text{C}\equiv\text{O}$, and $\text{C}=\text{O}$ bonds are among the strongest. Not surprisingly, explosives are usually designed to produce the gaseous products $\text{N}_2(\text{g})$, $\text{CO}(\text{g})$, and $\text{CO}_2(\text{g})$. Water vapor is nearly always produced as well.

Many common explosives are organic molecules that contain nitro (NO_2) or nitrate (NO_3) groups attached to a carbon skeleton. The Lewis structures of two of the most familiar explosives, nitroglycerin and trinitrotoluene (TNT), are

shown here (resonance structures are not shown for clarity). TNT contains the six-membered ring characteristic of benzene.



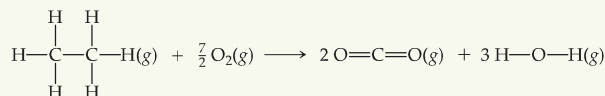
Nitroglycerin



Trinitrotoluene (TNT)

SAMPLE EXERCISE 8.12 | Using Average Bond Enthalpies

Using Table 8.4, estimate ΔH for the following reaction (where we explicitly show the bonds involved in the reactants and products):



SOLUTION

Analyze: We are asked to estimate the enthalpy change for a chemical process by using average bond enthalpies for the bonds that are broken in the reactants and formed in the products.

Plan: Among the reactants, we must break six $\text{C}-\text{H}$ bonds and a $\text{C}-\text{C}$ bond in C_2H_6 ; we also break $\frac{7}{2} \text{O}_2$ bonds. Among the products, we form four $\text{C}=\text{O}$ bonds (two in each CO_2) and six $\text{O}-\text{H}$ bonds (two in each H_2O).

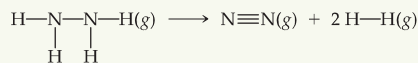
Solve: Using Equation 8.12 and data from Table 8.4, we have

$$\begin{aligned} \Delta H &= 6D(\text{C}-\text{H}) + D(\text{C}-\text{C}) + \frac{7}{2}D(\text{O}_2) - 4D(\text{C}=\text{O}) - 6D(\text{O}-\text{H}) \\ &= 6(413 \text{ kJ}) + 348 \text{ kJ} + \frac{7}{2}(495 \text{ kJ}) - (4(799 \text{ kJ}) + 6(463 \text{ kJ})) \\ &= 4558 \text{ kJ} - 5974 \text{ kJ} \\ &= -1416 \text{ kJ} \end{aligned}$$

Check: This estimate can be compared with the value of -1428 kJ calculated from more accurate thermochemical data; the agreement is good.

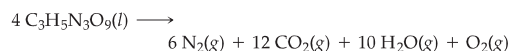
PRACTICE EXERCISE

Using Table 8.4, estimate ΔH for the reaction



Answer: -86 kJ

Nitroglycerin is a pale yellow, oily liquid. It is highly *shock-sensitive*: Merely shaking the liquid can cause its explosive decomposition into nitrogen, carbon dioxide, water, and oxygen gases:



The large bond enthalpies of the N_2 molecules (941 kJ/mol), CO_2 molecules (2×799 kJ/mol), and water molecules (2×463 kJ/mol) make this reaction enormously exothermic. Nitroglycerin is an exceptionally unstable explosive because it is in nearly perfect *explosive balance*: With the exception of a small amount of $\text{O}_2(g)$ produced, the only products are N_2 , CO_2 , and H_2O . Note also that, unlike combustion reactions (Section 3.2), explosions are entirely self-contained. No other reagent, such as $\text{O}_2(g)$, is needed for the explosive decomposition.

Because nitroglycerin is so unstable, it is difficult to use as a controllable explosive. The Swedish inventor Alfred Nobel (Figure 8.15▶) found that mixing nitroglycerin with an absorbent solid material such as diatomaceous earth or cellulose gives a solid explosive (*dynamite*) that is much safer than liquid nitroglycerin.

Related Exercises: 8.93 and 8.94



▲ **Figure 8.15 Alfred Nobel (1833–1896), the Swedish inventor of dynamite.** By many accounts Nobel's discovery that nitroglycerin could be made more stable by absorbing it onto cellulose was an accident. This discovery made Nobel a very wealthy man. He was also a complex and lonely man, however, who never married, was frequently ill, and suffered from chronic depression. He had invented the most powerful military explosive to date, but he strongly supported international peace movements. His will stated that his fortune be used to establish prizes awarding those who "have conferred the greatest benefit on mankind," including the promotion of peace and "fraternity between nations." The Nobel Prize is probably the most coveted award that a scientist, writer, or peace advocate can receive.

Bond Enthalpy and Bond Length

Just as we can define an average bond enthalpy, we can also define an average bond length for a number of common bond types. Some of these are listed in Table 8.5 ▼. Of particular interest is the relationship among bond enthalpy, bond length, and the number of bonds between the atoms. For example, we can use data in Tables 8.4 and 8.5 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 |

As the number of bonds between the carbon atoms increases, the bond enthalpy increases and the bond length decreases; 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.*

TABLE 8.5 ■ 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 | | |

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

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 most important one. (d) Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from $\text{CO}(g)$ and $\text{Cl}_2(g)$.

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

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

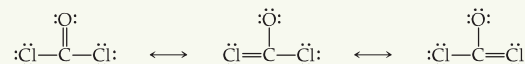
$$(16.17 \text{ g O}) \left(\frac{1 \text{ mol O}}{16.00 \text{ g O}} \right) = 1.011 \text{ mol O}$$

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

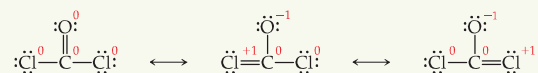
The ratio of the number of moles of each element, obtained by dividing each number of moles by the smallest quantity, indicates that there is one C and one O for each two Cl in the empirical formula, COCl_2 .

The molar mass of the empirical formula is $12.01 + 16.00 + 2(35.45) = 98.91 \text{ g/mol}$, 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, three structures satisfy the octet rule:

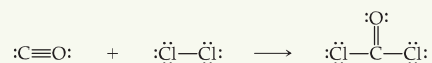


(c) Calculating the formal charges on each atom gives



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

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



Thus, the reaction involves breaking a $\text{C}\equiv\text{O}$ bond and a Cl--Cl bond and forming a C=O bond and two C--Cl bonds. Using bond enthalpies from Table 8.4, we have

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

CHAPTER REVIEW

SUMMARY AND KEY TERMS

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 can be viewed as an attempt by atoms to achieve a noble-gas electron configuration.

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.

Section 8.3 A covalent bond results from the sharing of electrons. 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 unshared electron 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** between two bonded atoms is the distance between the two nuclei. The bond length decreases as the number of bonds between the atoms increases.

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.

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. Most acceptable Lewis structures will have low formal charges with any negative formal charges residing on more electronegative atoms.

Sometimes a single 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 .

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. In this last case we envision using the unfilled d orbitals of the large atom to "expand" the valence shell of the atom. Expanded valence shells are observed for atoms in the third row and beyond in the periodic table, for which low-energy d orbitals are available.

Section 8.8 The strength of a covalent bond is measured by its **bond enthalpy**, which is the molar enthalpy change upon breaking a particular bond. Average bond enthalpies can be determined for a wide variety of covalent bonds. The strengths of covalent bonds increase with the number of electron pairs shared between two atoms.

We can use bond enthalpies to estimate the enthalpy change during chemical reactions in which bonds are broken and new bonds formed. 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.

KEY SKILLS

- Write Lewis symbols for atoms and ions.
- Understand lattice energy and be able to arrange compounds in order of increasing lattice energy based on the charges and sizes of the ions involved.
- Use atomic electron configurations and the octet rule to write Lewis structures for molecules to determine their electron distribution.
- Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds.
- Calculate charge separation in diatomic molecules based on the experimentally measured dipole moment and bond distance.
- Calculate formal charges from Lewis structures and use those formal charges to identify the most favorable Lewis structures.
- Recognize molecules where resonance structures are needed to describe the bonding.
- Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed.
- Understand the relationship between bond type (single, double, and triple), bond strength (or enthalpy) and bond length.
- Use bond enthalpies to estimate enthalpy changes for reactions involving gas phase reactants and products.

KEY EQUATIONS

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

$$\mu = Qr \quad [8.11]$$

$$\Delta H_{rxn} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed}) \quad [8.12]$$

The potential energy of two interacting charges

The dipole moment of two charges of equal magnitude but opposite sign, separated by a distance r

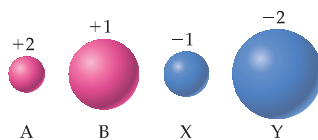
The enthalpy change as a function of bond enthalpies for reactions involving gas phase molecules.

VISUALIZING CONCEPTS

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

(a) $\cdot\ddot{X}\cdot$ (b) $\cdot X\cdot$ (c) $\cdot\ddot{X}\cdot$

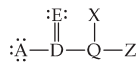
8.2 Illustrated at right are four ions—A, B, X, and Y—showing their relative ionic radii. The ions shown in red carry positive charges: a 2+ charge for A and a 1+ charge for B. Ions shown in blue carry negative charges: a 1− charge for X and a 2− charge for Y. (a) Which combinations of these ions produce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



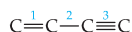
8.3 The orbital diagram below shows the valence electrons for a 2+ ion of an element. (a) What is the element? (b) What is the electron configuration of an atom of this element? [Section 8.2]



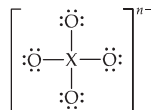
- 8.4 In the Lewis structure shown below, A, D, E, Q, X, and Z represent elements in the first two rows of the periodic table (H—Ne). Identify all six elements so that the formal charges of all atoms are zero. [Section 8.3]



- 8.5 The partial Lewis structure below 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) Determine where the hydrogen atoms are in the molecule. (b) Rank the carbon–carbon bonds in order of increasing bond length. (c) Rank the carbon–carbon bonds in order of increasing bond enthalpy. [Section 8.3 and 8.8]



- 8.6 Consider the Lewis structure for the polyatomic oxyanion shown below, where X is an element from the 3rd 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. (d) If the Lewis structure you drew in part (c) differs from the Lewis structure shown below, which one do you think is the best one (if you were able to choose only a single Lewis structure)? [Sections 8.5, 8.6, and 8.7]



EXERCISES

Lewis Symbols

- 8.7 (a) What are valence electrons? (b) How many valence electrons does a nitrogen atom possess? (c) An atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$. How many valence electrons does the atom have?
- 8.8 (a) What is the octet rule? (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 $1s^2 2s^2 2p^3$, how many electrons must it gain to achieve an octet?
- 8.9 Write the electron configuration for phosphorus. Identify the valence electrons in this configuration and the nonvalence electrons. From the standpoint of chemical reactivity, what is the important difference between them?
- 8.10 (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) Both 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?
- 8.11 Write the Lewis symbol for atoms of each of the following elements: (a) Al, (b) Br, (c) Ar, (d) Sr.
- 8.12 What is the Lewis symbol for each of the following atoms or ions: (a) Ca, (b) P, (c) Mg^{2+} , (d) S^{2-} ?

Ionic Bonding

- 8.13 Using Lewis symbols, diagram the reaction between magnesium and oxygen atoms to give the ionic substance MgO.
- 8.14 Use Lewis symbols to represent the reaction that occurs between Ca and F atoms.
- 8.15 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.
- 8.16 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?
- 8.17 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+} .
- 8.18 Write electron configurations for the following ions, and determine which have noble-gas configurations: (a) Zn^{2+} , (b) Te^{2-} , (c) Sc^{3+} , (d) Rh^{3+} , (e) Tl^+ , (f) Bi^{3+} .
- 8.19 (a) Define the term *lattice energy*. (b) Which factors govern the magnitude of the lattice energy of an ionic compound?
- 8.20 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 8.2. 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. Does this estimate agree with the prediction you made based upon the lattice energies?
- 8.21 The ionic substances KF, CaO, and ScN are isoelectronic (they have the same number of electrons). Examine the lattice energies for these substances in Table 8.2, and account for the trends you observe.
- 8.22 (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) Using a periodic table,

arrange the following substances according to their expected lattice energies, listing them from lowest lattice energy to the highest: ScN, KBr, MgO, NaF. Compare your list with the data in Table 8.2.

- 8.23** The lattice energies of KBr and CsCl are nearly equal (Table 8.2). What can you conclude from this observation?
- 8.24** Explain the following trends in lattice energy: (a) $\text{CaF}_2 > \text{BaF}_2$; (b) $\text{NaCl} > \text{RbBr} > \text{CsBr}$; (c) $\text{BaO} > \text{KF}$.
- 8.25** Energy is required to remove two electrons from Ca to form Ca^{2+} and is required to add two electrons to O to form O^{2-} . Why, then, is CaO stable relative to the free elements?
- 8.26** Construct a Born-Haber cycle for the formation of the hypothetical compound NaCl_2 , where the sodium ion

has a $2+$ charge (the 2nd 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 8.2), what value would you obtain for the standard enthalpy of formation, ΔH_f° , of NaCl_2 ?

- 8.27** Use data from Appendix C, Figure 7.12, and Figure 7.14 to calculate the lattice energy of RbCl. Is this value greater than or less than the lattice energy of NaCl? Explain.
- 8.28** (a) Based on the lattice energies of MgCl_2 and SrCl_2 given in Table 8.2, what is the range of values that you would expect for the lattice energy of CaCl_2 ? (b) Using data from Appendix C, Figure 7.12, and Figure 7.14 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

- 8.29** (a) What is meant by the term *covalent bond*? (b) Give three examples of covalent bonding. (c) A substance XY, formed from two different elements, boils at -33°C . Is XY likely to be a covalent or an ionic substance? Explain.
- 8.30** Which of these elements is unlikely to form covalent bonds: S, H, K, Ar, Si? Explain your choices.
- 8.31** Using Lewis symbols and Lewis structures, diagram the formation of SiCl_4 from Si and Cl atoms.
- 8.32** Use Lewis symbols and Lewis structures to diagram the formation of PF_3 from P and F atoms.
- 8.33** (a) Construct a Lewis structure for O_2 in which each atom achieves an octet of electrons. (b) Explain why it is necessary to form a double bond in the Lewis structure. (c) The bond in O_2 is shorter than the $\text{O}-\text{O}$ bond in compounds that contain an $\text{O}-\text{O}$ single bond. Explain this observation.
- 8.34** (a) Construct a Lewis structure for hydrogen peroxide, H_2O_2 , in which each atom achieves an octet of electrons. (b) Do you expect the $\text{O}-\text{O}$ bond in H_2O_2 to be longer or shorter than the $\text{O}-\text{O}$ bond in O_2 ?
- 8.35** (a) What is meant by the term electronegativity? (b) On the Pauling scale what is the range of electronegativity values for the elements? (c) Which element has the greatest electronegativity? (d) Which element has the smallest electronegativity?
- 8.36** (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) How do periodic trends in electronegativity relate to those for ionization energy and electron affinity?
- 8.37** Using only the periodic table as your guide, select the most electronegative atom in each of the following sets: (a) Se, Rb, O, In; (b) Al, Ca, C, Si; (c) Ge, As, P, Sn; (d) Li, Rb, Be, Sr.
- 8.38** By referring only to the periodic table, select (a) the most electronegative element in group 6A; (b) the least elec-

tronegative 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.

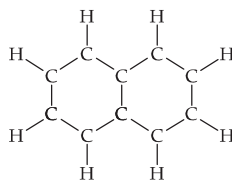
- 8.39** Which of the following bonds are polar: (a) $\text{B}-\text{F}$, (b) $\text{Cl}-\text{Cl}$, (c) $\text{Se}-\text{O}$, (d) $\text{H}-\text{I}$? Which is the more electronegative atom in each polar bond?
- 8.40** Arrange the bonds in each of the following sets in order of increasing polarity: (a) $\text{C}-\text{F}$, $\text{O}-\text{F}$, $\text{Be}-\text{F}$; (b) $\text{O}-\text{Cl}$, $\text{S}-\text{Br}$, $\text{C}-\text{P}$; (c) $\text{C}-\text{S}$, $\text{B}-\text{F}$, $\text{N}-\text{O}$.
- 8.41** The dipole moment and bond distance measured for the highly reactive gas phase OH molecule are 1.78 D and 0.98 \AA , respectively. (a) Given these values calculate the effective charges on the H and O atoms of the OH molecule in units of the electronic charges e . (b) Is this bond more or less polar than the $\text{H}-\text{Cl}$ bond in an HCl molecule? (c) Is that what you would have expected based on electronegativities?
- 8.42** The iodine monobromide molecule, IBr, has a bond length of 2.49 \AA and a dipole moment of 1.21 D. (a) Which atom of the molecule is expected to have a negative charge? Explain. (b) Calculate the effective charges on the I and Br atoms in IBr, in units of the electronic charge e .
- 8.43** 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 .
- 8.44** 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

- 8.45 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 .
- 8.46 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) C_2H_2 .
- 8.47 (a) When talking about atoms in a Lewis structure, what is meant by the term *formal charge*? (b) Does the formal charge of an atom represent the actual charge on that atom? Explain. (c) How does the formal charge of an atom in a Lewis structure differ from the oxidation number of the atom?
- 8.48 (a) Write a Lewis structure for the phosphorus trifluoride molecule, PF_3 . Is the octet rule satisfied for all the atoms in your structure? (b) Determine the oxidation numbers of the P and F atoms. (c) Determine the formal charges of the P and F atoms. (d) Is the oxidation number for the P atom the same as its formal charge? Explain why or why not.
- 8.49 Write Lewis structures that obey the octet rule for each of the following, and assign oxidation numbers and formal charges to each atom: (a) NO^+ , (b) POCl_3 (P is bonded to the three Cl atoms and to the O), (c) ClO_4^- , (d) HClO_3 (H is bonded to O).
- 8.50 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 distance.
- 8.51 (a) Write one or more appropriate Lewis structures 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?

- 8.52 Consider the nitryl cation, NO_2^+ . (a) Write one or more appropriate Lewis structures for this ion. (b) Are resonance structures needed to describe the structure? (c) With what familiar molecule is it isoelectronic?
- 8.53 Predict the ordering of the C—O bond lengths in CO , CO_2 , and CO_3^{2-} .
- 8.54 Based on Lewis structures, predict the ordering of N—O bond lengths in NO^+ , NO_2^- , and NO_3^- .
- 8.55 (a) Use the concept of resonance to explain why all six C—C bonds in benzene are equal in length. (b) Are the C—C bond lengths in benzene shorter than C—C single bonds? Are they shorter than C=C double bonds?
- 8.56 Mothballs are composed of naphthalene, C_{10}H_8 , a molecule of which consists of two six-membered rings of carbon fused along an edge, as shown in this incomplete Lewis structure:



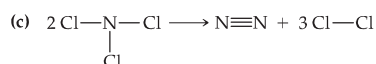
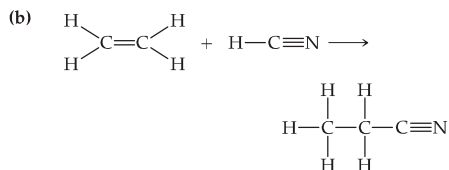
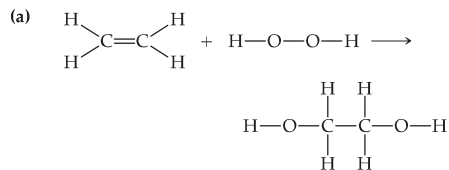
- (a) Write two complete Lewis structures for naphthalene. (b) The observed C—C bond lengths in the molecule are intermediate between C—C single and C=C double bonds. Explain. (c) Represent the resonance in naphthalene in a way analogous to that used to represent it in benzene.

Exceptions to the Octet Rule

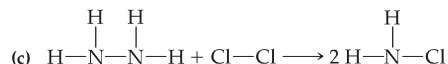
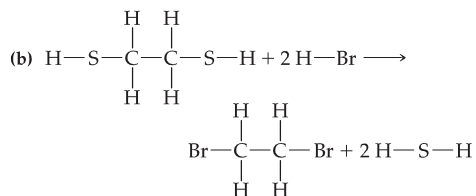
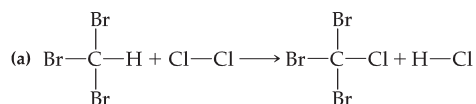
- 8.57 (a) State the octet rule. (b) Does the octet rule apply to ionic as well as to covalent compounds? Explain, using examples as appropriate.
- 8.58 Considering the nonmetals, what is the relationship between the group number for an element (carbon, for example, belongs to group 4A; see the periodic table on the inside front cover) and the number of single covalent bonds that element needs to form to conform to the octet rule?
- 8.59 What is the most common exception to the octet rule? Give two examples.
- 8.60 For elements in the third row of the periodic table and beyond, the octet rule is often not obeyed. What factors are usually cited to explain this fact?
- 8.61 Draw the Lewis structures for each of the following ions or molecules. Identify those that do not obey the octet rule, and explain why they do not. (a) SO_3^{2-} , (b) AlH_3 , (c) N_3^- , (d) CH_2Cl_2 , (e) SbF_5 .
- 8.62 Draw the Lewis structures for each of the following molecules or ions. Which do not obey the octet rule? (a) NH_4^+ , (b) SCN^- , (c) PCl_3 , (d) TeF_4 , (e) XeF_2 .
- 8.63 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 forms are possible that satisfy the octet rule? (c) Using formal charges, select the resonance form from among all the Lewis structures that is most important in describing BeCl_2 .
- 8.64 (a) Describe the molecule chlorine dioxide, ClO_2 , using three possible resonance structures. (b) Do any of these resonance structures satisfy the octet rule for every atom in the molecule? Why or why not? (c) Using formal charges, select the resonance structure(s) that is (are) most important.

Bond Enthalpies

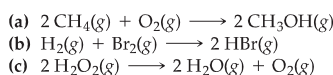
8.65 Using the bond enthalpies tabulated in Table 8.4, estimate ΔH for each of the following gas-phase reactions:



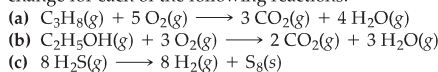
8.66 Using bond enthalpies (Table 8.4), estimate ΔH for the following gas-phase reactions:



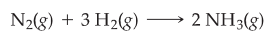
8.67 Using bond enthalpies (Table 8.4), estimate ΔH for each of the following reactions:



[8.68] Use bond enthalpies (Table 8.4) to estimate the enthalpy change for each of the following reactions:

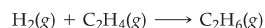


8.69 Ammonia is produced directly from nitrogen and hydrogen by using the Haber process. The chemical reaction is



(a) Use bond enthalpies (Table 8.4) to estimate the enthalpy change for the reaction, and tell whether this reaction is exothermic or endothermic. (b) Compare the enthalpy change you calculate in (a) to the true enthalpy change as obtained using ΔH_f° values.

8.70 (a) Use bond enthalpies to estimate the enthalpy change for the reaction of hydrogen with ethene:

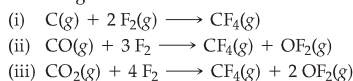


(b) Calculate the standard enthalpy change for this reaction, using heats of formation. Why does this value differ from that calculated in (a)?

8.71 Given the following bond-dissociation energies, calculate the average bond enthalpy for the Ti—Cl bond.

| | ΔH (kJ/mol) |
|---|---------------------|
| $\text{TiCl}_4(\text{g}) \longrightarrow \text{TiCl}_3(\text{g}) + \text{Cl}(\text{g})$ | 335 |
| $\text{TiCl}_3(\text{g}) \longrightarrow \text{TiCl}_2(\text{g}) + \text{Cl}(\text{g})$ | 423 |
| $\text{TiCl}_2(\text{g}) \longrightarrow \text{TiCl}(\text{g}) + \text{Cl}(\text{g})$ | 444 |
| $\text{TiCl}(\text{g}) \longrightarrow \text{Ti}(\text{g}) + \text{Cl}(\text{g})$ | 519 |

[8.72] (a) Using average bond enthalpies, predict which of the following reactions will be most exothermic:



(b) Explain the trend, if any, that exists between reaction exothermicity and the extent to which the carbon atom is bonded to oxygen.

ADDITIONAL EXERCISES

8.73 How many elements in the periodic table are represented by a Lewis symbol with a single dot? Are all these elements in the same group? Explain.

8.74 (a) Explain the following trend in lattice energy: 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. (b) The lattice energy of ZnH_2 is 2870 kJ/mol. Based on the data given in part (a), the radius of the Zn^{2+} ion is expected to be closest to that of which group 2A element?

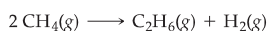
8.75 Based on data in Table 8.2, estimate (within 30 kJ/mol) the lattice energy for (a) LiBr, (b) CsBr, (c) CaCl_2 .

8.76 Would you expect AlN to have a lattice energy that is larger or smaller than ScN? Explain.

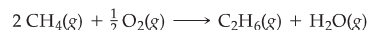
[8.77] From the ionic radii given in Figure 7.8, calculate the potential energy of a Ca^{2+} and O^{2-} ion pair that are just touching (the magnitude of the electronic charge is given on the back inside cover). Calculate the energy of a mole of such pairs. How does this value compare with

- the lattice energy of CaO (Table 8.2)? Explain the difference.
- [8.78] From Equation 8.4 and the ionic radii given in Figure 7.8, calculate the potential energy of the following pairs of ions. Assume that the ions are separated by a distance equal to the sum of their ionic radii: (a) Na^+ , Br^- ; (b) Rb^+ , Br^- ; (c) Sr^{2+} , S^{2-} .
- 8.79 (a) How does a polar molecule differ from a nonpolar one? (b) Atoms X and Y have different electronegativities. Will the diatomic molecule X—Y necessarily be polar? Explain. (c) What factors affect the size of the dipole moment of a diatomic molecule?
- 8.80 Which of the following molecules or ions contain polar bonds: (a) P_4 , (b) H_2S , (c) NO_2^- , (d) S_2^{2-} ?
- 8.81 To address energy and environmental issues, there is great interest in powering vehicles with hydrogen rather than gasoline. One of the most attractive aspects of the "hydrogen economy" is the fact that in principle the only emission would be water. However, two daunting obstacles must be overcome before this vision can become a reality. First, an economical method of producing hydrogen must be found. Second, a safe, lightweight, and compact way of storing hydrogen must be found. The hydrides of light metals are attractive for hydrogen storage because they can store a high weight percentage of hydrogen in a small volume. One of the most attractive hydrides is NaAlH_4 , which 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, what do you think is the identity of the polyatomic anion? Draw a Lewis structure for this ion.
- 8.82 For the following collection of nonmetallic elements, O, P, Te, I, 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 ? In each case explain your answer.
- 8.83 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? (c) 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. What is the identity of the yellow compound? What is the identity of the black compound? Be sure to use the appropriate naming convention depending upon whether the compound is better described as a molecular or ionic compound.
- 8.84 You and a partner are asked to complete a lab entitled "Fluorides of Group 6B Metals" 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 colorless liquid and the other a green powder. You also find the following notes in your partner's notebook—*Compound 1*: 47.7% Cr and 52.3% F (by mass), *Compound 2*: 45.7% Mo and 54.3% F (by mass). (a) What is the empirical formula for Compound 1? (b) What is the empirical formula for Compound 2? (c) Upon determining the melting points of these two compounds you find that the colorless liquid solidifies at 18 °C, while the green powder does not melt up to the maximum temperature of your apparatus, 1200 °C. What is the identity of the colorless liquid? What is the identity of the green powder? Be sure to use the appropriate naming convention depending upon whether the compound is better described as a molecular or ionic compound.
- [8.85] (a) Triazine, $\text{C}_3\text{H}_3\text{N}_3$, 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.
- [8.86] Using the electronegativities of Br and Cl, estimate the partial charges on the atoms in the Br—Cl molecule. Using these partial charges and the atomic radii given in Figure 7.7, estimate the dipole moment of the molecule. The measured dipole moment is 0.57 D.
- 8.87 Although I_3^- is known, F_3^- is not. Using Lewis structures, explain why F_3^- does not form.
- 8.88 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).
- 8.89 (a) Determine the formal charge on the chlorine atom in the hypochlorite ion, ClO^- , and the perchlorate ion, ClO_4^- , using resonance structures where the Cl atom has an octet. (b) What are the oxidation numbers of chlorine in ClO^- and in ClO_4^- ? (c) Is it uncommon for the formal charge and the oxidation state to be different? Explain. (d) Perchlorate is a much stronger oxidizing agent than hypochlorite. Would you expect there to be any relationship between the oxidizing power of the oxyanion and either the oxidation state or the formal charge of chlorine?
- 8.90 The following three Lewis structures can be drawn for N_2O :
- $$:\text{N}\equiv\text{N}-\ddot{\text{O}}: \longleftrightarrow :\ddot{\text{N}}-\text{N}\equiv\text{O}: \longleftrightarrow :\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$$
- (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 $\text{N}\equiv\text{N}$ bond; and the N—O bond length is 1.19 Å, slightly shorter than a typical $\text{N}=\text{O}$ bond. (See Table 8.5.) Rationalize these observations in terms of the resonance structures shown previously and your conclusion for (a).

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

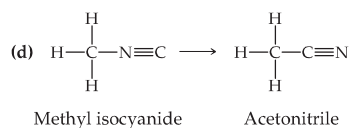
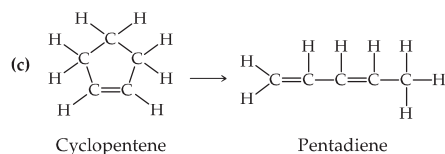
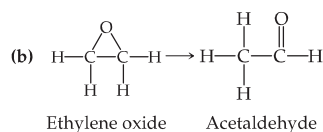
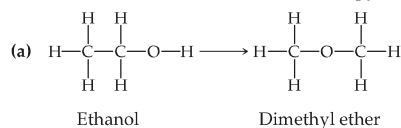


In practice, this reaction is carried out in the presence of oxygen, which converts the hydrogen produced to water.



Use bond enthalpies (Table 8.4) to estimate ΔH for these two reactions. Why is the conversion of methane to ethane more favorable when oxygen is used?

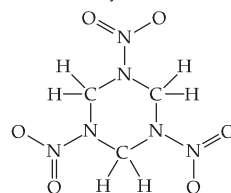
- 8.92 Two compounds are isomers if they have the same chemical formula but a different arrangement of atoms. Use bond enthalpies (Table 8.4) to estimate ΔH for each of the following gas-phase isomerization reactions, and indicate which isomer has the lower enthalpy:



- [8.93] With reference to the "Chemistry Put to Work" box on explosives, (a) use bond enthalpies to estimate the enthalpy change for the explosion of 1.00 g of nitroglycerin. (b) Write a balanced equation for the decomposition of TNT.

Assume that, upon explosion, TNT decomposes into $\text{N}_2(\text{g})$, $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{C}(\text{s})$.

- [8.94] The "plastic" explosive C-4, often used in action movies, contains the molecule *cyclotrimethylenetrinitramine*, which is often called RDX (for Royal Demolition eXplosive):



Cyclotrimethylenetrinitramine (RDX)

- (a) Complete the Lewis structure for the molecule by adding unshared electron pairs where they are needed. (b) Does the Lewis structure you drew in part (a) have any resonance structures? If so, how many? (c) The molecule causes an explosion by decomposing into $\text{CO}(\text{g})$, $\text{N}_2(\text{g})$, and $\text{H}_2\text{O}(\text{g})$. Write a balanced equation for the decomposition reaction. (d) With reference to Table 8.4, which is the weakest type of bond in the molecule? (e) Use average bond enthalpies to estimate the enthalpy change when 5.0 g of RDX decomposes.
- 8.95 The bond lengths of carbon-carbon, carbon-nitrogen, carbon-oxygen, and nitrogen-nitrogen single, double, and triple bonds are listed in Table 8.5. Plot bond enthalpy (Table 8.4) versus bond length for these bonds. What do you conclude about the relationship between bond length and bond enthalpy? What do you conclude about the relative strengths of C-C, C-N, C-O, and N-N bonds?
- 8.96 Use the data in Table 8.5 and the following data: S-S distance in S_8 = 2.05 Å; S-O distance in SO_2 = 1.43 Å to answer the following questions: (a) Predict the bond length in a S-N single bond. (b) Predict the bond length in a S-O single bond. (c) Why is the S-O bond length in SO_2 considerably shorter than your predicted value for the S-O single bond? (d) When elemental sulfur, S_8 , is carefully oxidized, a compound S_8O is formed, in which one of the sulfur atoms in the S_8 ring is bonded to an oxygen atom. The S-O bond length in this compound is 1.48 Å. In light of this information, write Lewis structures that can account for the observed S-O bond length. Does the sulfur bearing the oxygen in this compound obey the octet rule?

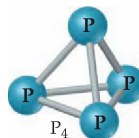
INTEGRATIVE EXERCISES

- 8.97 The Ti^{2+} ion is isoelectronic with the Ca atom. (a) Are there any differences in the electron configurations of Ti^{2+} and Ca? (b) With reference to Figure 6.25, comment on the changes in the ordering of the 4s and 3d subshells in Ca and Ti^{2+} . (c) Will Ca and Ti^{2+} have the same number of unpaired electrons? Explain.
- [8.98] (a) Write the chemical equations that are used in calculating the lattice energy of $\text{SrCl}_2(\text{s})$ via a Born-Haber cycle. (b) The second ionization energy of Sr(g) is 1064 kJ/mol. Use this fact along with data in Appendix C, Figure 7.12, Figure 7.14, and Table 8.2 to calculate ΔH_f° for $\text{SrCl}_2(\text{s})$.
- [8.99] The electron affinity of oxygen is -141 kJ/mol, corresponding to the reaction
- $$\text{O}(\text{g}) + \text{e}^- \longrightarrow \text{O}^-(\text{g})$$
- The lattice energy of $\text{K}_2\text{O}(\text{s})$ is 2238 kJ/mol. Use these data along with data in Appendix C and Figure 7.12 to calculate the "second electron affinity" of oxygen, corresponding to the reaction
- $$\text{O}^-(\text{g}) + \text{e}^- \longrightarrow \text{O}^{2-}(\text{g})$$

- 8.100** The reaction of indium, In, with sulfur leads to three binary compounds, which we will assume to be purely ionic. The three compounds have the following properties:

| Compound | Mass % In | Melting Point (°C) |
|----------|-----------|--------------------|
| A | 87.7 | 653 |
| B | 78.2 | 692 |
| C | 70.5 | 1050 |

- (a) Determine the empirical formulas of compounds A, B, and C. (b) Give the oxidation state of In in each of the three compounds. (c) Write the electron configuration for the In ion in each compound. Do any of these configurations correspond to a noble-gas configuration? (d) In which compound is the ionic radius of In expected to be smallest? Explain. (e) The melting point of ionic compounds often correlates with the lattice energy. Explain the trends in the melting points of compounds A, B, and C in these terms.
- [8.101]** 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: $\text{electronegativity} = k(\text{IE} - \text{EA})$, 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. Do these values follow the trend shown in Figure 8.6?
- 8.102** The compound chloral hydrate, known in detective stories as knockout drops, is composed of 14.52% C, 1.83% H, 64.30% Cl, and 19.35% 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.
- 8.103** 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.
- 8.104** Acetylene (C₂H₂) and nitrogen (N₂) 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 and compare their reactivities. (c) Write balanced chemical equations for the complete oxidation of N₂ to form N₂O₅(g) and of acetylene to form CO₂(g) and H₂O(g). (d) Calculate the enthalpy of oxidation per mole of N₂ and C₂H₂ (the enthalpy of formation of N₂O₅(g) is 11.30 kJ/mol). How do these comparative values relate to your response to part (b)? Both N₂ and C₂H₂ possess triple bonds with quite high bond enthalpies (Table 8.4). What aspect of chemical bonding in these molecules or in the oxidation products seems to account for the difference in chemical reactivities?
- [8.105]** 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⁻¹. 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 S₈ 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⁻¹. Estimate the average bond enthalpy in the compound.
- [8.106]** A common form of elemental phosphorus is the tetrahedral P₄ molecule, where all four phosphorus atoms are equivalent:



At room temperature phosphorus is a solid. (a) Do you think there are any unshared pairs of electrons in the P₄ molecule? (b) How many P—P bonds are there in the molecule? (c) Can you draw a Lewis structure for a linear P₄ molecule that satisfies the octet rule? (d) Using formal charges, what can you say about the stability of the linear molecule vs. that of the tetrahedral molecule?

- [8.107]** Consider benzene (C₆H₆) in the gas phase. (a) Write the reaction for breaking all the bonds in C₆H₆(g), and use data in Appendix C to determine the enthalpy change for this reaction. (b) Write a reaction that corresponds to breaking all the carbon-carbon bonds in C₆H₆(g). (c) By combining your answers to parts (a) and (b) and using the average bond enthalpy for C—H from Table 8.4, calculate the average bond enthalpy for the carbon-carbon bonds in C₆H₆(g). (d) Comment on your answer from part (c) as compared to the values for C—C single bonds and C=C double bonds in Table 8.4.
- 8.108** Average bond enthalpies are generally defined for gas-phase molecules. Many substances are liquids in their standard state. \rightleftharpoons (Section 5.7) By using appropriate thermochemical data from Appendix C, calculate average bond enthalpies in the liquid state for the following bonds, and compare these values to the gas-phase values given in Table 8.4: (a) Br—Br, from Br₂(l); (b) C—Cl, from CCl₄(l); (c) O—O, from H₂O₂(l) (assume that the O—H bond enthalpy is the same as in the gas phase). (d) What can you conclude about the process of breaking bonds in the liquid as compared to the gas phase? Explain the difference in the ΔH values between the two phases.