

# 9 The Basics of Chemical Bonding

## Chapter Outline

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This mountain climber's fate hangs on the strength of the chemical bonds between the atoms forming the fibers in the rope keeping her from falling to her death. Chemical bonds affect the chemical and physical properties of substances, both of which are important criteria when selecting materials for practical uses. In this chapter we begin our study of the way atoms bond to each other. | Love Images/© Corbis

## This Chapter in Context

In Chapter 3 you learned that we can classify substances into two broad categories, ionic or molecular. Ionic compounds, such as ordinary table salt, consist of electrically charged particles (ions) that bind to each other by electrostatic forces of attraction. We also said that in molecular substances, such as water, the atoms are held to each other by the sharing of electrons. Now that you've learned about the electronic structures of atoms, we can explore the attractions between atoms or ions, called **chemical bonds**, in greater depth. Our goal is to gain some insight into the reasons certain combinations of atoms prefer electron transfer and the formation of ions (leading to *ionic bonding*), while other combinations bind by electron sharing (leading to *covalent bonding*).

As with electronic structure, models of chemical bonding have also evolved, and in this chapter we introduce you to relatively simple theories. Although more complex theories exist (some of which we describe in Chapter 10), the basic concepts you will study in this chapter still find many useful applications in modern chemical thought.

## 9.1 | Energy Requirements for Bond Formation

■ The heat of reaction is just one factor that determines whether or not a chemical reaction can occur spontaneously. We will discuss this in detail in Chapter 19.



**Figure 9.1 | Exothermic reaction of sodium with chlorine.**

A small piece of melted sodium immediately ignites when dipped into a flask containing chlorine gas, producing light and releasing a lot of heat. The smoke coming from the flask is composed of fine crystals of sodium chloride.

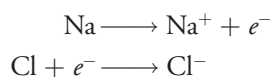
(Richard Megna/Fundamental Photographs)

For a *stable* compound to be formed from its elements, the reaction must be exothermic. In other words,  $\Delta H_f^\circ$  must be negative. Two examples of such reactions are the formation of  $\text{H}_2\text{O}$  by the reaction of  $\text{H}_2$  with  $\text{O}_2$  (Figure 1.22, page 20) and the formation of  $\text{NaCl}$  by the reaction of  $\text{Na}$  with  $\text{Cl}_2$ , shown in Figure 9.1. Both of these reactions release a large amount of energy when they occur and produce very stable compounds. Typically, compounds with positive heats of formation tend to be unstable with respect to decomposition. Sometimes that decomposition can occur violently, as with nitroglycerine, a powerful explosive.

When a reaction is exothermic, the potential energy of the particles in the system decreases. Therefore, to understand the formation of chemical bonds, we need to understand how bond formation can lead to a lowering of the potential energy of the atoms involved. In the pages ahead we will examine this for both ionic and molecular substances.

## 9.2 | Ionic Bonding

You learned in Chapter 3 that when sodium chloride is formed from its elements, each sodium atom loses one electron to form a sodium ion,  $\text{Na}^+$ , and each chlorine atom gains one electron to become a chloride ion,  $\text{Cl}^-$ .



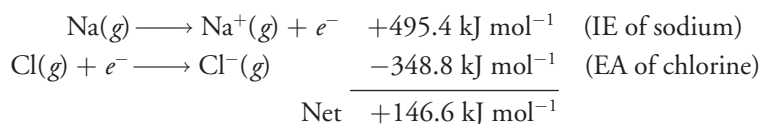
Once formed, these ions become tightly packed together, as illustrated in Figure 9.2, because their opposite charges attract. *This attraction between positive and negative ions in an ionic compound is what we call an ionic bond.*

The attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions may seem reasonable, but *why* are electrons transferred between these and other atoms? *Why* does sodium form  $\text{Na}^+$  and not  $\text{Na}^-$  or  $\text{Na}^{2+}$ ? And *why* does chlorine form  $\text{Cl}^-$  instead of  $\text{Cl}^+$  or  $\text{Cl}^{2-}$ ? To answer such questions we have to consider factors that are related to the potential energy of the system

of reactants and products. As noted above, for any stable compound to form from its elements, there must be a net lowering of the potential energy and the reaction must be exothermic.

## Importance of the Lattice Energy

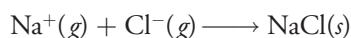
In the formation of an ionic compound such as NaCl, it is not the electron transfer itself that leads to a stable substance. We can see this if we examine the ionization energy of Na and the electron affinity of Cl. Dealing with a mole-sized collection of gaseous atoms, we have



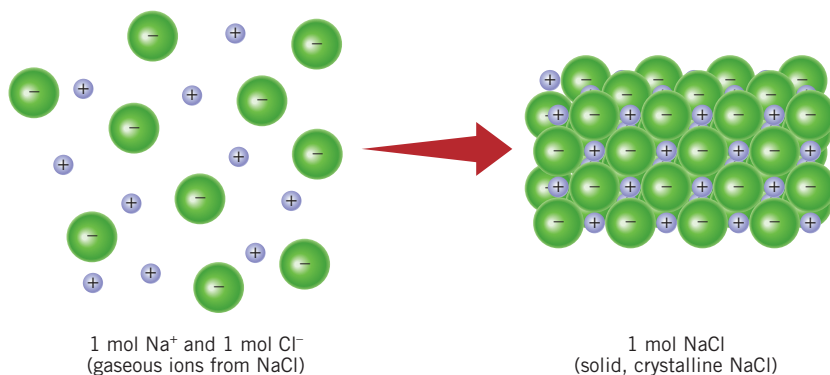
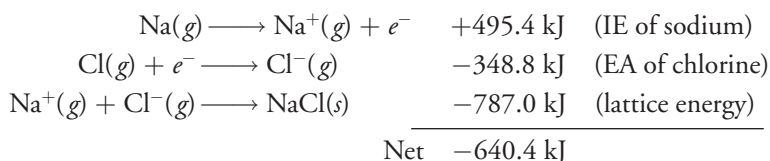
Notice that forming gaseous sodium and chloride ions from gaseous sodium and chlorine atoms requires a substantial *increase* in the potential energy. This tells us that if the IE and EA were the only energy changes involved, ionic sodium chloride would not form from atoms of sodium and chlorine. So where does the stability of the compound come from?

In the calculation above, we looked at the formation of gaseous ions, but salt is not a gas; it's a solid. Therefore, we need to see how the energy would change if the gaseous ions are condensed to give the solid, and to do this we must examine a quantity called the lattice energy.

The **lattice energy** is the energy change that would occur if the ions at infinite separation (*i.e.*, a cloud of gaseous ions) are brought together to form one mole of the solid compound.<sup>1</sup> For sodium chloride, the change associated with the lattice energy is pictured in Figure 9.3, and in equation form can be represented as



Because  $\text{Na}^+$  and  $\text{Cl}^-$  ions attract each other, their potential energy decreases as they come together, so the process releases energy and is exothermic. In fact, the lattice energy for sodium chloride is very exothermic and is equal to  $-787 \text{ kJ mol}^{-1}$ . If we include the lattice energy along with the ionization energy of Na and electron affinity of Cl, we have



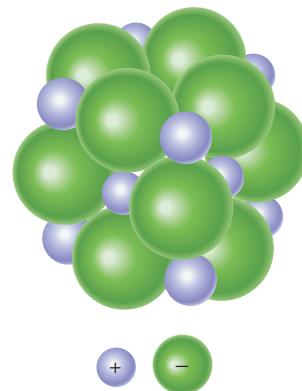
<sup>1</sup>In some books, the lattice energy is defined as the energy needed to separate the ions in one mole of a solid to give a cloud of gaseous ions. This would correspond to the change



The *magnitude* of the energy change is the same as for the process described above in the body of the text, but the algebraic sign of the energy change would be positive instead of negative (endothermic instead of exothermic).

■ Keep in mind the relationship between potential energy changes and endothermic and exothermic processes:

endothermic  $\Leftrightarrow$  increase in PE  
exothermic  $\Leftrightarrow$  decrease in PE



**Figure 9.2 | The packing of ions in NaCl.** Electrostatic forces hold the ions in place in the solid. These forces constitute ionic bonds.

■ The name lattice energy comes from the word *lattice*, which is used to describe the regular pattern of ions or atoms in a crystal. Lattice energies are exothermic and so are given negative signs.

**Figure 9.3 | The lattice energy of NaCl.** The energy released when one mole of gaseous  $\text{Na}^+$  and one mole of gaseous  $\text{Cl}^-$  condenses to one mole of solid NaCl is the lattice energy. For NaCl, this amounts to 787 kJ.

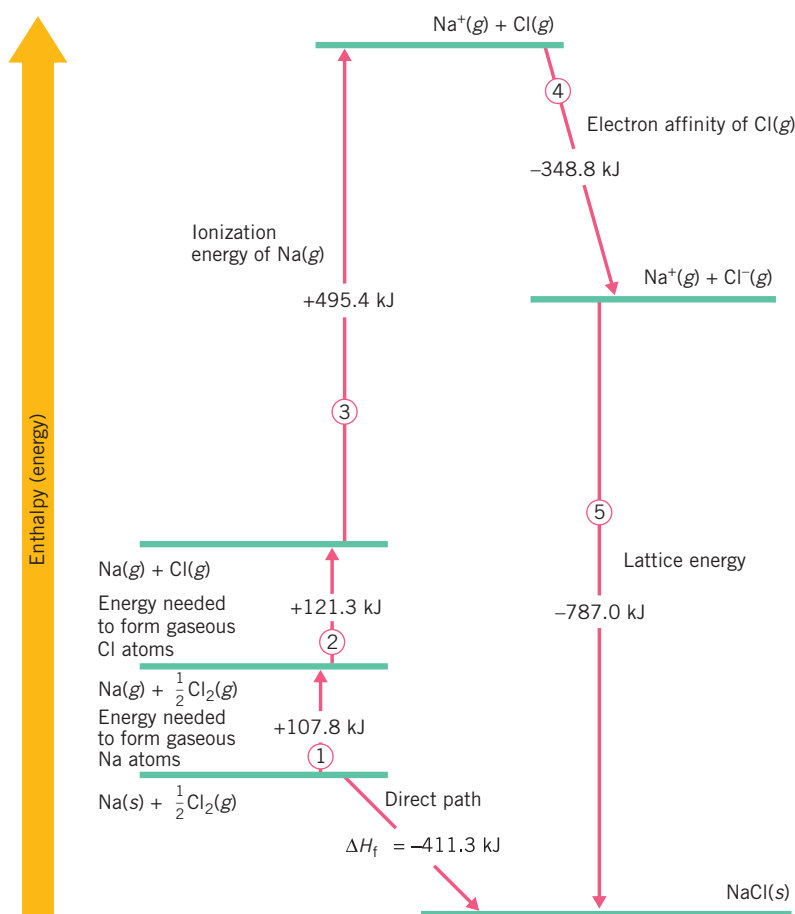
Thus, the release of energy equal to the lattice energy provides a large net lowering of the potential energy as solid NaCl is formed. We can also say that *it is the lattice energy that provides the stabilization necessary for the formation of NaCl*. Without it, the compound could not exist.

## Determining Lattice Energies

At this point, you may be wondering about our starting point in these energy calculations—namely, gaseous sodium atoms and chlorine atoms. In nature, sodium is a solid metal and chlorine consists of gaseous  $\text{Cl}_2$  molecules. Let's look at a complete analysis of the energy changes taking this into account. To perform the analysis we will use an enthalpy diagram similar to the type discussed in Chapter 7. It is called a **Born–Haber cycle** after the scientists who were the first to use it to calculate lattice energies.

In Chapter 7 you learned that the enthalpy change for a process is the same regardless of the path we follow from start to finish. With this in mind, we will construct two different paths from the free elements (solid sodium and gaseous chlorine molecules) to the solid ionic compound, sodium chloride, as shown in Figure 9.4.

The starting point for both paths is the same: the free elements sodium and chlorine. The path that starts at the lower left takes us directly to the product,  $\text{NaCl}(s)$ , and has as its enthalpy change the heat of formation of NaCl,  $\Delta H_f^\circ$ .



**Figure 9.4 | Analysis of the enthalpy changes in the formation of sodium chloride.** One path leads directly from the elements  $\text{Na}(s)$  and  $\text{Cl}_2(g)$  to  $\text{NaCl}(s)$ . The second (upper) path follows a series of changes that include the lattice energy and take us to the same final product,  $\text{NaCl}(s)$ .

The alternative path is divided into a number of steps. The first two, labeled 1 and 2, have  $\Delta H^\circ$  values that can be measured experimentally and both are endothermic. They change  $\text{Na}(s)$  and  $\text{Cl}_2(g)$  into gaseous atoms,  $\text{Na}(g)$  and  $\text{Cl}(g)$ . The next two steps (Steps 3 and 4) change the atoms to ions, first by the endothermic ionization energy (IE) of Na followed by the exothermic electron affinity (EA) of Cl. This brings us to the gaseous ions,  $\text{Na}^+(g) + \text{Cl}^-(g)$ , depicted on the right in Figure 9.4. Notice that at this point, if we add all the energy changes, the ions are at a considerably higher energy than the reactants. If these were the only energy terms involved in the formation of NaCl, the heat of formation would be endothermic and the compound would be unstable; it could not be formed by the direct combination of the elements.

The last step on the right in Figure 9.4 (Step 5) finally brings us to solid NaCl and corresponds to the lattice energy. To make the net energy changes the same along both paths, the energy released when the ions condense to form the solid must equal  $-787.0$  kJ. Therefore, the calculated lattice energy of NaCl must be  $-787.0$  kJ mol $^{-1}$ .

What we see in this analysis is that it is the lattice energy that permits NaCl to be formed from its elements. In fact, *for any ionic compound, the chief stabilizing influence is the lattice energy, which when released is large enough to overcome the net energy input required to form the ions from the elements.*

Besides affecting the ability of ionic compounds to form, lattice energies are also important in determining the solubilities of ionic compounds in water and other solvents. We will explore this topic in Chapter 14.

### Effect of Ionic Size and Charge on the Lattice Energy

The lattice energies of some ionic compounds are given in Table 9.1. As you can see, they are all very large exothermic quantities. Their magnitudes depend on a number of factors, including the charges on the ions and their sizes.

For two ions with charges  $q_1$  and  $q_2$  separated by a distance  $r$ , the potential energy can be calculated from **Coulomb's law**:

$$E = \frac{q_1 q_2}{k r} \quad (9.1)$$

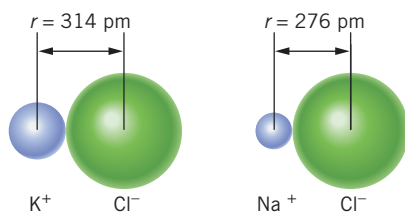
where  $k$  is a proportionality constant.<sup>2</sup> In an ionic solid,  $q_1$  and  $q_2$  have opposite signs, so  $E$  is calculated to be a negative quantity. That's why the lattice energy has a negative sign.

When the charges on the ions become larger (i.e., when  $q_1$  and  $q_2$  become larger),  $E$  becomes more negative, which means the potential energy becomes lower (more negative).

**Table 9.1** Lattice Energies of Some Ionic Compounds

Compound	Ions	Lattice Energy (kJ mol $^{-1}$ )
LiCl	$\text{Li}^+$ and $\text{Cl}^-$	-845
NaCl	$\text{Na}^+$ and $\text{Cl}^-$	-787
KCl	$\text{K}^+$ and $\text{Cl}^-$	-709
LiF	$\text{Li}^+$ and $\text{F}^-$	-1033
$\text{CaCl}_2$	$\text{Ca}^{2+}$ and $\text{Cl}^-$	-2258
$\text{AlCl}_3$	$\text{Al}^{3+}$ and $\text{Cl}^-$	-5492
CaO	$\text{Ca}^{2+}$ and $\text{O}^{2-}$	-3401
$\text{Al}_2\text{O}_3$	$\text{Al}^{3+}$ and $\text{O}^{2-}$	-15,916

<sup>2</sup>In this case, we're using the symbol  $q$  to mean electric charge, not heat as in Chapter 7. Because the number of letters in the alphabet is limited, it's not uncommon in science for the same letter to be used to stand for different quantities. This usually doesn't present a problem as long as the symbol is defined in the context in which it is used.



**Figure 9.5 | The effect of ionic size on the lattice energy.**

Because  $\text{Na}^+$  is smaller than  $\text{K}^+$ , the distance between ions is smaller in  $\text{NaCl}$  than in  $\text{KCl}$ . This causes the lattice energy of  $\text{NaCl}$  to be larger than that of  $\text{KCl}$ .

This explains why salts of  $\text{Ca}^{2+}$  have larger lattice energies than comparable salts of  $\text{Na}^+$ , and those containing  $\text{Al}^{3+}$  have even larger lattice energies.

Because the distance between the ions,  $r$ , appears in the denominator in Equation 9.1,  $E$  becomes a larger negative quantity as  $r$  becomes smaller. As a result, compounds formed from small ions (which can get close together) have larger lattice energies than those formed from large ions. For example, a  $\text{Na}^+$  ion is smaller than a  $\text{K}^+$  ion, and in Figure 9.5 we compare the cation–anion distances observed in solid  $\text{NaCl}$  and  $\text{KCl}$ . The smaller  $\text{Na–Cl}$  distance causes  $\text{NaCl}$  to have a larger lattice energy than  $\text{KCl}$ .

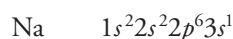
### Factors That Determine the Formation of Cations and Anions

We've shown that for an ionic compound to form, the energy lowering produced by release of the lattice energy must exceed the energy rise associated with forming the ions from the neutral atoms. This requires that the cation be formed from an atom of relatively low ionization energy; such atoms are found among the metals. Nonmetals, at the upper right of the periodic table, have large ionization energies but generally exothermic electron affinities. A nonmetal atom has little tendency to lose electrons, but forming an anion from a nonmetal atom can actually help to lower the energy. As a result, cations are formed from metals and anions are formed from nonmetals because this leads to the greatest lowering of the energy. In fact, metals combine with nonmetals to form ionic compounds simply because ionic bonding is favored energetically over other types whenever atoms with small ionization energies combine with atoms that have large exothermic electron affinities.

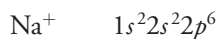
## 9.3 | Electron Configurations of Ions

### Stability of the Noble Gas Configuration

Earlier we raised the question about why sodium forms  $\text{Na}^+$  and chlorine forms  $\text{Cl}^-$ . To find the answer, let's begin by examining what happens when a sodium atom loses an electron. The electron configuration of  $\text{Na}$  is

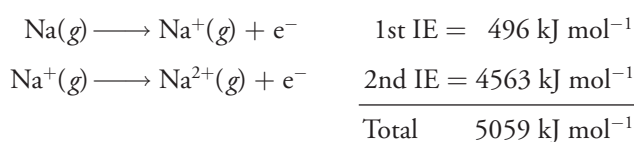


The electron that is lost is the one least tightly held, which is the single outer  $3s$  electron. The electronic structure of the  $\text{Na}^+$  ion, then, is



Notice that this is identical to the electron configuration of the noble gas neon. We say the  $\text{Na}^+$  ion has achieved a *noble gas configuration*.

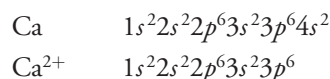
The energy needed to remove the first electron from  $\text{Na}$  is relatively small and can easily be recovered by the release of the lattice energy when an ionic compound containing  $\text{Na}^+$  is formed. However, removal of a second electron from sodium is *very* difficult because it involves breaking into the  $2s^2 2p^6$  core. Forming the  $\text{Na}^{2+}$  ion is therefore very endothermic, as we can see by adding the first and second ionization energies (Table 8.2, page 343).



Even though the  $\text{Na}^{2+}$  ion would give a compound such as  $\text{NaCl}_2$  a larger lattice energy than  $\text{NaCl}$  (e.g., see the lattice energy for  $\text{CaCl}_2$ ), it would not be large enough to make the formation of the compound exothermic. As a result,  $\text{NaCl}_2$  cannot form. The same

applies to other compounds of sodium, so when sodium forms a cation, electron loss stops once the  $\text{Na}^+$  ion is formed and a noble gas electron configuration is reached.

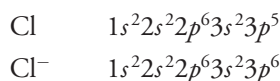
Similar situations exist for other metals, too. For example, the first two electrons to be removed from a calcium atom come from the  $4s$  valence shell (outer shell).



The energy needed to accomplish this can be recovered by the release of the lattice energy when a compound containing  $\text{Ca}^{2+}$  forms. Electron loss ceases at this point, however, because of the huge amount of energy needed to break into the noble gas core. As a result, a calcium atom loses just two electrons when it reacts.

For sodium and calcium, as well as other metals of Groups 1A and 2A and aluminum, the large ionization energy of the noble gas core just below their outer shells limits the number of electrons they lose, so the ions that are formed have noble gas electron configurations.

Nonmetals also tend to achieve noble gas configurations when they form anions. For example, when a chlorine atom reacts, it gains one electron.



At this point, we have a noble gas configuration (that of argon). Electron gain ceases, because if another electron were to be added, it would have to enter an orbital in the next higher shell, which is very energetically unfavorable. Similar arguments apply to the other nonmetals as well.

## The Octet Rule

In the preceding discussion you learned that a balance of energy factors causes many atoms to form ions that have a noble gas electron configuration. Historically, this is expressed in the form of a generalization: *When they form ions, atoms of most of the representative elements tend to gain or lose electrons until they have obtained an electron configuration identical to that of the nearest noble gas.* Because all the noble gases except helium have outer shells with eight electrons, this rule has become known as the **octet rule**, which can be stated as follows: *Atoms tend to gain or lose electrons until they have achieved an outer shell that contains an **octet of electrons** (eight electrons).*

## Cations That Do Not Obey the Octet Rule

The octet rule, as applied to ionic compounds, really works well only for the cations of the Group 1A and 2A metals and aluminum, and for the anions of the nonmetals. It does not work well for the transition metals and post-transition metals (the metals that follow a row of transition metals).

To obtain the correct electron configurations of the cations of these metals, we apply the following rules:

### Obtaining the Electron Configuration of a Cation

1. The first electrons to be lost by an atom or ion are *always* those from the shell with the largest value of  $n$  (i.e., the outer shell).
2. As electrons are removed from a given shell, they come from the highest-energy occupied subshell first, before any are removed from a lower-energy subshell. Within a given shell, the energies of the subshells vary as follows:  $s < p < d < f$ . This means that  $f$  is emptied before  $d$ , which is emptied before  $p$ , which is emptied before  $s$ .

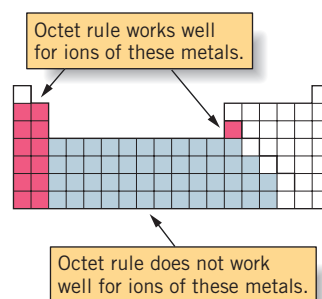
Let's look at two examples.

■ For calcium:

1st IE = 590 kJ/mol  
2nd IE = 1146 kJ/mol  
3rd IE = 4940 kJ/mol



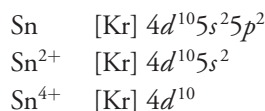
Electron configurations of ions of the representative elements.



Order in which electrons are lost from an atom.

■ Applying these rules to the metals of Groups 1A and 2A also gives the correct electron configurations.

Tin (a post-transition metal) forms two ions,  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ . The electron configurations are



Notice that the  $\text{Sn}^{2+}$  ion is formed by the loss of the higher energy  $5p$  electrons first. Then, further loss of the two  $5s$  electrons gives the  $\text{Sn}^{4+}$  ion. However, neither of these ions has a noble gas configuration.

For the transition elements, the first electrons lost are the  $s$  electrons of the outer shell. Then, if additional electrons are lost, they come from the underlying  $d$  subshell. An example is iron, which forms the ions  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . The element iron has the electron configuration



Iron loses its  $4s$  electrons fairly easily to give  $\text{Fe}^{2+}$ , which has the electron configuration



The  $\text{Fe}^{3+}$  ion results when another electron is removed, this time from the  $3d$  subshell.



Iron is able to form  $\text{Fe}^{3+}$  because the  $3d$  subshell is close in energy to the  $4s$ , so it is not very difficult to remove the third electron. Notice once again that the first electrons to be removed come from the shell with the largest value of  $n$  (the  $4s$  subshell). Then, after this shell is emptied, the next electrons are removed from the shell below.

Because so many of the transition elements are able to form ions in a way similar to that of iron, the ability to form more than one positive ion is usually cited as one of the characteristic properties of the transition elements. Frequently, one of the ions formed has a  $2+$  charge, which arises from the loss of the two outer  $s$  electrons. Ions with larger positive charges result when additional  $d$  electrons are lost. Unfortunately, it is not easy to predict exactly which ions can form for a given transition metal, nor is it simple to predict their relative stabilities with respect to being oxidized or reduced.

## Example 9.1

### Writing Electron Configurations of Ions

How do the electron configurations change (a) when a nitrogen atom forms the  $\text{N}^{3-}$  ion and (b) when an antimony atom forms the  $\text{Sb}^{3+}$  ion?

■ **Analysis:** For the nonmetals, you've learned that the octet rule does work, so the ion that is formed by nitrogen will have a noble gas configuration.

Antimony is a post-transition element, so we don't expect its cation to obey the octet rule. We will have to examine the electron configuration of the neutral atoms and determine which electrons are lost.

■ **Assembling the Tools:** The octet rule serves as the tool to determine the electron configuration of  $\text{N}^{3-}$ . To determine the electron configuration of  $\text{Sb}^{3+}$ , our tools will be the procedure for writing abbreviated electron configurations for atoms as well as the rules describing the order in which electrons are lost from an atom.

■ **Solution:** (a) Following the method for writing abbreviated configurations, the electron configuration for nitrogen is

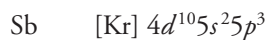


To form  $\text{N}^{3-}$ , three electrons are gained. These enter the  $2p$  subshell because it is the lowest available energy level. Filling the  $2p$  subshell completes the octet; the configuration for the ion is therefore





(b) The rules tell us that when a cation is formed, electrons are removed first from the outer shell of the atom (the shell with the largest value of the principal quantum number,  $n$ ). Within a given shell, electrons are always removed first from the subshell highest in energy. Let's begin with the ground state electron configuration for antimony, obtained in the usual way.



To form the  $\text{Sb}^{3+}$  ion, three electrons must be removed. These will come from the outer shell, which has  $n = 5$ . Within this shell, the energies of the subshells increase in the order  $s < p < d < f$ . Therefore, the  $5p$  subshell is higher in energy than the  $5s$ , so all three electrons are removed from the  $5p$ . This gives



■ **Are the Answers Reasonable?** In Chapter 3 you learned to use the periodic table to figure out the charges on the anions of the nonmetals. For nitrogen, we would take three steps to the right to get to the nearest noble gas, neon. The electron configuration we obtained for  $\text{N}^{3-}$  is that of neon, so our answer should be correct.

For antimony, we had to remove three electrons, which completely emptied the  $5p$  subshell. That's also good news, because ions do not tend to have partially filled  $s$  or  $p$  subshells (although partially filled  $d$  subshells are not uncommon for the transition metals). If we had taken the electrons from any other subshells, the  $\text{Sb}^{3+}$  ion would have had a partially filled  $5p$  subshell.

## Example 9.2

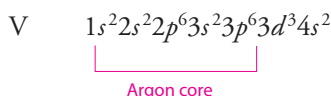
### Writing Electron Configurations of Ions

What is the electron configuration of the  $\text{V}^{3+}$  ion? Give the orbital diagram for the ion.

■ **Analysis:** To obtain the electron configuration of a cation, always begin with the electron configuration of the neutral atom. In this case we will remove three electrons to obtain the electron configuration of the ion.

■ **Assembling the Tools:** Once again, our tools will be the method for deriving electron configurations of atoms and the rules that tell us the order in which electrons are lost by an atom. We will also use Hund's rule, which tells us how electrons populate orbitals of a given subshell.

■ **Solution:** Following the usual method, the electron configuration of vanadium is



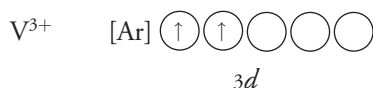
Notice that we've written the configuration showing the outer shell  $4s$  electrons farthest to the right. To form the  $\text{V}^{3+}$  cation, three electrons must be removed from the neutral atom. We have to keep in mind that the electrons are lost first from the occupied shell with highest  $n$ . Therefore, the first two come from the  $4s$  subshell and the third comes from the  $3d$ . This means we won't have to take any from the  $3s$  or  $3p$  subshells, so the argon core will remain intact. Therefore, let's rewrite the electron configuration in abbreviated form.



Removing the three electrons gives



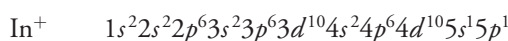
To form the orbital diagram, we show all five orbitals of the  $3d$  subshell and then spread out the two electrons with spins unpaired (Hund's rule). This gives



■ **Is the Answer Reasonable?** First, we check that we've written the correct electron configuration of vanadium, which we have. (A quick count of the electrons gives 23, which is the atomic number of vanadium.) We've also taken electrons away from the atom following the rules, so the electron configuration of the ion seems okay. Finally, we remembered to show all five orbitals of the  $3d$  subshell, even though only two of them are occupied.

## Practice Exercises

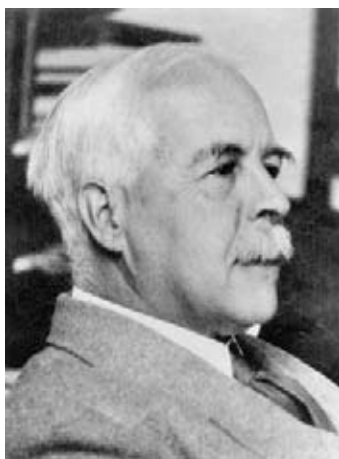
**9.1** | What is wrong with the following electron configuration of the  $\text{In}^+$  ion? What should the electron configuration be?



(Hint: Check the rules that tell us the order in which electrons are lost by an atom or ion.)

**9.2** | How do the electron configurations change when a chromium atom forms the following ions: (a)  $\text{Cr}^{2+}$ , (b)  $\text{Cr}^{3+}$ , (c)  $\text{Cr}^{6+}$ ?

**9.3** | How are the electron configurations of  $\text{S}^{2-}$  and  $\text{Cl}^-$  related?



Gilbert N. Lewis, chemistry professor at the University of California, helped develop theories of chemical bonding. In 1916, he proposed that atoms form bonds by sharing pairs of electrons.

(Bettmann/© Corbis)



Lewis symbols

## 9.4 | Lewis Symbols: Keeping Track of Valence Electrons

In the previous section you saw how the valence shells of atoms change when electrons are transferred during the formation of ions. We will soon see the way many atoms share their valence electrons with each other when they form covalent bonds. In these discussions it is useful to be able to keep track of valence electrons. To help us do this, we use a simple bookkeeping device called Lewis symbols, named after their inventor, the American chemist, G. N. Lewis (1875–1946).

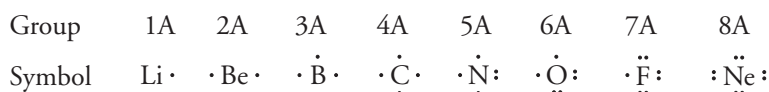
To draw the **Lewis symbol** for an element, we write its chemical symbol surrounded by dots (or some other similar mark), each of which represents a valence electron of the atom. For example, the element lithium has the Lewis symbol



in which the single dot stands for lithium's single valence electron. In fact, each element in Group 1A has a similar Lewis symbol, because each has only one valence electron. The Lewis symbols for all of the Group 1A metals are



The Lewis symbols for the eight A-group elements of Period 2 are<sup>3</sup>



<sup>3</sup>For beryllium, boron, and carbon, the number of unpaired electrons in the Lewis symbol doesn't agree with the number predicted from the atom's electron configuration. Boron, for example, has two electrons paired in its  $2s$  orbital and a third electron in one of its  $2p$  orbitals; therefore, there is actually only one unpaired electron in a boron atom. The Lewis symbols are drawn as shown, however, because when beryllium, boron, and carbon form bonds, they *behave* as if they have two, three, and four unpaired electrons, respectively.

The elements below each of these in their respective groups have identical Lewis symbols except, of course, for the chemical symbol of the element. Notice that when an atom has more than four valence electrons, the additional electrons are shown to be paired with others. Also notice that *for the representative elements, the group number is equal to the number of valence electrons* when the North American convention for numbering groups in the periodic table is followed.

■ This is one of the advantages of the North American convention for numbering groups in the periodic table.

### Example 9.3 Writing Lewis Symbols

What is the Lewis symbol for arsenic?

■ **Analysis:** We need to know the number of valence electrons, which we can obtain from the group number. Then we distribute the electrons (dots) around the chemical symbol.

■ **Assembling the Tools:** Our tool is the method described above for constructing the Lewis symbol.

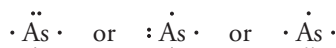
■ **Solution:** The symbol for arsenic is As and we find it in Group 5A. The element therefore has five valence electrons. The first four are placed around the symbol for arsenic as follows:



The fifth electron is paired with one of the first four. This gives



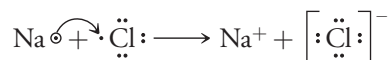
The location of the fifth electron doesn't really matter, so equally valid Lewis symbols are



■ **Is the Answer Reasonable?** There's not much to check here. Have we got the correct chemical symbol? Yes. Do we have the right number of dots? Yes.

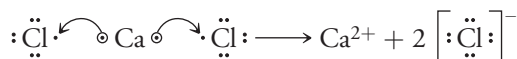
## Using Lewis Symbols to Represent Ionic Compounds

Although we will use Lewis symbols mostly to follow the fate of valence electrons in covalent bonds, they can also be used to describe what happens during the formation of ions. For example, when a sodium atom reacts with a chlorine atom, the sodium loses an electron to the chlorine, which we might depict as



The valence shell of the sodium atom is emptied, so no dots remain. The outer shell of chlorine, which formerly had seven electrons, gains one to give a total of eight. The brackets are drawn around the chloride ion to show that all eight electrons are the exclusive property of the  $\text{Cl}^-$  ion.

We can diagram a similar reaction between calcium and chlorine atoms.



## Example 9.4

### Using Lewis Symbols

Use Lewis symbols to diagram the reaction that occurs between sodium and oxygen atoms to give  $\text{Na}^+$  and  $\text{O}^{2-}$  ions.

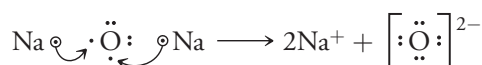
■ **Analysis:** For electrical neutrality, the formula will be  $\text{Na}_2\text{O}$ , so we will use two sodium atoms and one oxygen atom. Each sodium will lose one electron to give  $\text{Na}^+$  and the oxygen will gain two electrons to give  $\text{O}^{2-}$ .

■ **Assembling the Tools:** The principal tool is the method for constructing the Lewis symbol for an element and its ions.

■ **Solution:** Our first task is to draw the Lewis symbols for Na and O.



It takes two electrons to complete the octet around oxygen. Each Na supplies one. Therefore,



Notice that we have put brackets around the oxide ion.

■ **Is the Answer Reasonable?** We have accounted for all the valence electrons (an important check), the net charge is the same on both sides of the arrow (the equation is balanced), and we've placed the brackets around the oxide ion to emphasize that the octet belongs exclusively to that ion.

### Practice Exercises

**9.4** | Use Lewis symbols to diagram the formation of  $\text{CaI}_2$  from Ca and I atoms. (*Hint:* Begin by determining how many electrons are gained or lost by each atom.)

**9.5** | Diagram the reaction between magnesium and oxygen atoms to give  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions.

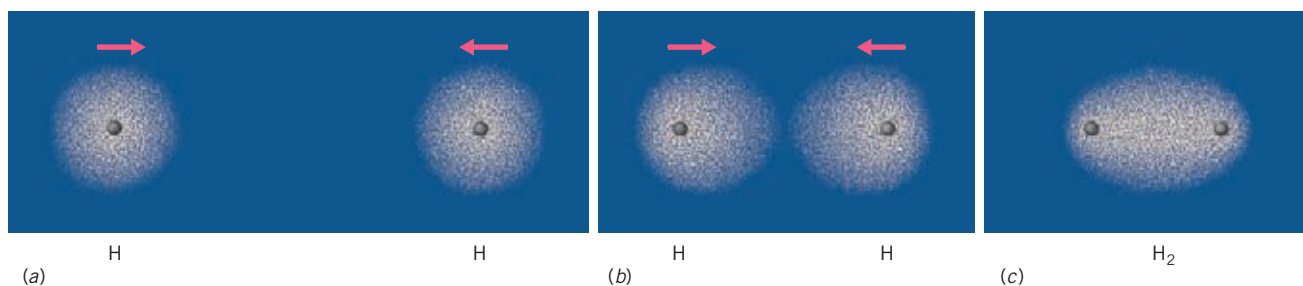
## 9.5 | Covalent Bonds

Most of the substances we encounter in our daily lives are not ionic. Instead, they are composed of electrically neutral molecules. The chemical bonds that bind the atoms to each other in such molecules are electrical in nature, but arise from the sharing of electrons rather than by electron transfer.

### Energy Changes on Bond Formation

In Section 9.2 we saw that for ionic bonding to occur, the energy-lowering effect of the lattice energy must be greater than the combined net energy-raising effects of the ionization energy (IE) and electron affinity (EA). Many times this is not possible, particularly when the ionization energies of all the atoms involved are large. This happens, for example, when nonmetals combine with each other to form molecules. In such cases, nature uses a different way to lower the energy—electron sharing.

Let's look at what happens when two hydrogen atoms join to form an  $\text{H}_2$  molecule (Figure 9.6). As the two atoms approach each other, the electron of each atom begins to feel the attraction of both nuclei. This causes the electron density around each nucleus to shift toward the region between the two atoms. Therefore, as the distance between the nuclei decreases, there is an increase in the probability of finding either electron near either nucleus. In effect, as the molecule is formed, each of the hydrogen atoms in the  $\text{H}_2$  molecule acquires a share of two electrons.



**Figure 9.6 | Formation of a covalent bond between two hydrogen atoms.** (a) Two H atoms separated by a large distance. (b) As the atoms approach each other, their electron densities are pulled into the region between the two nuclei. (c) In the  $H_2$  molecule, the electron density is concentrated between the nuclei. Both electrons in the bond are distributed over both nuclei.

In the  $H_2$  molecule, the buildup of electron density between the two atoms attracts both nuclei and pulls them together. Being of the same charge, however, the two nuclei also repel each other, as do the two electrons. In the molecule that forms, therefore, the atoms are held at a distance at which all these attractions and repulsions are balanced. Overall, the nuclei are kept from separating, and the net force of attraction produced by sharing the pair of electrons is called a **covalent bond**.

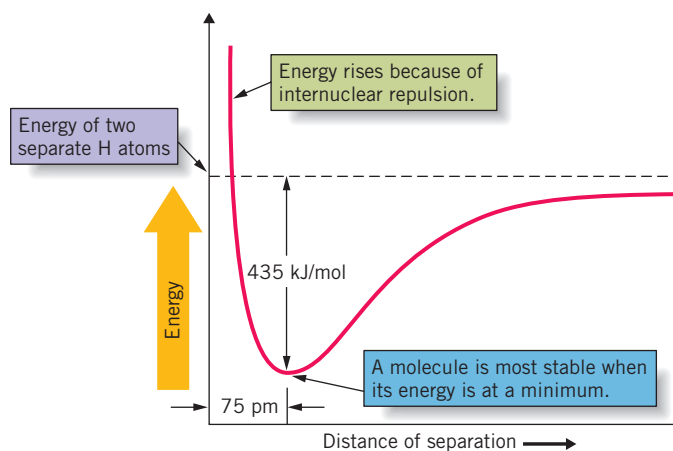
### Bond Energy and Bond Length

Every covalent bond is characterized by two quantities—namely, the average distance between the nuclei held together by the bond and the amount of energy needed to separate the two atoms to produce neutral atoms again. In the hydrogen molecule, the attractive forces pull the nuclei to a distance of 75 pm, and this distance is called the **bond length** (or sometimes the **bond distance**). Because a covalent bond holds atoms together, work must be done (energy must be supplied) to separate them. The amount of energy needed to “break” the bond (or the energy released when the bond is formed) is called the **bond energy**.

Figure 9.7 shows how the potential energy changes when two hydrogen atoms come together to form  $H_2$ . We see that the minimum potential energy occurs at a bond length of 75 pm, and that 1 mol of hydrogen molecules is more stable than 2 mol of hydrogen atoms by 435 kJ. In other words, the bond energy of  $H_2$  is 435 kJ/mol.

In general, forming any covalent bond leads to a lowering of the energy and breaking covalent bonds leads to an increase in energy. As noted in Chapter 7, the net energy change we observe in a chemical reaction is the result of energies associated with the breaking and making of bonds.

■ As the distance between the nuclei and the electron cloud that lies between them decreases, the potential energy decreases.



**Figure 9.7 | Changes in the total potential energy of two hydrogen atoms as they form  $H_2$ .** The energy of the molecule reaches a minimum when there is a balance between the attractions and repulsions.

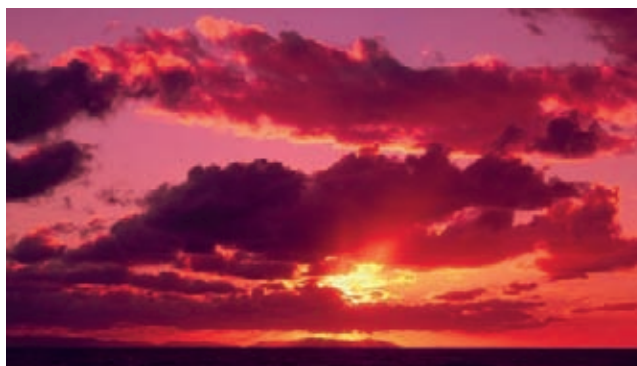
## CHEMISTRY AND CURRENT AFFAIRS | 9.1

## Sunlight and Skin Cancer

The ability of light to provide the energy for chemical reactions enables life to exist on our planet. Green plants absorb sunlight and, with the help of chlorophyll, convert carbon dioxide and water into carbohydrates (e.g., sugars and cellulose), which are essential constituents of the food chain. However, not all effects of sunlight are so beneficial.

As you know, light packs energy that's proportional to its frequency, and if the photons that are absorbed by a substance have enough energy, they can rupture chemical bonds and initiate chemical reactions. Light that is able to do this has frequencies in the ultraviolet (UV) region of the electromagnetic spectrum, and the sunlight bombarding the earth contains substantial amounts of UV radiation. Fortunately, a layer of ozone (O<sub>3</sub>) in the stratosphere, a region of the atmosphere extending from about 45 to 55 km altitude, absorbs most of the incoming UV, protecting life on the surface. However, some UV radiation does get through, and the part of the spectrum of most concern is called "UV-B" with wavelengths between 280 and 320 nm.

What makes UV-B so dangerous is its ability to affect the DNA in our cells. (The structure of DNA and its replication is discussed in Chapter 23.) Absorption of UV radiation causes constituents of the DNA, called *pyrimidine bases*, to undergo reactions that form bonds between them. This causes transcription errors when the DNA replicates during cell division, giving rise to genetic



Dawn of a new day brings the risk of skin cancer to those particularly susceptible. Fortunately, understanding the risk allows us to protect ourselves with clothing and sunblock creams. © Mick Roessler/© Corbis

mutations that can lead to skin cancers. These skin cancers fall into three classes—basal cell carcinomas, squamous cell carcinomas, and melanomas (the last being the most dangerous). Each year there are more than 1 million cases of skin cancer diagnosed. It is estimated that more than 90% of skin cancers are due to absorption of UV-B radiation.

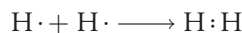
In recent years, concern has grown over the depletion of the ozone layer in the stratosphere apparently caused by the release of gases called chlorofluorocarbons (CFCs), which have been widely used in refrigerators and air conditioners. Some scientists have estimated a substantial increase in the rate of skin cancer caused by increased amounts of UV-B reaching the earth's surface due to this ozone depletion.

■ In Chapter 8 you learned that when two electrons occupy the same orbital and therefore share the same space, their spins must be paired. The pairing of electrons is an important part of the formation of a covalent bond.

## Pairing of Electrons in Covalent Bonds

Before joining to form H<sub>2</sub>, each of the separate hydrogen atoms has one electron in a 1s orbital. When these electrons are shared, the 1s orbital of each atom is, in a sense, filled. Because the electrons now share the same space, they become paired as required by the Pauli exclusion principle; that is, *m<sub>s</sub>* is + $\frac{1}{2}$  for one of the electrons and - $\frac{1}{2}$  for the other. In general, the electrons involved almost always become paired when atoms form covalent bonds. In fact, a covalent bond is sometimes referred to as an **electron pair bond**.

Lewis symbols are often used to keep track of electrons in covalent bonds. The electrons that are shared between two atoms are shown as a pair of dots placed between the symbols for the bonded atoms. The formation of H<sub>2</sub> from hydrogen atoms, for example, can be depicted as



Because the electrons are shared, each H atom is considered to have two electrons.



(Colored circles emphasize that two electrons can be counted around each of the H atoms.)

For simplicity, the electron pair in a covalent bond is usually depicted as a single dash. Thus, the hydrogen molecule is represented as



A formula such as this, which is drawn with Lewis symbols, is called a **Lewis formula** or **Lewis structure**. It is also called a **structural formula** because it shows which atoms are present in the molecule *and* how they are attached to each other.

## The Octet Rule and Covalent Bonding

You have seen that when a nonmetal atom forms an anion, electrons are gained until the  $s$  and  $p$  subshells of its valence shell are completed. The tendency of a nonmetal atom to finish with a completed valence shell, usually consisting of eight electrons, also influences the number of electrons the atom tends to acquire by sharing, and it thereby affects the number of covalent bonds the atom forms.

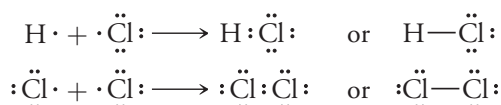
Hydrogen, with just one electron in its  $1s$  orbital, completes its valence shell by obtaining a share of just one electron from another atom, so a hydrogen atom forms just one covalent bond. When this other atom is hydrogen, the  $H_2$  molecule is formed.

Many atoms form covalent bonds by sharing enough electrons to give them complete  $s$  and  $p$  subshells in their outer shells. This is the noble gas configuration mentioned earlier and is the basis of the octet rule described in Section 9.3. As applied to covalent bonding, the **octet rule** can be stated as follows: *When atoms form covalent bonds, they tend to share sufficient electrons so as to achieve an outer shell having eight electrons.*

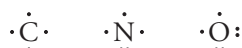
Often, the octet rule can be used to explain the number of covalent bonds an atom forms. This number normally equals the number of electrons the atom must acquire to have a total of eight (an octet) in its outer shell. For instance, the halogens (Group 7A) all have seven valence electrons. The Lewis symbol for a typical member of this group, chlorine, is



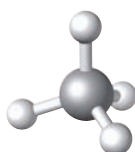
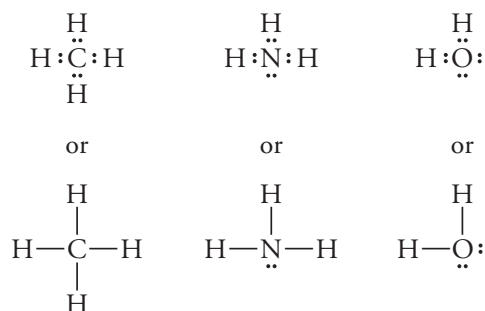
We can see that only one electron is needed to complete its octet. Of course, chlorine can actually gain this electron and become a chloride ion. This is what it does when it forms an ionic compound such as sodium chloride ( $\text{NaCl}$ ). When chlorine combines with another nonmetal, however, the complete transfer of an electron is not energetically favorable. Therefore, in forming such molecules as  $\text{HCl}$  or  $\text{Cl}_2$ , chlorine gets the one electron it needs by forming a covalent bond.



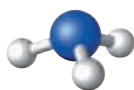
There are many nonmetals that form more than one covalent bond. For example, the three most important elements in biochemical systems are carbon, nitrogen, and oxygen.



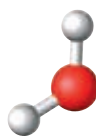
You've already encountered the simplest hydrogen compounds of these elements: methane,  $\text{CH}_4$ , ammonia,  $\text{NH}_3$ , and water,  $\text{H}_2\text{O}$ . Their Lewis structures are



Methane



Ammonia



Water

■ As you will see, it is useful to remember that hydrogen atoms form only one covalent bond.



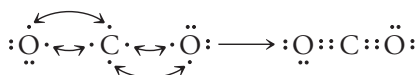
Octet rule and covalent bonding

In the ball-and-stick drawings of the molecules, the “sticks” represent the covalent bonds between the atoms.

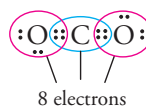
## Multiple Bonds

The bond produced by the sharing of *one* pair of electrons between two atoms is called a **single bond**. So far, these have been the only kind we’ve discussed. There are, however, many molecules in which more than a single pair of electrons are shared between two atoms. For example, we can diagram the formation of the bonds in CO<sub>2</sub> as follows.

■ The arrows here simply indicate how the electrons can combine to form the electron pair bonds in the molecule.



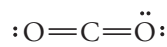
The carbon atom shares two of its valence electrons with one oxygen and two with the other. At the same time, each oxygen shares two electrons with carbon. The result is the formation of two **double bonds**. Notice that in the Lewis formula, both of the shared electron pairs are placed between the symbols for the two atoms joined by the double bond. Once again, if we circle the valence shell electrons that “belong” to each atom, we see that each has an octet.



■ How we place the unshared pairs of electrons around the oxygen is unimportant. Two equally valid Lewis structure for CO<sub>2</sub> are



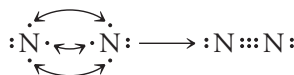
The Lewis structure for CO<sub>2</sub>, using dashes, is



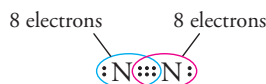
Sometimes three pairs of electrons are shared between two atoms. The most abundant gas in the atmosphere, nitrogen, occurs in the form of diatomic molecules, N<sub>2</sub>. As we’ve seen, the Lewis symbol for nitrogen is



and each nitrogen atom needs three electrons to complete its octet. When the N<sub>2</sub> molecule is formed, each of the nitrogen atoms shares three electrons with the other.



The result is called a **triple bond**. Again, notice that we place all three electron pairs of the bond between the two atoms. We count all of these electrons as though they belong to both of the atoms. Each nitrogen therefore has an octet.



The triple bond is usually represented by three dashes, so the bonding in the N<sub>2</sub> molecule is normally shown as



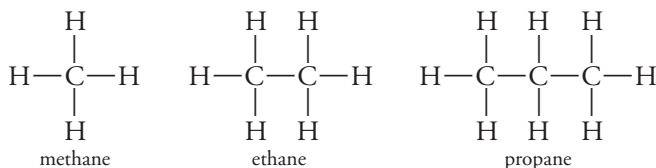


## 9.6 | Covalent Compounds of Carbon

Covalent bonds are found in many of the substances we encounter on a daily basis. Most of them are classified as **organic compounds** in which carbon atoms are covalently bonded to other carbon atoms and to a variety of other nonmetals. They include the foods we eat, the fabrics we wear, the medicines that cure us, the fuels that power vehicles, and the fibers in the rope supporting the mountain climber in the opening photo of this chapter. Because they are so common, organic compounds will be used frequently as examples in our discussions later in the book. For this reason, you will find it helpful to learn something now about their makeup.

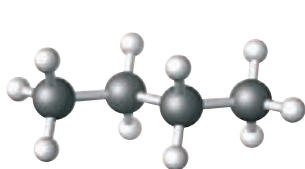
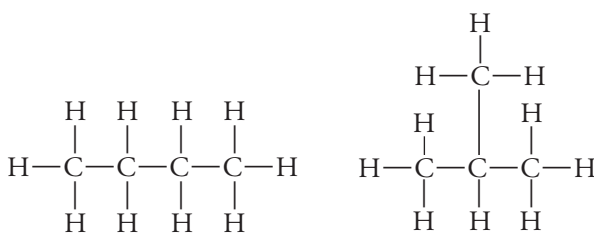
Organic compounds fall into different classes according to the elements that are bonded to carbon and how atoms of those elements are arranged in the molecules. The kinds of compounds we will study in this section will include those in which carbon is bonded to hydrogen, oxygen, and nitrogen. As you learned in Chapter 3, such substances can be considered to be derived from hydrocarbons—compounds of carbon and hydrogen in which the basic molecular “backbones” are composed of carbon atoms linked to one another in a chainlike fashion. (Hydrocarbons themselves are the principal constituents of petroleum.)

*One of the chief features of organic compounds is the tendency of carbon to complete its octet by forming four covalent bonds.* For example, in the alkane series of hydrocarbons (which we described briefly on page 92) all of the bonds are single bonds. The structures of the first three alkanes (methane, ethane, and propane) are

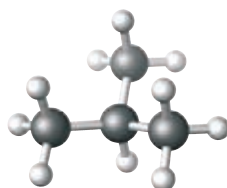
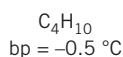
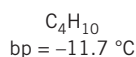


The shapes of their molecules are illustrated as space-filling models in Figure 3.19 on page 93.

When more than four carbon atoms are present, matters become more complex because there is more than one way to arrange the atoms. For example, butane has the formula  $\text{C}_4\text{H}_{10}$ , but there are two ways to arrange the carbon atoms. These two arrangements occur in compounds commonly called butane and isobutane.



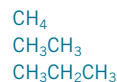
Butane

Methylpropane  
(isobutane)

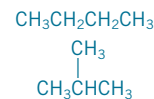
■ If you are also enrolled in a course in biology, you will find some knowledge of organic chemistry useful in understanding that subject as well.

■ A more comprehensive discussion of organic compounds is found in Chapter 23. In this section we look at some simple ways carbon atoms combine with other atoms to form certain important classes of organic substances that we encounter frequently.

■ These structures can be written in a condensed form as

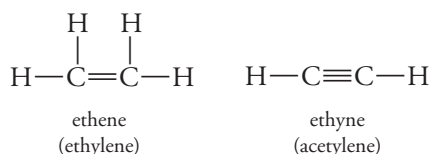


■ Butane and isobutane are said to be isomers of each other. In condensed form, we can write their structures as



Even though they have the same molecular formula, these are actually different compounds with different properties, as you can see from the boiling points listed below their structures. The ability of atoms to arrange themselves in more than one way to give different compounds that have the same molecular formula is called **isomerism** and is discussed more fully in Chapters 22 and 23. The existence of *isomers* is one of the reasons there are so many organic compounds. For example, there are 366,319 different compounds, or isomers, that have the formula  $C_{20}H_{42}$ ; they differ only in the way the carbon atoms are attached to each other.

Carbon can also complete its octet by forming double or triple bonds. The Lewis structures of ethene,  $C_2H_4$ , and ethyne,  $C_2H_2$  (commonly called ethylene and acetylene, respectively) are as follows:<sup>4</sup>

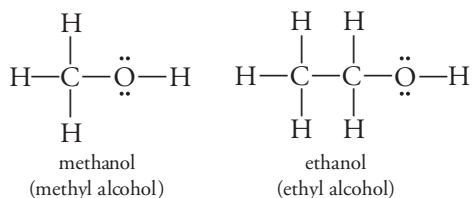


## Compounds That Also Contain Oxygen and Nitrogen

Most organic compounds contain elements in addition to carbon and hydrogen. As we mentioned in Chapter 3, it is convenient to consider such compounds to be derived from hydrocarbons by replacing one or more hydrogens by other groups of atoms. Such compounds can be divided into various families according to the nature of the groups, called **functional groups**, attached to the parent hydrocarbon fragment. Some such families are summarized in Table 9.2, in which the hydrocarbon fragment to which the functional group is attached is symbolized by the letter R.

### Alcohols

In Chapter 3 we noted that alcohols are organic compounds in which one of the hydrogen atoms of a hydrocarbon is replaced by OH. The family name for these compounds is **alcohol**. Examples are methanol (methyl alcohol) and ethanol (ethyl alcohol), which have the following structures:



Some **condensed formulas** that we might write for these are  $CH_3OH$  and  $CH_3CH_2OH$ , or  $CH_3-OH$  and  $CH_3CH_2-OH$ . Methanol is used as a solvent and a fuel; ethanol is found in alcoholic beverages and is blended with gasoline to yield a fuel called E85, containing 85% ethanol.

### Ketones

In alcohols, the oxygen forms two single bonds to complete its octet, just as in water. But oxygen can also form double bonds, as you saw for  $CO_2$ . One family of compounds in which a doubly bonded oxygen replaces a pair of hydrogen atoms is called **ketones**. The



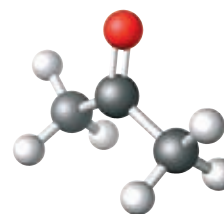
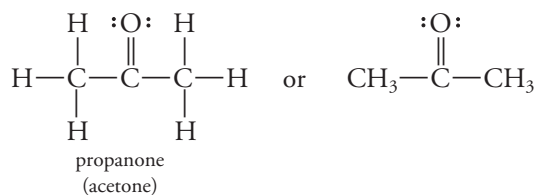
This container of “Canned Heat” contains methanol as the fuel. It is commonly used to heat food at buffets. (*Andy Washmik*)

<sup>4</sup>In the IUPAC system for naming organic compounds, *meth-*, *eth-*, *prop-*, and *but-* indicate carbon chains of 1, 2, 3, and 4 carbon atoms, respectively. Organic nomenclature is discussed more fully in Chapter 23.

Table 9.2 Some Families of Oxygen- and Nitrogen-Containing Organic Compounds		
Family Name	General Formula <sup>a</sup>	Example
Alcohols	$\text{R}-\ddot{\text{O}}-\text{H}$	$\text{CH}_3-\ddot{\text{O}}-\text{H}$ methanol
Aldehydes	$\text{R}-\overset{\text{:O:}}{\parallel}{\text{C}}-\text{H}$	$\text{CH}_3-\overset{\text{:O:}}{\parallel}{\text{C}}-\text{H}$ ethanal (acetaldehyde)
Ketones	$\text{R}-\overset{\text{:O:}}{\parallel}{\text{C}}-\text{R}$	$\text{CH}_3-\overset{\text{:O:}}{\parallel}{\text{C}}-\text{CH}_3$ propanone (acetone)
Acids	$\text{R}-\overset{\text{:O:}}{\parallel}{\text{C}}-\ddot{\text{O}}-\text{H}$	$\text{CH}_3-\overset{\text{:O:}}{\parallel}{\text{C}}-\ddot{\text{O}}-\text{H}$ ethanoic acid (acetic acid)
Amines	$\text{R}-\ddot{\text{N}}\text{H}_2$ $\text{R}-\ddot{\text{N}}\text{H}-\text{R}$ $\text{R}-\ddot{\text{N}}-\text{R}$   R	$\text{CH}_3-\ddot{\text{N}}\text{H}_2$ methylamine

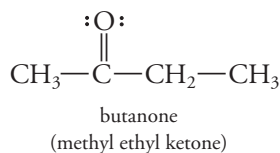
<sup>a</sup>R stands for a hydrocarbon fragment such as  $\text{CH}_3-$  or  $\text{CH}_3\text{CH}_2-$ .

simplest example is propanone, better known as acetone, a solvent often used in nail polish remover.



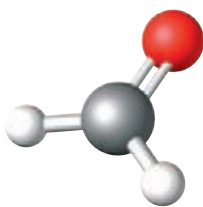
Acetone

Ketones are found in many useful solvents that dissolve various plastics. An example is methyl ethyl ketone.



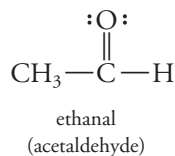
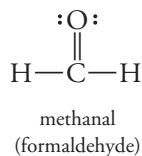
### Aldehydes

Notice that in ketones the carbon bonded to the oxygen is also attached to *two* other carbon atoms. If at least one of the atoms attached to the  $\text{C}=\text{O}$  group (called a **carbonyl group**, pronounced *car-bon-EEL*) is a hydrogen, a different family of compounds is formed



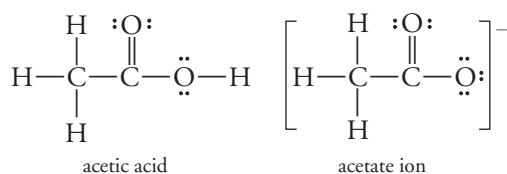
Formaldehyde

called **aldehydes**. Examples are formaldehyde (used to preserve biological specimens, for embalming, and to make plastics) and acetaldehyde (used in the manufacture of perfumes, dyes, plastics, and other products).

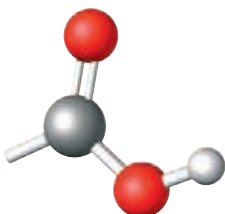


### Organic Acids

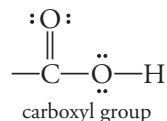
**Organic acids**, also called **carboxylic acids**, constitute another very important family of oxygen-containing organic compounds. An example is acetic acid, which we described in Chapter 5. The shape of the molecule was illustrated in Figure 5.11 (page 165), showing the single hydrogen atom that is capable of ionizing in the formation of  $\text{H}_3\text{O}^+$ . The Lewis structures of acetic acid and the acetate ion are



In general, the structures of organic acids are characterized by the presence of the **carboxyl group**,  $-\text{CO}_2\text{H}$ .



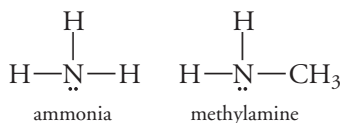
The carboxyl group



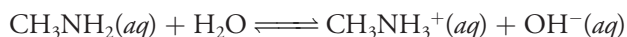
Notice that organic acids have both a doubly bonded oxygen and an OH group attached to the end carbon atom.

### Amines

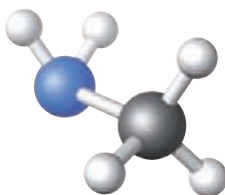
Nitrogen atoms need three electrons to complete an octet, and in most of its compounds, nitrogen forms three bonds. The common nitrogen-containing organic compounds can be imagined as being derived from ammonia by replacing one or more of the hydrogens of  $\text{NH}_3$  with hydrocarbon groups. They're called amines, and an example is methylamine,  $\text{CH}_3\text{NH}_2$ .



Amines are strong-smelling compounds and often have a “fishy” odor. Like ammonia, they're weakly basic.<sup>5</sup>

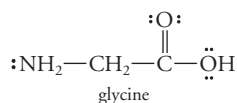


As we noted in Chapter 5, the  $\text{H}^+$  that is added to an amine becomes attached to the nitrogen atom.

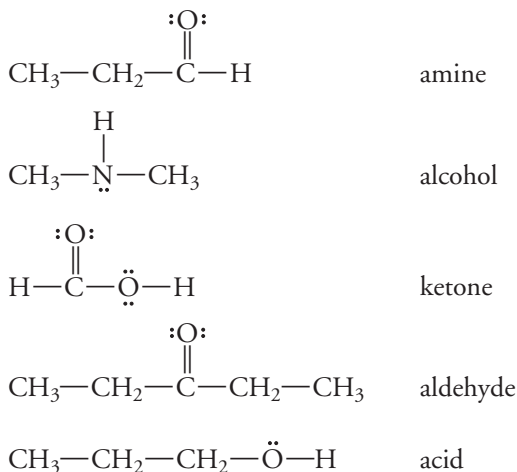


Methylamine

<sup>5</sup>Amino acids, which are essential building blocks of proteins in our bodies, contain both an amine group ( $-\text{NH}_2$ ) and a carboxyl group ( $-\text{CO}_2\text{H}$ ). The simplest of these is the amino acid glycine,



**9.6** | Match the structural formulas on the left with the correct names of the families of organic compounds to which they belong.



**9.7** | The following questions apply to the compounds in Practice Exercise 9.6. (a) Which produces a basic solution in water? (b) Which produces an acidic aqueous solution? (c) For the acid, what is the Lewis structure of the anion formed when it is neutralized?

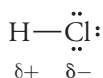
## Practice Exercises

## 9.7 | Bond Polarity and Electronegativity

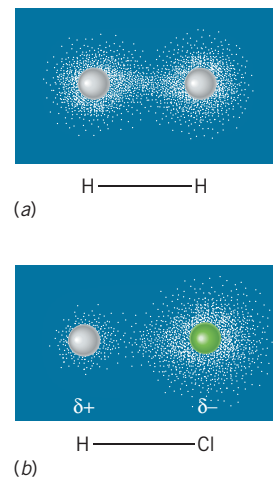
When two identical atoms form a covalent bond, as in  $\text{H}_2$  or  $\text{Cl}_2$ , each atom has an equal share of the bond's electron pair. The electron density at both ends of the bond is the same, because the electrons are equally attracted to both nuclei. However, when different kinds of atoms combine, as in  $\text{HCl}$ , one nucleus usually attracts the electrons in the bond more strongly than the other.

### Polar and Nonpolar Bonds

The result of unequal attractions for the bonding electrons is an unbalanced distribution of electron density within the bond. For example, chlorine atoms have a greater attraction for electrons in a bond than do hydrogen atoms. In the  $\text{HCl}$  molecule, therefore, the electron cloud is pulled more tightly around the  $\text{Cl}$ , and that end of the molecule experiences a slight buildup of negative charge. The electron density that shifts toward the chlorine is removed from the hydrogen, which causes the hydrogen end to acquire a slight positive charge. These charges are less than full  $1+$  and  $1-$  charges and are called **partial charges**, which are usually indicated by the lowercase Greek letter delta,  $\delta$  (see Figure 9.8). Partial charges can also be indicated on Lewis structures. For example,



A bond that carries partial positive and negative charges on opposite ends is called a **polar covalent bond**, or often simply a **polar bond** (the word *covalent* is understood). The term *polar* comes from the notion of *poles* of equal but opposite charge at either end of the bond. Because *two poles* of electric charge are involved, the bond is said to be an **electric dipole**.



**Figure 9.8 | Equal and unequal sharing of electrons in a covalent bond.** Each of the diagrams illustrates the distribution of electron density of the shared electron pair in a bond. (a) In  $\text{H}_2$ , the electron density in the bond is spread equally over both atoms. (b) In  $\text{HCl}$ , more than half of the electron density of the bond is concentrated around chlorine, causing opposite ends of the bond to carry partial electrical charges.

The polar bond in HCl causes the molecule as a whole to have opposite charges on either end, so the HCl molecule as a whole is an electric dipole. We say that HCl is a **polar molecule**. The magnitude of its polarity is expressed quantitatively by its **dipole moment** (symbol  $\mu$ ), which is equal to the amount of charge on either end of the molecule,  $q$ , multiplied by the distance between the charges,  $r$ .



Dipole moment

$$\mu = q \times r \quad (9.2)^6$$

Table 9.3 lists the dipole moments and bond lengths for some diatomic molecules. The dipole moments are reported in **debye** units (symbol D), where  $1 \text{ D} = 3.34 \times 10^{-30} \text{ C m}$  (coulomb  $\times$  meter).

By separate experiments, it is possible to measure both  $\mu$  and  $r$  (which corresponds to the bond length in a diatomic molecule such as HCl). Knowledge of  $\mu$  and  $r$  makes it possible to calculate the amount of charge on opposite ends of the dipole. For HCl, such calculations show that  $q$  equals  $0.17$  electronic charge units, which means the hydrogen carries a charge of  $+0.17e^-$  and the chlorine a charge of  $-0.17e^-$ .

One of the main reasons we are concerned about whether a molecule is polar or not is because many physical properties, such as melting point and boiling point, are affected by it. This is because polar molecules attract each other more strongly than do nonpolar molecules. The positive end of one polar molecule attracts the negative end of another. The strength of the attraction depends on both the amount of charge on either end of the molecule and the distance between the charges; in other words, it depends on the molecule's dipole moment.

Table 9.3

Dipole Moments and Bond Lengths for Some Diatomic Molecules<sup>a</sup>

Compound	Dipole Moment (D)	Bond Length (pm)
HF	1.83	91.7
HCl	1.09	127
HBr	0.82	141
HI	0.45	161
CO	0.11	113
NO	0.16	115

<sup>a</sup>Source: National Institute of Standards and Technology.

## Example 9.5

### Calculating the Charge on the End of a Polar Molecule

The HF molecule has a dipole moment of 1.83 D and a bond length of 91.7 pm. What is the amount of charge, in electronic charge units, on either end of the bond?

■ **Analysis:** This is going to involve substituting values into Equation 9.2. However, to answer the problem correctly, we will have to be especially careful of the units. The debye has charge expressed in coulombs, but we have to express the answer in electronic charge units.

■ **Assembling the Tools:** The primary tool for solving the problem is Equation 9.2. In the calculation we are also going to have to convert between coulombs (C) and electronic charge units. From the table on the inside rear cover of the book we find that the charge on an electron (i.e., an electronic charge unit) equals  $1.602 \times 10^{-19} \text{ C}$ , which we can express as

$$1 e^- \Leftrightarrow 1.602 \times 10^{-19} \text{ C}$$

■ **Solution:** We will solve Equation 9.2 for  $q$ .

$$q = \frac{\mu}{r}$$

The debye unit,  $\text{D} = 3.34 \times 10^{-30} \text{ C m}$ , so the dipole moment of HF is

$$\mu = (1.83 \cancel{\text{D}}) (3.34 \times 10^{-30} \text{ C m}/\cancel{\text{D}}) = 6.11 \times 10^{-30} \text{ C m}$$

<sup>6</sup>Once again, we're using the symbol  $q$  to mean electric charge, not heat as in Chapter 7.

The SI prefix p (pico) means  $\times 10^{-12}$ , so the bond length  $r = 91.7 \times 10^{-12}$  m. Substituting in the equation above gives

$$q = \frac{6.11 \times 10^{-30} \text{ C} \cdot \cancel{\text{m}}}{91.7 \times 10^{-12} \cancel{\text{m}}} = 6.66 \times 10^{-20} \text{ C}$$

The value of  $q$  in electronic charge units is therefore

$$q = 6.66 \times 10^{-20} \cancel{\text{C}} \times \left( \frac{1 e^-}{1.602 \times 10^{-19} \cancel{\text{C}}} \right) = 0.416 e^-$$

As in HCl, the hydrogen carries the positive charge, so the charge on the hydrogen end of the molecule is  $+0.416 e^-$  and the charge on the fluorine end is  $-0.416 e^-$ .

■ **Is the Answer Reasonable?** If we look at the units, we see that they cancel correctly, so that gives us confidence that we've done the calculation correctly. The fact that our answer is between zero and one electronic charge unit, and therefore a partial electrical charge, further suggests we've solved the problem correctly.

**9.8** | The chlorine end of the chlorine monoxide molecule carries a charge of  $+0.167 e^-$ . The bond length is 154.6 pm. Calculate the dipole moment of the molecule in debye units. (*Hint:* Be sure to convert the charge to coulombs.)

**9.9** | Although isolated  $\text{Na}^+$  and  $\text{Cl}^-$  ions are unstable, these ions can exist in the gaseous state as *ion pairs*. An ion pair consists of an NaCl unit in which the bond length is 236 pm. The dipole moment of the ion pair is 9.00 D. What are the actual amounts of charge on the sodium and chlorine atoms in this NaCl pair? What percentage of full  $1+$  and  $1-$  charges are these? (This is the *percentage ionic character* in the NaCl pair.)

## Practice Exercises

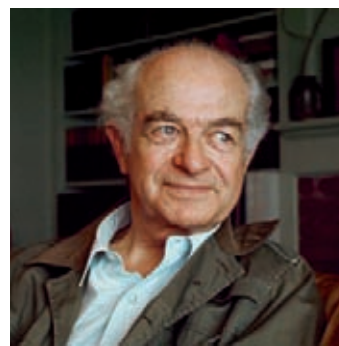
## Electronegativity

The degree to which a covalent bond is polar depends on the difference in the abilities of the bonded atoms to attract electrons. The greater the difference, the more polar the bond, and the more the electron density is shifted toward the atom that attracts electrons more.

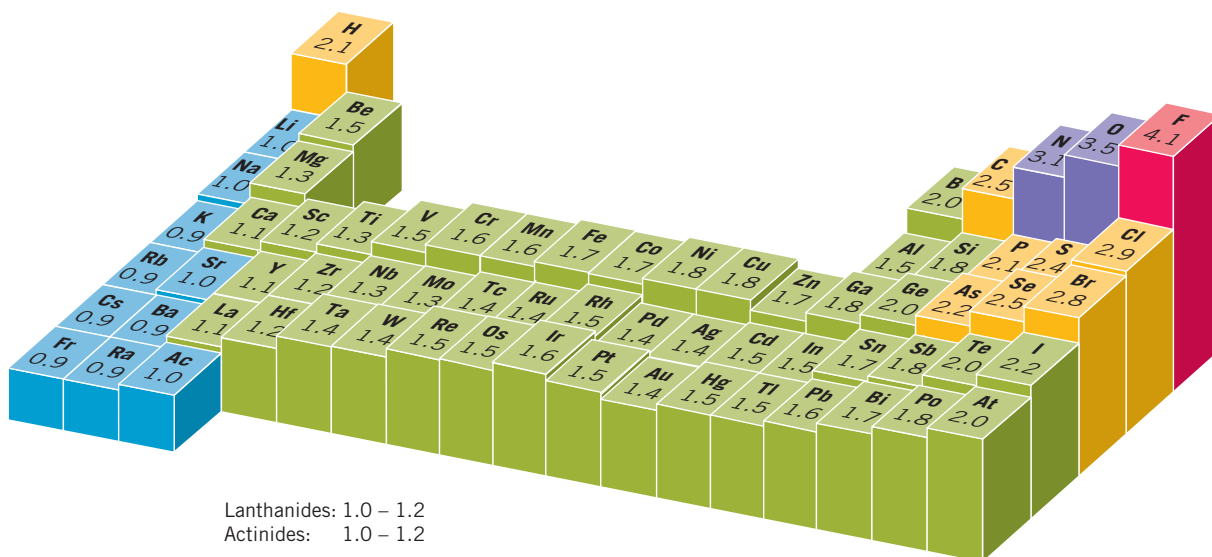
The term that we use to describe the attraction an atom has for the electrons in a bond is called **electronegativity**. In HCl, for example, chlorine is *more electronegative* than hydrogen. This causes the electron pair of the covalent bond to spend more of its time around the more electronegative atom, which is why the Cl end of the bond acquires a partial negative charge.

The first scientist to develop numerical values for electronegativity was Linus Pauling (1901–1994). He observed that polar bonds have a bond energy larger than would be expected if the opposite ends of the bonds were electrically neutral. Pauling reasoned that the extra bond energy is caused by the attraction between the partial charges on opposite ends of the bond. By estimating the extra bond energy, he was able to develop a scale of electronegativities for the elements. Other scientists have used different approaches to measuring electronegativities, with similar results.

A set of numerical values for the electronegativities of the elements is shown in Figure 9.9. These data are useful because the *difference* in electronegativity provides an estimate of the degree of polarity of a bond. For instance, the data tell us fluorine is more electronegative than chlorine, so we expect HF to be more polar than HCl. (This is confirmed by the larger dipole moment of the HF molecule.) In addition, the relative magnitudes of the electronegativities indicate which ends of a bond carry the partial positive and negative charges. Thus, hydrogen is less electronegative than

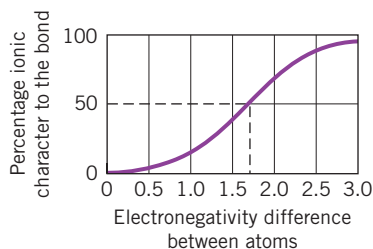
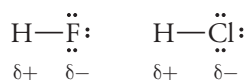


Linus Pauling (1901–1994) contributed greatly to our understanding of chemical bonding. He was the winner of two Nobel Prizes, in 1954 for chemistry and in 1962 for peace. (Ted Streshinsky/© Corbis)



**Figure 9.9 | The electronegativities of the elements.** The noble gases are assigned electronegativities of zero and are omitted from the table.

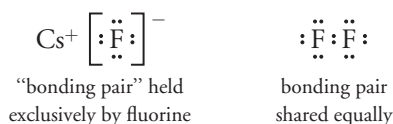
either fluorine or chlorine, so in both of these molecules the hydrogen bears the partial positive charge.



**Figure 9.10 | Variation in the percentage ionic character of a bond with electronegativity difference.**

The bond becomes about 50% ionic when the electronegativity difference equals 1.7, which means that the atoms in the bond carry a partial charge of approximately  $\pm 0.5 e^-$ .

By studying electronegativity values and their differences we find that there is no sharp dividing line between ionic and covalent bonding. Ionic bonding and *nonpolar covalent bonding* simply represent the two extremes. A bond is mostly ionic when the difference in electronegativity between two atoms is very large; the more electronegative atom acquires essentially complete control of the bonding electrons. In a **nonpolar covalent bond**, there is no difference in electronegativity, so the pair of bonding electrons is shared equally.



The degree to which the bond is polar, which we might think of as the amount of **ionic character** of the bond, varies in a continuous way with changes in the electronegativity difference (Figure 9.10). The bond becomes more than 50% ionic when the electronegativity difference exceeds approximately 1.7.

## Practice Exercises

**9.10** | Bromine and chlorine form a molecular substance with the formula BrCl. Is the bond polar? If so, which atom carries the partial negative charge? (*Hint*: Compare electronegativities.)

**9.11** | For each of the following bonds, choose the atom that carries the partial negative charge. Arrange them in order of increasing bond polarity: (a) P—Br, (b) Si—Cl, (c) S—Cl.



## Periodic Trends in Electronegativity

An examination of Figure 9.9 reveals that within the periodic table, *electronegativity increases from bottom to top in a group, and from left to right in a period*. These trends follow those for ionization energy (IE); an atom that has a small IE will lose an electron more easily than an atom with a large IE, just as an atom with a small electronegativity will lose its share of an electron pair more readily than an atom with a large electronegativity.

Elements located in the same region of the table (for example, the nonmetals) have similar electronegativities, which means that if they form bonds with each other, the electronegativity differences will be small and the bonds will be more covalent than ionic. On the other hand, if elements from widely separated regions of the table combine, large electronegativity differences occur and the bonds will be predominantly ionic. This is what happens, for example, when an element from Group 1A or Group 2A reacts with a nonmetal from the upper right-hand corner of the periodic table.



Periodic trends in electronegativity

■ It is found that the electronegativity is proportional to the average of the ionization energy and the electron affinity of an element.

## Reactivities of the Elements and Electronegativity

There are parallels between an element's electronegativity and its **reactivity**—its tendency to undergo redox reactions.

### Reactivities of Metals Relate to Their Ease of Oxidation

In nearly every compound containing a metal, the metal exists in a positive oxidation state. Therefore, for a metal, *reactivity* relates to how easily the metal is oxidized. For example, a metal like sodium, which is very easily oxidized, is said to be very reactive, whereas a metal like platinum, which is very difficult to oxidize, is said to be unreactive.

There are several ways to compare how easily metals are oxidized. In Chapter 6 we saw that by comparing the abilities of metals to displace each other from compounds we are able to establish their relative ease of oxidation. This was the basis for the activity series (Table 6.3).

Figure 9.11 illustrates how the ease of oxidation (reactivity) of metals varies in the periodic table. In general, these trends roughly follow the variations in electronegativity, with the metal being less easily oxidized as its electronegativity increases. You might expect this, because electronegativity is a measure of how strongly the atom of an element attracts electrons when combining with an atom of a different element. The more strongly the atom attracts electrons, the more difficult it is to oxidize. This relationship between reactivity and electronegativity is only approximate, however, because many other factors affect the stability of the compounds that are formed.

■ *Reactivity* refers in general to the tendency of a substance to react with something. The *reactivity of a metal* refers to its tendency specifically to undergo oxidation.



Trends in the reactivity of metals in the periodic table

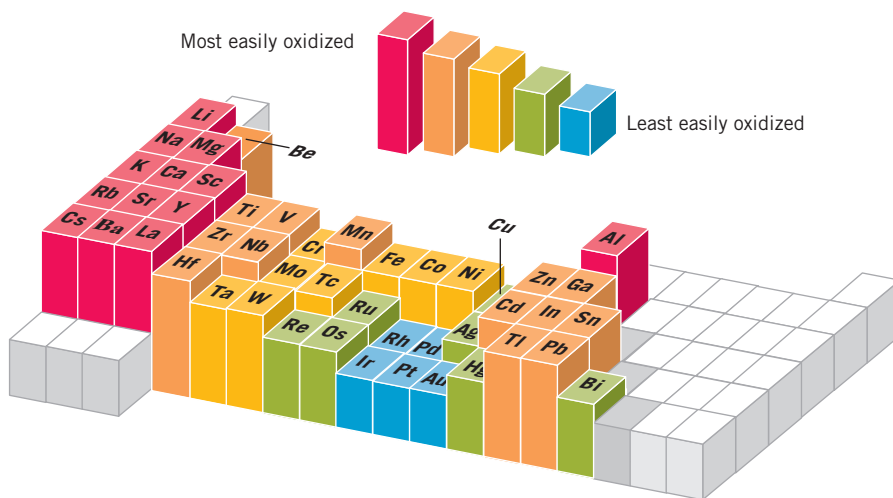


Figure 9.11 | Variations in the ease of oxidation of metals.

### Elements of Groups 1A and 2A

In Figure 9.11, we see that the metals that are most easily oxidized are found at the far left in the periodic table. These are elements with very low electronegativities. The metals in Group 1A, for example, are so easily oxidized that all of them react with water to liberate hydrogen. Because of their reactivity toward moisture and oxygen, they have no useful applications that require exposure to the atmosphere, so we rarely encounter them as free metals. The same is true of the heavier metals in Group 2A, calcium through barium. These elements also react with water to liberate hydrogen. In Figure 9.9 we see that electronegativity decreases going down a group, which explains why the heavier elements in Group 2A are more reactive than those at the top of the group.

### Noble Metals

In Figure 9.11 we can also locate the metals that are the most difficult to oxidize. They occur for the most part among the heavier transition elements in the center of the periodic table. Here we find the elements platinum and gold, which are sometimes called **noble metals** because of their extremely low degree of reactivity. Their bright luster and lack of any tendency to corrode in air or water combine to make them particularly attractive for use in fine jewelry. Their lack of reactivity also is responsible for their industrial uses. Gold, for example, is used to coat the electrical contacts in low-voltage circuits found in microcomputers, because even a small amount of corrosion on a more reactive metal would be sufficient to impede the flow of electricity so much as to make the devices unreliable.



This statue of Prometheus overlooking the skating rink in Rockefeller Center in New York City is covered in a thin layer of gold, providing both beauty and weather resistance. (*Philipus/Alamy*)



Trends in the reactivity of nonmetals in the periodic table

#### Fluorine:



#### Chlorine:



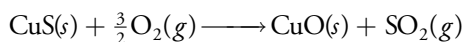
#### Bromine:



### The Oxidizing Power of Nonmetals

The reactivity of a nonmetal is determined by its ease of reduction, and therefore its ability to serve as an oxidizing agent. This ability also varies according to the element's electronegativity. Nonmetals with high electronegativities have strong tendencies to acquire electrons and are therefore strong oxidizing agents. In parallel with changes in electronegativities in the periodic table, *the oxidizing abilities of nonmetals increase from left to right across a period and from bottom to top in a group*. Thus, the most powerful oxidizing agent is fluorine, followed closely by oxygen, both of which appear in the upper right-hand corner of the periodic table.

Single replacement reactions (also called **displacement reactions**) occur among the nonmetals, just as with the metals (which you studied in Chapter 6). For example, heating a metal sulfide in oxygen causes the sulfur to be replaced by oxygen. The displaced sulfur then combines with additional oxygen to give sulfur dioxide. The equation for a typical reaction is



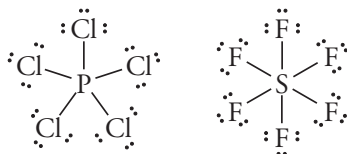
Displacement reactions are especially evident among the halogens, where a particular halogen in its elemental form will oxidize the *anion* of any halogen below it in Group 7A, as illustrated in the margin. Thus,  $\text{F}_2$  will oxidize  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ;  $\text{Cl}_2$  will oxidize  $\text{Br}^-$  and  $\text{I}^-$ , but not  $\text{F}^-$ ; and  $\text{Br}_2$  will oxidize  $\text{I}^-$ , but not  $\text{F}^-$  or  $\text{Cl}^-$ .

## 9.8 | Lewis Structures

In Section 9.5 we introduced you to Lewis structures and we have used them to describe various molecules, all of which obey the octet rule. Examples included  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{N}_2$ , as well as a variety of organic compounds.

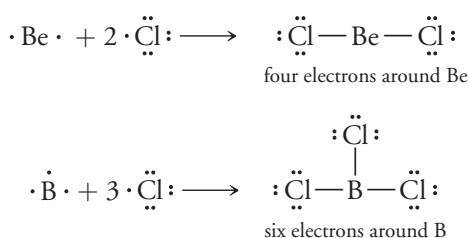
Lewis structures are very useful in chemistry because they give us a relatively simple way to describe the structures of molecules. As a result, much chemical reasoning is based on them. In fact, in Chapter 10 you will learn how to use Lewis structures to make reasonably accurate predictions about the shapes of molecules. In this section we will develop a simple method for drawing Lewis structures for both molecules and polyatomic ions (which are also held together by covalent bonds).

Although the octet rule is important in covalent bonding, it is not always obeyed. For instance, there are some molecules in which one or more atoms must have more than an octet in the valence shell. Examples are  $\text{PCl}_5$  and  $\text{SF}_6$ , whose Lewis structures are



In these molecules the formation of more than four bonds to the central atom requires that the central atom have a share of more than eight electrons.

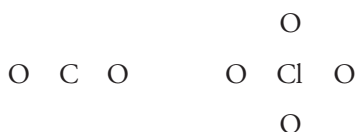
There are also some molecules (but not many) in which the central atom behaves as though it has less than an octet. The most common examples involve compounds of beryllium and boron.



Although Be and B sometimes have less than an octet, *the elements in Period 2 never exceed an octet*. The reason is because their valence shells, having  $n = 2$ , can hold a maximum of only 8 electrons. (This explains why the octet rule works so well for atoms of carbon, nitrogen, and oxygen.) However, elements in periods below Period 2, such as phosphorus and sulfur, sometimes do exceed an octet, because their valence shells can hold more than 8 electrons. For example, the valence shell for elements in Period 3, for which  $n = 3$ , could hold a maximum of 18 electrons, and the valence shell for Period 4 elements, which have  $s$ ,  $p$ ,  $d$ , and  $f$  subshells, could theoretically hold as many as 32 electrons.

## A Procedure for Drawing Lewis Structures

Figure 9.12 outlines a series of steps that provides a systematic method for drawing Lewis structures. The first step is to decide which atoms are bonded to each other, so that we know where to put the dots or dashes. This is not always a simple matter. Many times the formula suggests the way the atoms are arranged because the central atom, which is usually the least electronegative one, is usually written first. Examples are  $\text{CO}_2$  and  $\text{ClO}_4^-$ , which have the following **skeletal structures** (i.e., arrangements of atoms):



Sometimes, obtaining the skeletal structure is not quite so simple, especially when more than two elements are present. Some generalizations are possible, however. For example, the skeletal structure of nitric acid,  $\text{HNO}_3$ , is

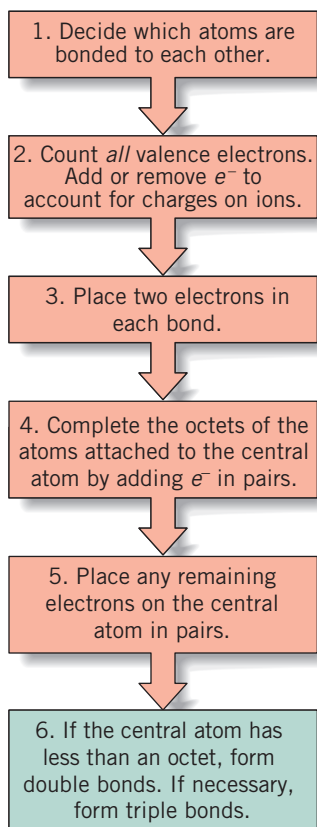


■ Lewis structures just describe which atoms are bonded to each other and the kinds of bonds involved. Thus, the Lewis structure for water can be drawn as  $\text{H}-\ddot{\text{O}}-\text{H}$ , but it does not mean the water molecule is linear, with all the atoms in a straight line. Actually, water isn't linear; the two  $\text{O}-\text{H}$  bonds form an angle of about  $104^\circ$ .

■ Although beryllium is a metal, many of its compounds are not ionic. Pure  $\text{BeCl}_2$  is molecular with covalent  $\text{Be}-\text{Cl}$  bonds.



Method for drawing Lewis structures



**Figure 9.12 | Summary of the steps in drawing a Lewis structure.** If you follow these steps, you will obtain a Lewis structure in which the octet rule is obeyed by the maximum number of atoms.

rather than one of the following:



Nitric acid is an oxoacid (Section 5.4), and it happens that the hydrogen atoms that can be released from molecules of oxoacids are always bonded to oxygen atoms, which are in turn bonded to the third nonmetal atom. Therefore, recognizing  $\text{HNO}_3$  as the formula of an oxoacid allows us to predict that the three oxygen atoms are bonded to the nitrogen, and the hydrogen is bonded to one of the oxygens. (It is also useful to remember that hydrogen forms only one bond, so we should not choose it to be a central atom.)

There are times when no reasonable basis can be found for choosing a particular skeletal structure. If you must make a guess, choose the most symmetrical arrangement of atoms, because it has the greatest chance of being correct.

After you've decided on the skeletal structure, the next step is to count all of the *valence electrons* to find out how many dots must appear in the final formula. Using the periodic table, locate the groups in which the elements in the formula occur to determine the number of valence electrons contributed by each atom. If the structure you wish to draw is that of an ion, *add one additional valence electron for each negative charge or remove a valence electron for each positive charge*. Some examples are as follows:

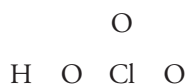
$\text{SO}_3$	Sulfur (Group 6A) contributes $6e^-$ . Each oxygen (Group 6A) contributes $6e^-$ .	$1 \times 6 = 6e^-$ $3 \times 6 = 18e^-$ <hr/> Total $24e^-$
$\text{ClO}_4^-$	Chlorine (Group 7A) contributes $7e^-$ . Each oxygen (Group 6A) contributes $6e^-$ . Add $1e^-$ for the $1-$ charge.	$1 \times 7 = 7e^-$ $4 \times 6 = 24e^-$ $+1e^-$ <hr/> Total $32e^-$
$\text{NH}_4^+$	Nitrogen (Group 5A) contributes $5e^-$ . Each hydrogen (Group 1A) contributes $1e^-$ . Subtract $1e^-$ for the $1+$ charge.	$1 \times 5 = 5e^-$ $4 \times 1 = 4e^-$ $-1e^-$ <hr/> Total $8e^-$

After we have determined the number of valence electrons, we place them into the skeletal structure in pairs following the steps outlined in Figure 9.12. Let's look at some examples of how we go about this.

## Example 9.6 Drawing Lewis Structures

What is the Lewis structure of the chloric acid molecule,  $\text{HClO}_3$ ?

■ **Analysis:** The first step is to select a reasonable skeletal structure. Because the substance is an oxoacid, we can expect the hydrogen to be bonded to an oxygen, which in turn is bonded to the chlorine. The other two oxygens would also be bonded to the chlorine. This gives

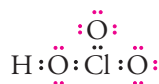


■ **Assembling the Tools:** Our tool is the procedure outlined in Figure 9.12.

■ **Solution:** The total number of valence electrons is 26 ( $1e^-$  from H,  $6e^-$  from each O, and  $7e^-$  from Cl). To distribute the electrons, we start by placing a pair of electrons in each bond, because we know that there must be at least one pair of electrons between each pair of atoms.



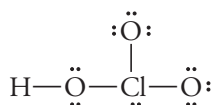
This has used  $8e^-$ , so we still have  $18e^-$  to go. Next, we work on the atoms surrounding the chlorine (which is the central atom in this structure). No additional electrons are needed around the H, because  $2e^-$  are all that can occupy its valence shell. Therefore, we next complete the octets of the oxygens, which uses 16 more electrons.



We have now used a total of  $24e^-$ , so there are two electrons left. “Left-over” electrons are always placed on the central atom in pairs (the Cl atom, in this case). This gives



which we can also write as follows, using dashes for the electron pairs in the bonds:



The chlorine and the three oxygens have octets, and the valence shell of hydrogen is complete with  $2e^-$ , so we are finished.

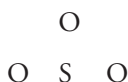
■ **Is the Answer Reasonable?** The most common error is to have either too many or too few valence electrons in the structure, so that’s always the best place to begin your check. Doing this will confirm that the number of  $e^-$  is correct.

■ The valence shell of hydrogen contains only the 1s subshell, which can hold a maximum of two electrons. This means hydrogen can have a share of only two electrons and can form just one covalent bond.

## Example 9.7 Drawing Lewis Structures

Draw the Lewis structure for the  $\text{SO}_3$  molecule.

■ **Analysis:** Sulfur is less electronegative than oxygen and it is written first in the formula, so we expect it to be the central atom, surrounded by the three O atoms. This gives the skeletal structure



■ **Assembling the Tools:** We follow the procedure in Figure 9.12.

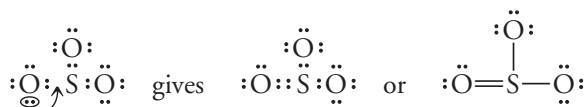
■ **Solution:** The total number of electrons in the formula is 24 ( $6e^-$  from the sulfur, plus  $6e^-$  from each oxygen). We begin to distribute the electrons by placing a pair in each bond. This gives



We have used  $6e^-$ , so there are  $18e^-$  left. We next complete the octets around the oxygens, which uses the remaining electrons.



At this point all of the electrons have been placed into the structure, but we see that the sulfur has only six electrons around it. We cannot simply add more dots because the total must be 24. Therefore, according to the last step of the procedure in Figure 9.12, we have to create a multiple bond. *To do this we move a pair of electrons that we have shown to belong solely to an oxygen into a sulfur–oxygen bond so that it can be counted as belonging to both the oxygen and the sulfur.* In other words, we place a double bond between sulfur and one of the oxygens. It doesn't matter which oxygen we choose for this honor.



Notice that each atom has an octet.

■ **Is the Answer Reasonable?** The key step in completing the structure is recognizing what we have to do to obtain an octet around the sulfur. We have to add more electrons to the valence shell of sulfur, but without removing them from any of the oxygen atoms. By forming the double bond, we accomplish this. A quick check also confirms that we've placed exactly the correct number of valence electrons into the structure.

## Example 9.8 Drawing Lewis Structures

What is the Lewis structure for the ion  $\text{IF}_4^-$ ?

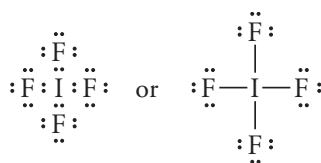
■ **Analysis:** Iodine is less electronegative than fluorine and is first in the formula, so we can anticipate that iodine will be the central atom. Our skeletal structure is



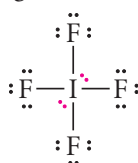
■ **Assembling the Tools:** As before, we follow the procedure in Figure 9.12. We begin by counting valence electrons, remembering to add an extra electron to account for the negative charge. Then we distribute the electrons in pairs.

■ **Solution:** The iodine and fluorine atoms are in Group 7A and each contribute 7 electrons, for a total of  $35e^-$ . The negative charge requires one additional electron to give a total of  $36e^-$ .

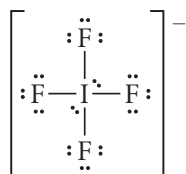
First we place  $2e^-$  into each bond, and then we complete the octets of the fluorine atoms. This uses 32 electrons.



There are four electrons left, and according to Step 5 in Figure 9.12 they are placed on the central atom as *pairs* of electrons. This gives



The last step is to add brackets around the formula and write the charge outside as a superscript.



■ **Is the Answer Reasonable?** We can recount the valence electrons, which tells us we have the right number of them, and all are in the Lewis structure. Each fluorine atom has an octet, which is proper. Notice that we have placed the “left-over” electrons onto the central atom. This gives iodine more than an octet, but that’s okay because iodine is not a Period 2 element.

**9.12** | Predict a reasonable skeletal structure for  $\text{H}_2\text{PO}_4^-$  and determine the number of valence electrons that should be in its Lewis structure. (*Hint:* It’s an ion derived from an oxoacid.)

**9.13** | Predict reasonable skeletal structures for  $\text{SO}_2$ ,  $\text{NO}_3^-$ ,  $\text{HClO}_3$ , and  $\text{H}_3\text{AsO}_4$ .

**9.14** | How many valence electrons should appear in the Lewis structures of  $\text{SO}_2$ ,  $\text{SeO}_4^{2-}$ , and  $\text{NO}^+$ ?

**9.15** | Draw Lewis structures for  $\text{OF}_2$ ,  $\text{NH}_4^+$ ,  $\text{SO}_2$ ,  $\text{NO}_3^-$ ,  $\text{ClF}_3$ , and  $\text{HClO}_4$ .

## Practice Exercises

## Formal Charges and Lewis Structures

Lewis structures are meant to describe how atoms share electrons in chemical bonds. Such descriptions are theoretical explanations or predictions that relate to the forces that hold molecules and polyatomic ions together. But, as you learned in Chapter 1, a theory is only as good as the observations on which it is based, so to have confidence in a theory about chemical bonding, we need to have a way to check it. We need experimental observations that relate to the description of bonding.

### Bond Properties That Depend on Bond Order

To compare bonds between the same two elements, it’s useful to define a quantity called the **bond order**, which is the number of electron pairs shared between two atoms. Thus, a single bond has a bond order of one, a double bond a bond order of two, and a triple bond a bond order of three.

Two properties that are related to the bond order are *bond length*, the distance between the nuclei of the bonded atoms, and *bond energy*, the energy required to separate the bonded atoms to give neutral particles. For example, we mentioned in Section 9.5 that measurements have shown the  $\text{H}_2$  molecule has a bond length of 75 pm and a bond

**Table 9.4** Average Bond Lengths and Bond Energies Measured for Carbon–Carbon Bonds

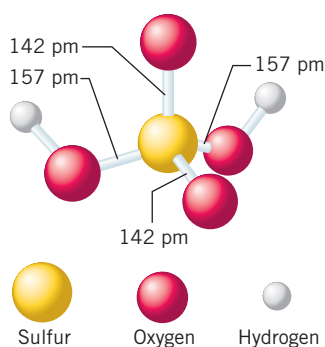
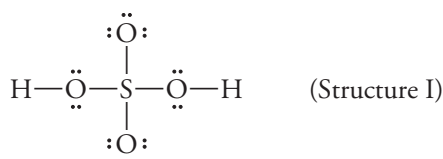
Bond	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	154	348
C=C	134	615
C≡C	120	812



Correlation between bond properties and bond order

As the bond order increases, the bond length decreases and the bond energy increases, provided we are comparing bonds between the same elements.

With this as background, let's examine the Lewis structure of sulfuric acid, drawn according to the procedure given in Figure 9.12.

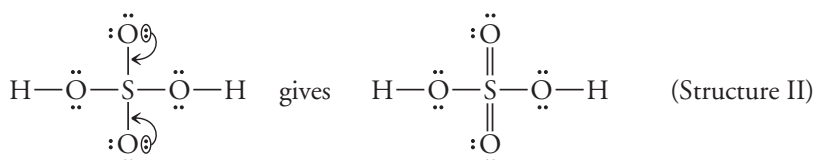


**Figure 9.13** | The structure of sulfuric acid in the vapor state.

Notice the difference in the sulfur–oxygen bond lengths.

It obeys the octet rule, and there doesn't seem to be any need to attempt to write any other structures for it. But a problem arises if we compare the predicted bond lengths with those found experimentally. In our Lewis structure, all four sulfur–oxygen bonds are shown as single bonds, which means they should have about the same bond lengths. However, experimentally it has been found that the bonds are not of equal length, as illustrated in Figure 9.13. The S—O bonds are shorter than the S—OH bonds, which means they must have a larger bond order. Therefore, we need to modify our Lewis structure to make it conform to reality.

Because sulfur is in Period 3, its valence shell has  $3s$ ,  $3p$ , and  $3d$  subshells, which together can accommodate more than eight electrons. Therefore, sulfur is able to form more than four bonds, so we are allowed to increase the bond order in the S—O bonds by moving electron pairs to create sulfur–oxygen double bonds as follows:



Now we have a Lewis structure that better fits experimental observations because the sulfur–oxygen double bonds are expected to be shorter than the sulfur–oxygen single bonds. Because this second Lewis structure agrees better with the actual structure of the molecule, it is the *preferred* Lewis structure, even though it violates the octet rule.

### Assigning Formal Charges to Atoms

Are there any criteria that we could have applied that would have allowed us to predict that the second Lewis structure for  $\text{H}_2\text{SO}_4$  is better than the one with only single bonds, even though it seems to violate the octet rule unnecessarily? To answer this question, let's take a closer look at the two Lewis structures we've drawn.

In Structure I, there are only single bonds between the sulfur and oxygen atoms. If the electrons in the bonds are shared equally by S and O, then each atom "owns" half of the electron pair, or the equivalent of one electron. In other words, the four single bonds place the equivalent of four electrons in the valence shell of the sulfur. An isolated single atom of sulfur, however, has six valence electrons, so in Structure I the sulfur appears to have two electrons *less* than it does as just an isolated atom. Thus, at least in a *bookkeeping* sense, it

energy of 435 kJ/mol, which means that it takes 435 kJ to break the bonds of 1 mol of  $\text{H}_2$  molecules to give 2 mol of hydrogen atoms.

Bond order is a measure of the amount of electron density in the bond, and the greater the electron density, the more tightly the nuclei are held and the more closely they are drawn together. This is illustrated by the data in Table 9.4, which gives typical bond lengths and bond energies for single, double, and triple bonds between carbon atoms. In summary:



would appear that if sulfur obeyed the octet rule in  $\text{H}_2\text{SO}_4$ , it would have a charge of  $2+$ . This *apparent* charge on the sulfur atom is called its **formal charge**.

Notice that in defining formal charge, we've stressed the word "apparent." *The formal charge arises because of the bookkeeping we've done and should not be confused with whatever the actual charge is on an atom in the molecule.* (The situation is somewhat similar to the oxidation numbers you learned to assign in Chapter 6, which are artificial charges assigned according to a set of rules.) Here's how formal charges are assigned.

■ The actual charges on the atoms in a molecule are determined by the relative electronegativities of the atoms.

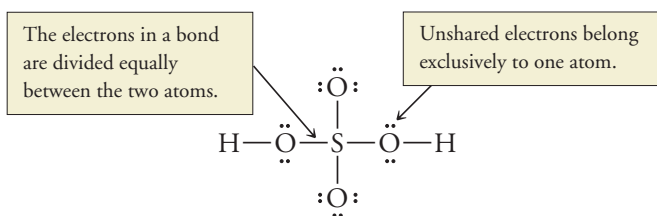


Calculating formal charges

### Calculating the Formal Charge on Atoms in a Lewis Structure

1. For each atom, write down the number of valence electrons in an isolated atom of the element.
2. Using the Lewis structure, add up the valence electrons that "belong to" the atom in the molecule or ion, and then subtract this total from the value in Step 1. The result is the formal charge on the atom.
3. The sum of the formal charges in a structure must equal the charge on the particle.

In performing the calculation in Step 2, electrons in bonds are divided equally between the two atoms, while unshared electrons are assigned exclusively to the atom on which they reside. For example, for Structure I above, we have



Therefore, the calculation of formal charge is summarized by the following equation:

$$\text{formal charge} = \left( \text{number of } e^- \text{ in valence shell of the isolated atom} \right) - \left( \text{number of bonds to the atom} + \text{number of unshared } e^- \right) \quad (9.3)$$

Calculated number of electrons in the valence shell of the atom in the Lewis structure

For example, for the sulfur in Structure I, we get

$$\text{formal charge on S} = 6 - (4 + 0) = +2$$

There are 4 bonds to the sulfur atom.

An isolated S atom has 6 electrons.

There are no unshared pairs on the sulfur.

Let's also calculate the formal charges on the hydrogen and oxygen atoms in Structure I. An isolated H atom has one electron. In Structure I each H has one bond and no unshared electrons. Therefore,

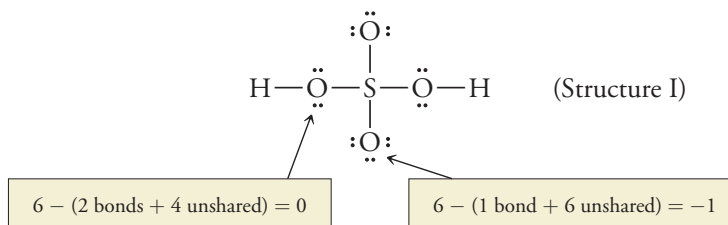
$$\text{formal charge on H} = 1 - (1 + 0) = 0$$

In Structure I, we also see that there are two kinds of oxygen to consider. An isolated oxygen atom has six electrons, so we have, for the oxygens also bonded to hydrogen,

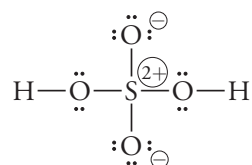
$$\text{formal charge} = 6 - (2 + 4) = 0$$

and for the oxygens not bonded to hydrogen,

$$\text{formal charge} = 6 - (1 + 6) = -1$$



Nonzero formal charges are indicated in a Lewis structure by placing them in circles alongside the atoms, as follows:



Notice that the sum of the formal charges in the molecule adds up to zero. *After you've assigned formal charges, it is important to always check that the sum of the formal charges in the Lewis structure adds up to the charge on the particle.*

Now let's look at the formal charges in Structure II. For sulfur we have

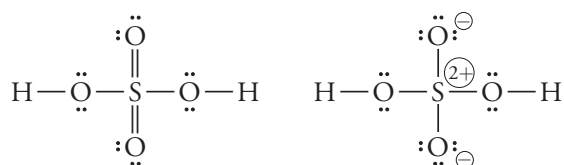
$$\text{formal charge on S} = 6 - (6 + 0) = 0$$

so the sulfur has no formal charge. The hydrogens and the oxygens that are also bonded to H are the same in this structure as before, so they have no formal charges. And finally, the oxygens that are not bonded to hydrogen have

$$\text{formal charge} = 6 - (2 + 4) = 0$$

These oxygens also have no formal charges.

Now let's compare the two structures side by side.



Imagine changing the one with the double bonds (no formal charges on any atoms) to the one with the single bonds (having two negative and two positive charges). In doing so, we've created two pairs of positive-negative charge from something electrically neutral. Because the process involves separating negative charges from positive charges, it would produce an increase in the potential energy. Our conclusion, therefore, is that the singly bonded structure on the right has a higher potential energy than the one with the double bonds. In general, the lower the potential energy of a molecule, the more stable it is. Therefore, the lower energy structure with the double bonds is, in principle, the more stable structure, so it is preferred over the one with only single bonds. This now gives us a rule that we can use in selecting the best Lewis structures for a molecule or ion:



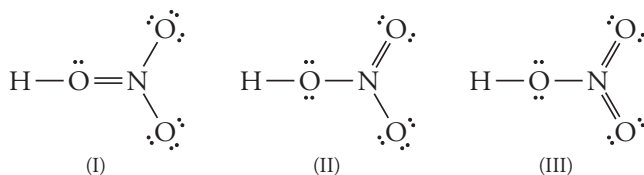
Selecting the best Lewis structure

When several Lewis structures are possible, the one with formal charges closest to zero is the most stable and is preferred.

## Example 9.9

## Selecting Lewis Structures Based on Formal Charges

A student drew the following three Lewis structures for the nitric acid molecule:



Which one is preferred?

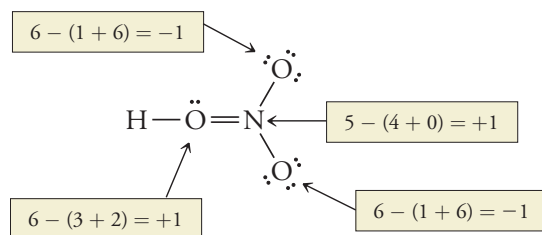
■ **Analysis:** When we have to select among several Lewis structures to find the best one, we first have to assign formal charges to each of the atoms. As a rule, the structure with the formal charges closest to zero will be the best structure. We have to be careful, however, that we don't select a structure in which an atom is assigned more electrons than its valence shell can actually hold. Such a structure must be eliminated from consideration.

■ **Assembling the Tools:** To assign the formal charges, the tool we use is Equation 9.3 on page 389.

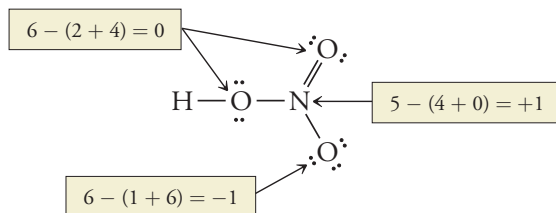
■ **Solution:** Except for hydrogen, all of the atoms in the molecule are from Period 2, and therefore can have a maximum of eight electrons in their valence shells. (Period 2 elements *never* exceed an octet because their valence shells have only *s* and *p* subshells and can accommodate a maximum of eight electrons.) Scanning the structures, we see that I and II show octets around both N and O. However, the nitrogen in Structure III has 5 bonds to it, which require 10 electrons. Therefore, this structure is not acceptable and can be eliminated immediately. Our choice is then between Structures I and II. Let's calculate formal charges on the atoms in each of them.

■ In Structure III, the formal charges are zero on each of the atoms, but this cannot be the "preferred structure" because the nitrogen atom has too many electrons in its valence shell.

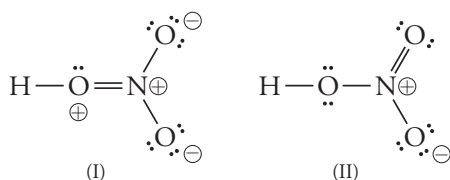
Structure I:



Structure II:



Next, we place the formal charges on the atoms in the structures.



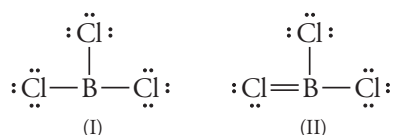
Because Structure II has fewer formal charges than Structure I, it is the lower-energy, preferred Lewis structure for  $\text{HNO}_3$ .

■ **Is the Answer Reasonable?** One simple check we can do is to add up the formal charges in each structure. The sum must equal the net charge on the particle, which is zero for  $\text{HNO}_3$ . Adding formal charges gives zero for each structure, so we can be confident we've assigned them correctly. This gives us confidence in our answer, too.

## Example 9.10

### Selecting Lewis Structures Based on Formal Charges

The following two structures can be drawn for  $\text{BCl}_3$ :

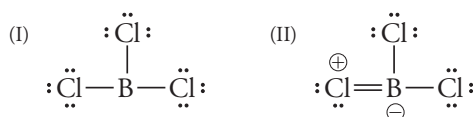


Why is the one that violates the octet rule preferred?

■ **Analysis:** We're asked to select between Lewis structures, which tells us that we have to consider formal charges. We'll assign them and then see whether we can answer the question.

■ **Assembling the Tools:** To assign formal charges we use Equation 9.3.

■ **Solution:** Assigning formal charges gives

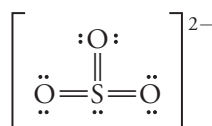


In Structure I all the formal charges are zero. In Structure II, two of the atoms have formal charges, so this alone would argue in favor of Structure I. There is another argument in favor as well. Notice that the formal charges in Structure II place the positive charge on the more electronegative chlorine atom and the negative charge on the less electronegative boron. If charges could form in this molecule, they certainly would not be expected to form in this way. Therefore, there are two factors that make the structure with the double bond unfavorable, so we usually write the Lewis structure for  $\text{BCl}_3$  as shown in (I).

■ **Is the Answer Reasonable?** We've assigned the formal charges correctly, and our reasoning seems sound, so we appear to have answered the question adequately.

## Practice Exercises

**9.16** | A student drew the following Lewis structure for the sulfite ion,  $\text{SO}_3^{2-}$ :



Is this the best Lewis structure for the ion? (*Hint:* Negative formal charges should be on the more electronegative atoms.)

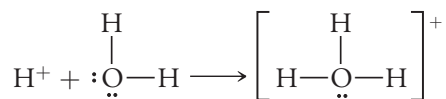
**9.17** | Assign formal charges to the atoms in the following Lewis structures:



**9.18** | Select the preferred Lewis structure for (a)  $\text{SO}_2$ , (b)  $\text{HClO}_3$ , and (c)  $\text{H}_3\text{PO}_4$ .

## Coordinate Covalent Bonds

Often we use Lewis structures to follow the course of chemical reactions. For example, we can diagram how a hydrogen ion combines with a water molecule to form the hydronium ion, a process that occurs in aqueous solutions of acids.



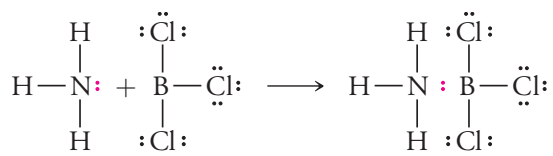
The formation of the bond between  $\text{H}^+$  and  $\text{H}_2\text{O}$  follows a different path than the covalent bonds we discussed earlier in this chapter. For instance, when two H atoms combine to form  $\text{H}_2$ , each atom brings one electron to the bond.



But in the formation of  $\text{H}_3\text{O}^+$ , both of the electrons that become shared between the  $\text{H}^+$  and the O originate on the oxygen atom of the water molecule. *This type of bond, in which both electrons of the shared pair come from just one of the two atoms, is called a **coordinate covalent bond**.*

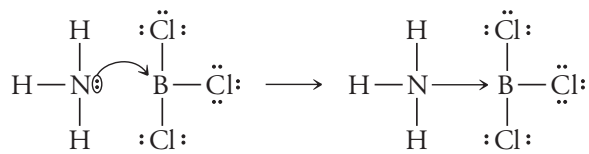
Although we can make a distinction about the origin of the electrons shared in the bond, once the bond is formed a coordinate covalent bond is really the same as any other covalent bond. In other words, we can't tell where the electrons in the bond came from *after* the bond has been formed. In the  $\text{H}_3\text{O}^+$  ion, for example, all three O—H bonds are identical once they've been formed.

The concept of a coordinate covalent bond is helpful in explaining what happens to atoms in a chemical reaction. For example, when ammonia is mixed with boron trichloride, an exothermic reaction takes place and the compound  $\text{NH}_3\text{BCl}_3$  is formed in which there is a boron–nitrogen bond. Using Lewis structures, we can diagram this reaction as follows.



In the reaction, we might say that “the boron forms a coordinate covalent bond with the nitrogen of the ammonia molecule.”

An arrow sometimes is used to represent the donated pair of electrons in a coordinate covalent bond. The direction of the arrow indicates the direction in which the electron pair is donated, in this case from the nitrogen to the boron.



Compounds like  $\text{BCl}_3\text{NH}_3$ , which are formed by simply joining two smaller molecules, are sometimes called **addition compounds**.

■ All electrons are alike. We are using different colors for them so we can see where the electrons in the bond came from.



The addition compound formed from ammonia and boron trichloride. The light blue colored atom is boron.

**9.19** | Use Lewis structures to show how the formation of  $\text{NH}_4^+$  from  $\text{NH}_3$  and  $\text{H}^+$  involves formation of a coordinate covalent bond. How does this bond differ from the other N—H bonds in  $\text{NH}_4^+$ ? (*Hint*: Keep in mind the definition of a coordinate covalent bond.)

**9.20** | Use Lewis structures to explain how the reaction between hydroxide ion and hydrogen ion involves the formation of a coordinate covalent bond.

## Practice Exercises

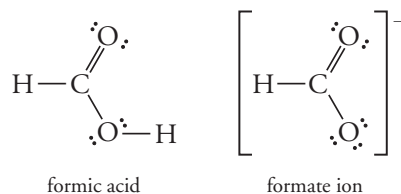
## 9.9 | Resonance Structures

■ The IUPAC name for formic acid is methanoic acid and the formate ion is the methanoate ion.



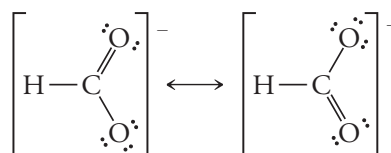
Formic acid is the substance that causes the stinging sensation in bites from fire ants. (WildPicture/Alamy)

There are some molecules and ions for which we cannot write Lewis structures that agree with experimental measurements of bond length and bond energy. An example is the formate ion,  $\text{CHO}_2^-$ , formed by neutralizing formic acid,  $\text{HCHO}_2$ . Following the usual steps, we would write the Lewis structure of the formate ion as shown on the right below.



This structure suggests that in the  $\text{CHO}_2^-$  ion, one carbon–oxygen bond should be longer than the other, but experiments show that the C–O bond lengths are identical, with lengths that are about halfway between the expected values for a single bond and a double bond. The Lewis structure doesn't match the experimental evidence, and there's no way to write one that does. It would require showing all of the electrons in pairs and, at the same time, showing 1.5 pairs of electrons in each carbon–oxygen bond.

The way we get around problems like this is through the use of a concept called **resonance**. We view the actual structure of the molecule or ion, which we cannot draw satisfactorily, as a composite, or average, of a number of Lewis structures that we can draw. For example, for formate ion we write



■ It is important to understand that when we draw resonance structures *no atoms are moved*; the electrons are just redistributed.



A zonkey is the hybrid offspring of a zebra and a donkey. It has characteristics of both of its parents, but is never exactly like either one of them. It certainly isn't a zebra one minute and a donkey the next! (JJIIPRESS/AFP/Getty Images, Inc.)

where we have simply shifted electrons around in going from one structure to the other. The bond between the carbon and a particular oxygen is depicted as a single bond in one structure and as a double bond in the other. The average of these is 1.5 bonds (halfway between a single and a double bond), which is in agreement with the experimental bond lengths. These two Lewis structures are called **resonance structures** or **contributing structures**. The actual structure of the ion, which we can't draw, is called a **resonance hybrid** of these two resonance structures. The double-ended arrow is used to show that we are drawing resonance structures and implies that the true hybrid structure is a composite of the two resonance structures.

Some students find the term *resonance* somewhat misleading. The word itself suggests that the actual structure flip-flops back and forth between the two structures shown. This is *not* the case! We are simply using structures that we are able to draw to describe an actual structure that we cannot draw. It's a bit like trying to imagine what a *zonkey* looks like by viewing photos of a zebra and a donkey. Although a zonkey may have characteristics of both parents, a zonkey is a zonkey; it doesn't flip back and forth between being a zebra one minute and a donkey the next. Similarly, a *resonance hybrid* also has characteristics of its "parents," but it doesn't flip back and forth between the contributing structures.

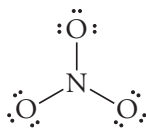


Determining resonance structures

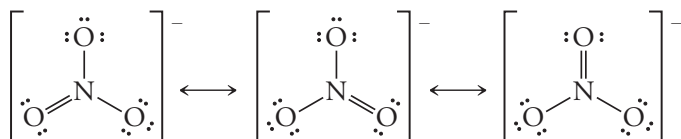
### When We Draw Resonance Structures

There is a simple way to determine when resonance should be applied to Lewis structures. If you find that you must move electrons to create one or more double bonds while following the procedures developed earlier, the number of resonance structures is equal

to the number of equivalent choices for the locations of the double bonds. For example, in drawing the Lewis structure for the  $\text{NO}_3^-$  ion, we reach the stage



A double bond must be created to give the nitrogen an octet. Since it can be placed in any one of three locations, there are three resonance structures for this ion.



■ The three oxygens in  $\text{NO}_3^-$  are said to be equivalent; that is, they are all alike in their chemical environment. Each oxygen is bonded to a nitrogen atom that's attached to two other oxygen atoms.

Notice that each structure is the same, except for the location of the double bond.

In the nitrate ion, the extra bond that appears to “move around” from one structure to another is actually divided among all three bond locations. Therefore, the **average bond order** in the N—O bonds is expected to be  $1\frac{1}{3}$ , or 1.33. In general, we can calculate the average bond order by adding up the total number of bonds and dividing by the number of equivalent positions. In the  $\text{NO}_3^-$  ion, we have a total of *four* bonds (two single bonds and a double bond) distributed over *three* equivalent positions, so the bond order is  $4/3 = 1\frac{1}{3}$ .

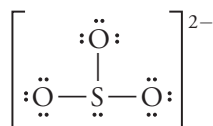


Calculating average bond orders

## Example 9.11 Drawing Resonance Structures

Use formal charges to show that resonance applies to the preferred Lewis structure for the sulfite ion,  $\text{SO}_3^{2-}$ . Draw the resonance structures and determine the average bond order of the S—O bonds.

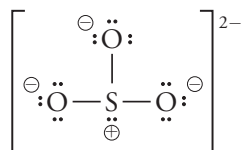
■ **Analysis:** Following our usual procedure we obtain the following Lewis structure:



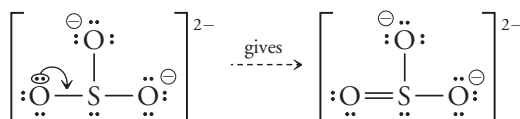
All of the valence electrons have been placed into the structure and we have octets around all of the atoms, so it doesn't seem that we need the concept of resonance. However, the question refers to the “preferred” structure, which suggests that we are going to have to assign formal charges and determine what the preferred structure is. Then we can decide whether the concept of resonance will apply.

■ **Assembling the Tools:** To assign formal charges, our tool is Equation 9.3. If a double bond occurs in the preferred structure, the number of equivalent positions equals the number of resonance structures. The average bond order will be calculated from the number of bonds distributed over the three equivalent bond locations.

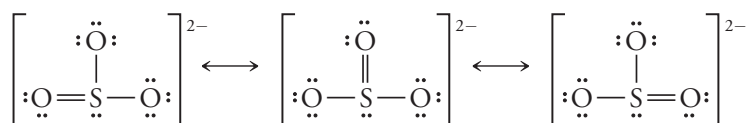
■ **Solution:** When we assign formal charges, we get



We can obtain a better Lewis structure if we can reduce the number of formal charges. This can be accomplished by moving an unshared electron pair from one of the oxygens into an S—O bond, thereby forming a double bond. Let's do this using the oxygen at the left.



However, we could have done this with any of the three S—O bonds, so there are three equivalent choices for the location of the double bond. Therefore, there are three resonance structures.

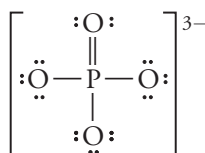


As with the nitrate ion, we expect an average bond order of 1.33.

■ **Is the Answer Reasonable?** If we can answer “yes” to the following questions, the problem is solved correctly: Have we counted valence electrons correctly? Have we properly placed the electrons into the skeletal structure? Do the formal charges we've calculated add up to the charge on the  $\text{SO}_3^{2-}$  ion? Have we correctly determined the number of equivalent positions for the double bond? Have we computed the average bond order correctly? All the answers are “yes”, so we have solved the problem correctly.

## Practice Exercises

**9.21** | The phosphate ion has the following Lewis structure, where we've used formal charges to obtain the best structure.



How many resonance structures are there for this ion? (*Hint:* How many equivalent positions are there for the double bond?)

**9.22** | Draw the resonance structures for  $\text{HCO}_3^-$ .

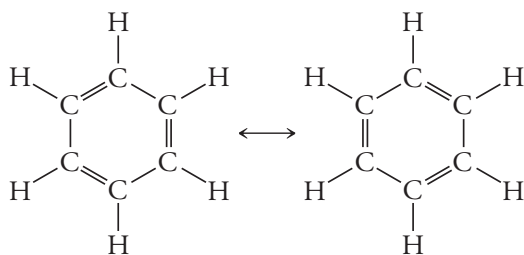
**9.23** | Determine the preferred Lewis structure for the bromate ion,  $\text{BrO}_3^-$ , and, if appropriate, draw resonance structures.

## Stability of Molecules with Resonance Structures

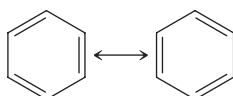
One of the benefits that a molecule or ion derives from existing as a resonance hybrid is that its total energy is lower than that of any one of its contributing structures. A particularly important example of this occurs with the compound benzene,  $\text{C}_6\text{H}_6$ . This is a flat hexagonal ring-shaped molecule (Figure 9.14) with a basic structure that appears in many important organic molecules, ranging from plastics to amino acids.



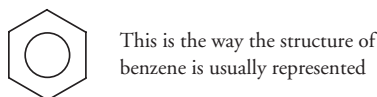
Two resonance structures are usually drawn for benzene.



These are generally represented as hexagons with dashes showing the locations of the double bonds. It is assumed that at each apex of the hexagon there is a carbon bonded to a hydrogen as well as to the adjacent carbon atoms.



Usually, the actual structure of benzene (that of its resonance hybrid) is represented as a hexagon with a circle in the center. This is intended to show that the electron density of the three extra bonds is evenly distributed around the ring.



Although the individual resonance structures for benzene show double bonds, the molecule does not react like other organic molecules that have true carbon–carbon double bonds. The reason appears to be that the resonance hybrid is considerably more stable than either of the resonance forms. In fact, it has been calculated that the actual structure of the benzene molecule is more stable than either of its resonance structures by approximately 146 kJ/mol. This extra stability achieved through resonance is called the **resonance energy**.

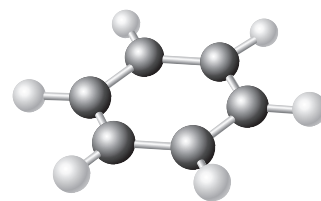
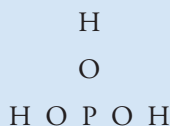


Figure 9.14 | **Benzene.** The molecule has a planar hexagonal structure.

## Analyzing and Solving Multi-Concept Problems

Phosphorous acid has the formula  $\text{H}_3\text{PO}_3$ . It was found that a sample of the acid weighing 0.3066 g was neutralized completely by 0.4196 g of KOH. Use these data to write the preferred Lewis structure for  $\text{H}_3\text{PO}_3$ .

■ **Analysis** At first, it seems like we should be able to follow the guidelines developed earlier in this chapter to arrive at the Lewis structure. For example, on page 384 you learned that for oxoacids, the hydrogens that can be released as  $\text{H}^+$  are bonded to oxygen, which in turn is bonded to the central atom of the oxoacid. The formula  $\text{H}_3\text{PO}_3$  suggests a triprotic acid, which would have the following skeletal structure.



We can use the data presented for the neutralization of the acid by KOH to confirm whether or not this is the correct arrangement of atoms.

From the neutralization data we can calculate the number of moles of KOH required to neutralize one mole of the acid. This will tell us the number of “acidic” hydrogens in a molecule of the acid. If the acid is indeed a triprotic acid as indicated by the skeletal structure above, three moles of KOH should be needed to neutralize one mole of acid.

If the stoichiometry of the neutralization reaction tells us the acid is triprotic, we can then proceed to add the necessary number of electrons to the skeletal structure above. However, if the neutralization reaction tells us  $\text{H}_3\text{PO}_3$  is not triprotic, then we have to refine the skeletal structure before proceeding further. Here, then, is our strategy.

*Part 1:* Use the neutralization data to determine the number of moles of KOH that reacts with 1.00 mol of  $\text{H}_3\text{PO}_3$ .

*Part 2:* Refine the skeletal structure, if necessary, to make it conform to the results of the computation in Part 1.

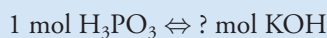
*Part 3:* Add the necessary number of electrons to obtain the complete Lewis structure. Then reduce formal charges, if possible, to obtain the preferred structure.

**PART 1**

■ **Assembling the Tools** The data we need to perform the calculation are the molar masses of  $\text{H}_3\text{PO}_3$  ( $81.994 \text{ g mol}^{-1}$ ) and  $\text{KOH}$  ( $56.108 \text{ g mol}^{-1}$ ). From the data in the problem, we can also set up the equivalence



■ **Solution** This part of the problem can be expressed as



Using dimensional analysis gives us.

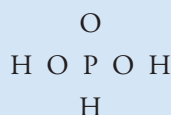
$$1 \cancel{\text{ mol H}_3\text{PO}_3} \times \frac{81.994 \text{ g H}_3\text{PO}_3}{1 \cancel{\text{ mol H}_3\text{PO}_3}} \times \frac{0.4196 \text{ g KOH}}{0.3066 \text{ g H}_3\text{PO}_3} \times \frac{1 \text{ mol KOH}}{56.108 \text{ g KOH}} = 2.00 \text{ mol KOH}$$

Because only 2 moles of  $\text{KOH}$  are needed to neutralize 1 mole of the acid, the acid must be diprotic. We are going to have to make changes in the skeletal structure to reflect this.

**PART 2**

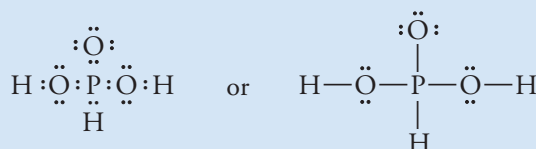
■ **Assembling the Tools** We need to use the general guidelines for constructing skeletal structures, modified as necessary to make the structure conform to the results of Part 1.

■ **Solution** On page 384 you learned that acidic hydrogens in an oxoacid are bonded to oxygen atoms, which are bonded in turn to the central atom. Because  $\text{H}_3\text{PO}_3$  is diprotic, only two such hydrogens are present. So what about the third hydrogen? If it's not bonded to oxygen, then it must be bonded to the phosphorus atom. This suggests the skeletal structure:

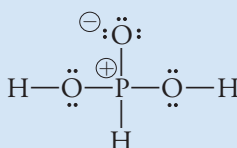
**PART 3**

■ **Assembling the Tools** Our tool is the procedure for drawing Lewis structures given on page 383. We will also use formal charges (page 389) to determine whether we have the preferred structure.

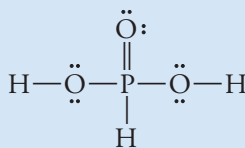
■ **Solution** Phosphorus (Group 5A) contributes 5 electrons; each oxygen (Group 6A) contributes 6 electrons, and each hydrogen contributes one electron. The total is  $26e^-$ . Following the usual procedure, the Lewis structure is



Assigning formal charges gives us



We can reduce the formal charges by moving a lone electron pair from the oxygen at the top into the phosphorus–oxygen bond, giving a double bond.



This structure has no formal charges and is the preferred structure of the molecule.

■ **Is the Answer Reasonable?** The fact that the stoichiometry calculation gives a whole number of moles of KOH per mole of  $\text{H}_3\text{PO}_3$  suggests this part of the problem has been solved correctly. Dimensional analysis also gives the correct units, so we can conclude the calculation is correct. The alternative skeletal structure agrees with the stoichiometry, so it is reasonable. Finally, we can check to be sure we've supplied the correct number of electrons, which we have, so our Lewis structure appears to be reasonable.

## Summary

**Ionic Bonding.** In ionic compounds, the forces of attraction between positive and negative ions are called **ionic bonds**. The formation of ionic compounds by electron transfer is favored when atoms of low ionization energy react with atoms of high electron affinity. The chief stabilizing influence in the formation of ionic compounds is the release of the **lattice energy**. When atoms of the elements in Groups 1A and 2A as well as the nonmetals form ions, they usually gain or lose enough electrons to achieve a noble gas electron configuration. Transition elements lose their outer *s* electrons first, followed by loss of *d* electrons from the shell below the outer shell. Post-transition metals lose electrons from their outer *p* subshell first, followed by electrons from the outer *s* subshell.

**Covalent Bonding.** Electron sharing between atoms occurs when electron transfer is energetically too “expensive.” Shared electrons attract the positive nuclei, and this leads to a lowering of the potential energy of the atoms as a covalent bond forms. Electrons generally become paired when they are shared. An atom tends to share enough electrons to complete its valence shell. Except for hydrogen, the valence shell usually holds eight electrons, which forms the basis of the octet rule. The **octet rule** states that atoms of the representative elements tend to acquire eight electrons in their outer shells when they form bonds. **Single, double, and triple bonds** involve the sharing of one, two, and three pairs of electrons, respectively, between two atoms. Boron and beryllium often have less than an octet in their compounds. Atoms of the elements of Period 2 cannot have more than an octet because their outer shells can hold only eight electrons. Elements in Periods 3, 4, 5, and 6 can exceed an octet if they form more than four bonds.

**Bond energy** (the energy needed to separate the bonded atoms) and **bond length** (the distance between the nuclei of the atoms connected by the bond) are two experimentally measurable quantities that can be related to the number of pairs of

electrons in the bond. For bonds between atoms of the same elements, bond energy increases and bond length decreases as the bond order increases.

**Electronegativity and Polar Bonds.** The attraction an atom has for the electrons in a bond is called the atom's **electronegativity**. When atoms of different electronegativities form a bond, the electrons are shared unequally and the bond is **polar**, with **partial positive** and **partial negative** charges at opposite ends. This causes the bond to be an electric **dipole**. In a **polar molecule**, such as HCl, the product of the charge at either end multiplied by the distance between the charges gives the **dipole moment**,  $\mu$ . When the two atoms have the same electronegativity, the bond is **nonpolar**. The extent of polarity of the bond depends on the electronegativity difference between the two bonded atoms. When the electronegativity difference is very large, ionic bonding results. A bond is approximately 50% ionic when the electronegativity difference is 1.7. In the periodic table, electronegativity increases from left to right across a period and from bottom to top in a group.

**Reactivity and Electronegativity.** The **reactivity** of metals is related to the ease with which they are oxidized (lose electrons); for nonmetals it is related to the ease with which they are reduced (gain electrons). Metals with low electronegativities lose electrons easily, are good reducing agents, and tend to be very reactive. The most reactive metals are located in Groups 1A and 2A, and their ease of oxidation increases going down the group. For nonmetals, the higher the electronegativity, the stronger is their ability to serve as oxidizing agents. In **displacement reactions**, a more electronegative nonmetal is often able to displace one of lower electronegativity from its compounds. The strongest oxidizing agent is fluorine. Among the halogens, oxidizing strength decreases from fluorine to iodine.

**Lewis Symbols and Lewis Structures.** Lewis symbols are a bookkeeping device used to keep track of valence electrons in ionic and covalent bonds. The **Lewis symbol** of an element consists of the element's chemical symbol surrounded by a number of dots equal to the number of valence electrons. In the **Lewis structure** for an ionic compound, the Lewis symbol for the anion is enclosed in brackets (with the charge written outside) to show that all the electrons belong entirely to the ion. The Lewis structure for a molecule or polyatomic ion uses pairs of dots between chemical symbols to represent shared pairs of electrons. The electron pairs in covalent bonds usually are represented by dashes; one dash equals two electrons. The following procedure is used to draw the Lewis structure: (1) decide on the **skeletal structure** (remember that the least electronegative atom is usually the central atom and is usually first in the formula); (2) count all the valence electrons, taking into account the charge, if any; (3) place a pair of electrons in each bond; (4) complete the octets of atoms other than the central atom (but remember that hydrogen can only have two electrons); (5) place any left-over electrons on the central atom in pairs; (6) if the central atom still has less than an octet, move electron pairs to make double or triple bonds.

**Formal Charges.** The **formal charge** assigned to an atom in a Lewis structure (which usually differs from the actual charge on the atom) is calculated as the difference between the number of valence electrons of an isolated atom of the element and the number of electrons that “belong” to the atom because of its bonds to other atoms and its unshared valence electrons. The sum of the formal charges always equals the net charge on the molecule or

ion. The most stable (lowest energy) Lewis structure for a molecule or ion is the one with formal charges closest to zero. This is usually the preferred Lewis structure for the particle.

**Coordinate Covalent Bonding.** For bookkeeping purposes, we sometimes single out a covalent bond whose electron pair originated from one of the two bonded atoms. An arrow is sometimes used to indicate the donated pair of electrons. Once formed, a coordinate covalent bond is no different from any other covalent bond.

**Resonance.** Two or more atoms in a molecule or polyatomic ion are *chemically equivalent* if they are attached to the same kinds of atoms or groups of atoms. Bonds to chemically equivalent atoms must be the same; they must have the same bond length and the same bond energy, which means they must involve the sharing of the same number of electron pairs. Sometimes the Lewis structures we draw suggest that the bonds to chemically equivalent atoms are not the same. Typically, this occurs when it is necessary to form multiple bonds during the drawing of a Lewis structure. When alternatives exist for the location of a multiple bond among two or more equivalent atoms, then each possible Lewis structure is actually a **resonance structure** or **contributing structure**, and we draw them all. In drawing resonance structures, the relative locations of the nuclei must be identical in all. The **average bond order** is calculated from the total number of bonds distributed over the equivalent bond locations. Remember that none of the resonance structures corresponds to a real molecule, but their composite—the **resonance hybrid**—does approximate the actual structure of the molecule or ion.



### Tools for Problem Solving

In this chapter you learned to apply the following concepts as tools in solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need.

#### Electron configurations of ions of the representative elements (page 363)

Metals in Groups 1A and 2A, aluminum, and the nonmetals obey the octet rule when they form ions. This knowledge is helpful when you have to write the electron configurations of ions of these elements.

#### Order in which electrons are lost from an atom (page 363)

Electrons are lost first from the shell with largest  $n$ . For a given shell, electrons are lost from subshells in the following order:  $f$  before  $d$  before  $p$  before  $s$ . Use this knowledge to obtain electron configurations of ions of the transition and post-transition metals.

#### Lewis symbols (page 366)

Lewis symbols are a bookkeeping device that we use to keep track of valence electrons in atoms and ions. For a neutral atom of the representative elements, the Lewis symbol consists of the atomic symbol surrounded by dots equal in number to the group number.

#### Octet rule and covalent bonding (page 371)

The octet rule helps us construct Lewis structures for covalently bonded molecules. Elements in Period 2 never exceed an octet in their valence shells.

**Dipole moment** (page 378)

Dipole moments are a measure of the polarity of molecules, so they can be used to compare molecular polarity. The dipole moment ( $\mu$ ) of a diatomic molecule is calculated as the charge on an end of the molecule,  $q$ , multiplied by the bond length,  $r$ . Dipole moments are expressed in debye units.

$$\mu = q \times r$$

**Periodic trends in electronegativity** (page 381)

The trends revealed in Figure 9.9 allow us to use the locations of elements in the periodic table to estimate the degree of polarity of bonds and to estimate which of two atoms in a bond is the most electronegative.

**Trends in the reactivity of metals in the periodic table** (page 381)

A knowledge of where the most reactive and least reactive metals are located in the periodic table gives a qualitative feel for how reactive a metal is.

**Trends in the reactivity of nonmetals in the periodic table** (page 382)

The periodic table correlates the position of a nonmetal with its strength as an oxidizing agent. Oxidizing ability increases from left to right across a period and from bottom to top in a group.

**Method for drawing Lewis structures** (page 383)

The method described in Figure 9.12 yields Lewis structures in which the maximum number of atoms obey the octet rule.

**Correlation between bond properties and bond order** (page 388)

The correlations allow us to compare experimental covalent bond properties (bond energy and bond length) with those predicted by theory.

**Method for calculating formal charges** (page 389)

Use formal charges to select the best Lewis structure for a molecule or polyatomic ion. The best structure is usually the one with the fewest formal charges. Assign formal charges to atoms as follows:

$$\text{Formal charge} = \left[ \begin{array}{l} \text{number of } e^- \text{ in valence} \\ \text{shell of the isolated atom} \end{array} \right] - \left[ \begin{array}{l} \text{number of bonds} \\ \text{to the atom} \end{array} + \begin{array}{l} \text{number of} \\ \text{unshared } e^- \end{array} \right]$$

**Selecting the best Lewis structure** (page 390)

The structure having the smallest formal charges is preferred. Be sure none of the atoms in the structure appears to have more electrons than permitted by its location in the periodic table.

**Determining resonance structures** (page 394)

Expect resonance structures when there is more than one option for assigning the location of a double bond. Determine the number of equivalent positions for the double bond. That number is the number of resonance structures you should draw.

**Calculating average bond order** (page 395)

To calculate the average bond order for resonance structures, add up the total number of bonds and divide by the number of equivalent positions in which they are drawn.



= WileyPLUS, an online teaching and learning solution. *Note to instructors:* Many of the end-of-chapter problems are available for assignment via the WileyPLUS system. [www.wileyplus.com](http://www.wileyplus.com). **ILW** = An Interactive Learningware solution is available for this problem. **OH** = An Office Hour video is available for this problem. Review Problems are presented in pairs separated by blue rules. Answers to problems whose numbers appear in blue are given in Appendix B. More challenging problems are marked with an asterisk \*.

## | Review Questions

### Ionic Bonding

- 9.1** What must be true about the change in the total potential energy of a collection of atoms for a stable compound to be formed from the elements?
- 9.2** What is an *ionic bond*?
- 9.3** How is the tendency to form ionic bonds related to the IE and EA of the atoms involved?

- 9.4 Define the term *lattice energy*. In what ways does the lattice energy contribute to the stability of ionic compounds?
- 9.5 Magnesium forms compounds containing the ion  $\text{Mg}^{2+}$  but not the ion  $\text{Mg}^{3+}$ . Why?
- 9.6 Why doesn't chlorine form the ion  $\text{Cl}^{2-}$  in compounds?
- 9.7 Why do many of the transition elements in Period 4 form ions with a 2+ charge?
- 9.8 If we were to compare the first, second, third, and fourth ionization energies of aluminum, between which pair of successive ionization energies would there be the largest difference? (Refer to the periodic table when answering this question.)
- 9.9 In each of the following pairs of compounds, which would have the larger lattice energy: (a)  $\text{CaO}$  or  $\text{Al}_2\text{O}_3$ , (b)  $\text{BeO}$  or  $\text{SrO}$ , (c)  $\text{NaCl}$  or  $\text{NaBr}$ ?

### Lewis Symbols

- 9.10 The Lewis symbol for an atom only accounts for electrons in the valence shell of the atom. Why are we not concerned with the other electrons?
- 9.11 Which of these Lewis symbols is incorrect?  
(a)  $\cdot\ddot{\text{O}}\cdot$  (b)  $\cdot\ddot{\text{Cl}}\cdot$  (c)  $:\ddot{\text{N}}\text{e}:$  (d)  $:\ddot{\text{S}}\text{b}:$

### Electron Sharing

- 9.12 In terms of the potential energy change, why doesn't ionic bonding occur when two nonmetals react with each other?
- 9.13 Describe what happens to the electron density around two hydrogen atoms as they come together to form an  $\text{H}_2$  molecule.
- 9.14 What happens to the energy of two hydrogen atoms as they approach each other? What happens to the spins of the electrons?
- 9.15 Is the formation of a covalent bond endothermic or exothermic?
- 9.16 What factors control the bond length in a covalent bond?

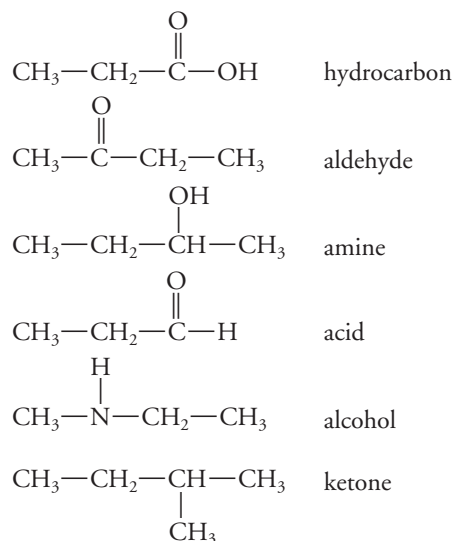
### Covalent Bonding and the Octet Rule

- 9.17 What is the *octet rule*? What is responsible for it?
- 9.18 How many covalent bonds are normally formed by (a) hydrogen, (b) carbon, (c) oxygen, (d) nitrogen, and (e) chlorine?
- 9.19 Why do Period 2 elements never form more than four covalent bonds? Why are Period 3 elements able to exceed an octet?
- 9.20 Define (a) *single bond*, (b) *double bond*, and (c) *triple bond*.
- 9.21 The Lewis structure for hydrogen cyanide is  $\text{H}-\text{C}\equiv\text{N}:$ . Draw circles enclosing electrons to show that carbon and nitrogen obey the octet rule.
- 9.22 Why doesn't hydrogen obey the octet rule?

### Compounds of Carbon

- 9.23 Sketch the Lewis structures for (a) methane, (b) ethane, and (c) propane.

- 9.24 Draw the structure for a hydrocarbon that has a chain of six carbon atoms linked by single bonds. How many hydrogen atoms does the molecule have? What is the molecular formula for the compound?
- 9.25 How many *different* molecules have the formula  $\text{C}_5\text{H}_{12}$ ? Sketch their structures.
- 9.26 What is a carbonyl group? In which classes of organic molecules that we've studied do we find a carbonyl group?
- 9.27 Match the compounds on the left with the family types on the right.



- 9.28 Write a chemical equation for the ionization in water of the acid in Question 9.27. Is the acid strong or weak? Draw the Lewis structure for the ion formed by the acid when it ionizes.
- 9.29 Write a chemical equation for the reaction of the amine in Question 9.27 with water. Draw the Lewis structure for the ion formed by the amine.
- 9.30 Write the net ionic equation for the aqueous reaction of the acid and amine in Question 9.27 with each other. (Use molecular formulas.)
- 9.31 Draw the structures of (a) ethylene and (b) acetylene.

### Polar Bonds and Electronegativity

- 9.32 What is a polar covalent bond?
- 9.33 Define *dipole moment* in the form of an equation. What is the value of the *debye* (with appropriate units)?
- 9.34 Define electronegativity. On what basis did Pauling develop his scale of electronegativities?
- 9.35 Which element has the highest electronegativity? Which is the second most electronegative element?
- 9.36 Among the following bonds, which are more ionic than covalent? (a)  $\text{Si}-\text{O}$ , (b)  $\text{Ba}-\text{O}$ , (c)  $\text{Se}-\text{Cl}$ , (d)  $\text{K}-\text{Br}$
- 9.37 If an element has a low electronegativity, is it likely to be classified as a metal or a nonmetal? Explain your answer.

**Electronegativity and the Reactivities of the Elements**

- 9.38 When we say that aluminum is more *reactive* than iron, which kind of reaction of these elements are we describing?
- 9.39 In what groups in the periodic table are the most reactive metals found? Where do we find the least reactive metals?
- 9.40 How is the electronegativity of a metal related to its reactivity?
- 9.41 Arrange the following metals in their approximate order of reactivity (most reactive first, least reactive last) based on their locations in the periodic table: (a) iridium, (b) silver, (c) calcium, (d) iron.
- 9.42 Complete and balance the following equations. If no reaction occurs, write "N.R."
- (a)  $\text{KCl} + \text{Br}_2 \longrightarrow$                       (d)  $\text{CaBr}_2 + \text{Cl}_2 \longrightarrow$   
 (b)  $\text{NaI} + \text{Cl}_2 \longrightarrow$                       (e)  $\text{AlBr}_3 + \text{F}_2 \longrightarrow$   
 (c)  $\text{KCl} + \text{F}_2 \longrightarrow$                       (f)  $\text{ZnBr}_2 + \text{I}_2 \longrightarrow$
- 9.43 In each pair, choose the better oxidizing agent.
- (a)  $\text{O}_2$  or  $\text{F}_2$                       (d)  $\text{P}_4$  or  $\text{S}_8$   
 (b)  $\text{As}_4$  or  $\text{P}_4$                       (e)  $\text{Se}_8$  or  $\text{Cl}_2$   
 (c)  $\text{Br}_2$  or  $\text{I}_2$                       (f)  $\text{As}_4$  or  $\text{S}_8$

**Failure of the Octet Rule**

- 9.44 How many electrons are in the valence shells of (a) Be in  $\text{BeCl}_2$ , (b) B in  $\text{BCl}_3$ , and (c) H in  $\text{H}_2\text{O}$ ?
- 9.45 What is the minimum number of electrons that would be expected to be in the valence shell of As, in  $\text{AsCl}_5$ ?
- 9.46 Nitrogen and arsenic are in the same group in the periodic table. Arsenic forms both  $\text{AsCl}_3$  and  $\text{AsCl}_5$ , but with chlorine, nitrogen only forms  $\text{NCl}_3$ . On the basis of the electronic structures of N and As, explain why this is so.

**Bond Length and Bond Energy**

- 9.47 Define *bond length* and *bond energy*.
- 9.48 Define *bond order*. How are bond energy and bond length related to bond order? Why are there these relationships?

- 9.49 The energy required to break the H—Cl bond to give  $\text{H}^+$  and  $\text{Cl}^-$  ions would not be called the H—Cl bond energy. Why?

**Formal Charge**

- 9.50 What is the definition of *formal charge*?
- 9.51 How are formal charges used to select the best Lewis structure for a molecule? What is the basis for this method of selection?
- 9.52 What are the formal charges on the atoms in the HCl molecule? What are the actual charges on the atoms in this molecule? (*Hint*: See Section 9.6.) Are formal charges the same as actual charges?

**Coordinate Covalent Bonds**

- 9.53 What is a *coordinate covalent bond*?
- 9.54 Once formed, how (if at all) does a coordinate covalent bond differ from an ordinary covalent bond?
- 9.55  $\text{BCl}_3$  has an incomplete valence shell. Use Lewis structures to show how it could form a coordinate covalent bond with a water molecule.

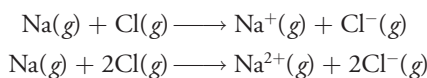
**Resonance**

- 9.56 Why is the concept of resonance needed?
- 9.57 What is a resonance hybrid? How does it differ from the resonance structures drawn for a molecule?
- 9.58 Draw the resonance structures of the benzene molecule. Why is benzene more stable than one would expect if the ring contained three carbon–carbon double bonds?
- 9.59 Polystyrene plastic is a hydrocarbon that consists of a long chain of carbon atoms joined by single bonds in which every other carbon is attached to a benzene ring. The ring is attached by replacing a hydrogen of benzene with a single bond to the carbon chain. Sketch a portion of a polystyrene molecule that contains five benzene rings.

# Review Problems

**Lattice Energy**

- 9.60 Use data from the tables of ionization energies and electron affinities on pages 343 and 348 to calculate the energy changes for the following reactions.



Approximately how many times larger would the lattice energy of  $\text{NaCl}_2$  have to be compared to the lattice energy of  $\text{NaCl}$  for  $\text{NaCl}_2$  to be more stable than  $\text{NaCl}$ ?

- 9.61 Changing 1 mol of  $\text{Mg}(s)$  and 1/2 mol of  $\text{O}_2(g)$  to gaseous atoms requires a total of approximately 150 kJ of energy. The first and second ionization energies of magnesium are 737 and 1450 kJ/mol, respectively; the first and second electron affinities of oxygen are  $-141$  and  $+844$  kJ/mol, respectively; and the standard heat of formation of  $\text{MgO}(s)$  is  $-602$  kJ/mol. Construct an enthalpy diagram similar to the one in Figure 9.4 (page 360) and use it to calculate the lattice energy of magnesium oxide. How does the lattice energy of  $\text{MgO}$  compare with that of  $\text{NaCl}$ ? What might account for the difference?

### Electron Configurations of Ions

**9.62** Explain what happens to the electron configurations of Mg and Br when they react to form magnesium bromide.

**9.63** Describe what happens to the electron configurations of lithium and nitrogen when they react to form the lithium nitride.

**ILW OH 9.64** What are the electron configurations of the  $\text{Pb}^{2+}$  and  $\text{Pb}^{4+}$  ions?

**9.65** What are the electron configurations of the  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  ions?

**9.66** Write the abbreviated electron configuration of the  $\text{Mn}^{3+}$  ion. How many unpaired electrons does the ion contain?

**9.67** Write the abbreviated electron configuration of the  $\text{Co}^{3+}$  ion. How many unpaired electrons does the ion contain?

### Lewis Symbols

**9.68** Write Lewis symbols for the following atoms: (a) Si, (b) Sb, (c) Ba, (d) Al, (e) S.

**9.69** Write Lewis symbols for the following atoms: (a) K, (b) Ge, (c) As, (d) Br, (e) Se.

**9.70** Use Lewis symbols to diagram the reactions between (a) Ca and Br, (b) Al and O, and (c) K and S.

**OH 9.71** Use Lewis symbols to diagram the reactions between (a) Mg and S, (b) Mg and Cl, and (c) Mg and N.

### Dipole Moments

**9.72** Use the data in Table 9.3 (page 378) to calculate the amount of charge on the oxygen and nitrogen in the nitrogen monoxide molecule, expressed in electronic charge units ( $e = 1.60 \times 10^{-19}$  C). Which atom carries the positive charge?

**9.73** The molecule bromine monofluoride has a dipole moment of 1.42 D and a bond length of 176 pm. Calculate the charge on the ends of the molecule, expressed in electronic charge units ( $e = 1.60 \times 10^{-19}$  C). Which atom carries the positive charge?

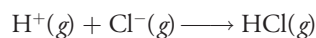
**9.74** The dipole moment of HF is 1.83 D and the bond length is 917 pm. Calculate the amount of charge (in electronic charge units) on the hydrogen and the fluorine atoms in the HF molecule.

**OH 9.75** In the vapor state, cesium and fluoride ions pair to give  $\text{CsF}$  formula units that have a bond length of 0.255 nm and a dipole moment of 7.88 D. What is the actual charge on the cesium and fluorine atoms in  $\text{CsF}$ ? What percentage of full  $1+$  and  $1-$  charges is this?

### Bond Energy

**9.76** How much energy, in joules, is required to break the bond in *one* chlorine molecule? The bond energy of  $\text{Cl}_2$  is 242.6 kJ/mol.

**9.77** How much energy is released in the formation of one molecule of HCl by the following reaction?



The bond energy of HCl is 431 kJ mol<sup>-1</sup>. Additional data can be found in tables in Chapter 8.

**9.78** The reason there is danger in exposure to high-energy radiation (e.g., ultraviolet and X rays) is that the radiation can rupture chemical bonds. In some cases, cancer can be caused by it. A carbon–carbon single bond has a bond energy of approximately 348 kJ per mole. What wavelength of light is required to provide sufficient energy to break the C–C bond? In which region of the electromagnetic spectrum is this wavelength located?

**9.79** A mixture of  $\text{H}_2$  and  $\text{Cl}_2$  is stable, but a bright flash of light passing through it can cause the mixture to explode. The light causes  $\text{Cl}_2$  molecules to split into Cl atoms, which are highly reactive. What wavelength of light is necessary to cause the  $\text{Cl}_2$  molecules to split? The bond energy of  $\text{Cl}_2$  is 242.6 kJ per mole.

### Covalent Bonds and the Octet Rule

**9.80** Use Lewis structures to diagram the formation of (a)  $\text{Br}_2$ , (b)  $\text{H}_2\text{O}$ , and (c)  $\text{NH}_3$  from neutral atoms.

**OH 9.81** Chlorine tends to form only one covalent bond because it needs just one electron to complete its octet. What are the Lewis structures for the simplest compound formed by chlorine with (a) nitrogen, (b) carbon, (c) sulfur, and (d) bromine?

**9.82** Use the octet rule to predict the formula of the simplest compound formed from hydrogen and (a) selenium, (b) arsenic, and (c) silicon. (Remember that the valence shell of hydrogen can hold only two electrons.)

**9.83** What would be the formula for the simplest compound formed from (a) phosphorus and chlorine, (b) carbon and fluorine, and (c) iodine and chlorine?

### Electronegativity

**9.84** Use Figure 9.9 to choose the atom in each of the following bonds that carries the partial positive charge: (a) N–S, (b) Si–I, (c) N–Br, (d) C–Cl.

**9.85** Use Figure 9.9 to choose the atom that carries the partial negative charge in each of the following bonds: (a) Hg–I, (b) P–I, (c) Si–F, (d) Mg–N.

**9.86** Which of the bonds in Problem 9.84 is the most polar?

**9.87** Which of the bonds in the Problem 9.85 is the least polar?

### Drawing Lewis Structures

**ILW 9.88** Draw Lewis structures for (a)  $\text{AsCl}_4^+$ , (b)  $\text{ClO}_2^-$ , (c)  $\text{HNO}_2$ , and (d)  $\text{XeF}_2$ .

**9.89** Draw Lewis structures for (a)  $\text{TeF}_4$ , (b)  $\text{ClF}_5$ , (c)  $\text{PF}_6^-$ , and (d)  $\text{XeF}_4$ .



9.90 Draw Lewis structures for (a)  $\text{SiCl}_4$ , (b)  $\text{PF}_3$ , (c)  $\text{PH}_3$ , and (d)  $\text{SCl}_2$ .

9.91 Draw Lewis structures for (a)  $\text{HIO}_3$ , (b)  $\text{H}_2\text{CO}_3$ , (c)  $\text{HCO}_3^-$ , and (d)  $\text{PCl}_4^+$ .

9.92 Draw Lewis structures for (a) carbon disulfide and (b) cyanide ion.

9.93 Draw Lewis structures for (a) selenium trioxide and (b) selenium dioxide.

9.94 Draw Lewis structures for (a)  $\text{AsH}_3$ , (b)  $\text{HClO}_2$ , (c)  $\text{H}_2\text{SeO}_3$ , and (d)  $\text{H}_3\text{AsO}_4$ .

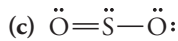
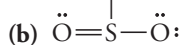
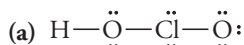
OH 9.95 Draw Lewis structures for (a)  $\text{NO}^+$ , (b)  $\text{NO}_2^-$ , (c)  $\text{SbCl}_6^-$ , and (d)  $\text{IO}_3^-$ .

9.96 Draw the Lewis structure for (a)  $\text{CH}_2\text{O}$  (the central atom is carbon, which is attached to two hydrogens and an oxygen), and (b)  $\text{SOCl}_2$  (the central atom is sulfur, which is attached to an oxygen and two chlorines).

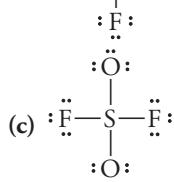
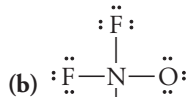
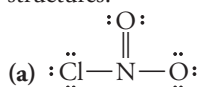
9.97 Draw Lewis structures for (a)  $\text{GeCl}_4$ , (b)  $\text{CO}_3^{2-}$ , (c)  $\text{PO}_4^{3-}$ , and (d)  $\text{O}_2^{2-}$ .

### Formal Charge

9.98 Assign formal charges to each atom in the following structures:



9.99 Assign formal charges to each atom in the following structures:



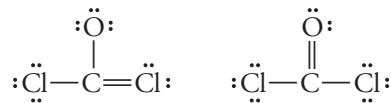
ILW 9.100 Draw the Lewis structure for  $\text{HClO}_4$  according to the procedure described in Figure 9.12. Assign formal charges to each atom in the formula. Determine the preferred Lewis structure for this compound.

9.101 Draw the Lewis structure for  $\text{SO}_2\text{Cl}$  (sulfur bonded to two Cl and one O). Assign formal charges to each atom. Determine the preferred Lewis structure for this molecule.

9.102 Below are two structures for  $\text{BeCl}_2$ . Give two reasons why the one on the left is the preferred structure.



9.103 The following are two Lewis structures that can be drawn for phosgene, a substance that has been used as a war gas.

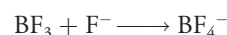


Which is the better Lewis structure? Why?

### Coordinate Covalent Bonds

9.104 Use Lewis structures to show that the hydronium ion,  $\text{H}_3\text{O}^+$ , can be considered to be formed by the creation of a coordinate covalent bond between  $\text{H}_2\text{O}$  and  $\text{H}^+$ .

9.105 Use Lewis structures to show that the reaction

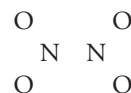


involves the formation of a coordinate covalent bond.

### Resonance

9.106 Draw the resonance structures for  $\text{CO}_3^{2-}$ . Calculate the average C—O bond order.

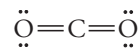
ILW 9.107 Draw all of the resonance structures for the  $\text{N}_2\text{O}_4$  molecule and determine the average N—O bond order. The skeletal structure of the molecule is



OH 9.108 How should the N—O bond lengths compare in the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  ions?

9.109 Arrange the following in order of increasing C—O bond length:  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CO}_2$ ,  $\text{HCO}_2^-$  (formate ion, page 394).

9.110 The Lewis structure of  $\text{CO}_2$  was given as



but two other resonance structures can also be drawn for it. What are they? On the basis of formal charges, why are they not preferred structures?

9.111 Use formal charges to establish the preferred Lewis structures for the  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  ions. Draw resonance structures for both ions and determine the average Cl—O bond order in each. Which of these ions would be expected to have the shorter Cl—O bond length?

## Additional Exercises

**9.112** Use an enthalpy diagram to calculate the lattice energy of  $\text{CaCl}_2$  from the following information. Energy needed to vaporize one mole of  $\text{Ca}(s)$  is 192 kJ. For calcium, the first IE = 589.5 kJ mol<sup>-1</sup>, the second IE = 1146 kJ mol<sup>-1</sup>. The electron affinity of Cl is 348 kJ mol<sup>-1</sup>. The bond energy of  $\text{Cl}_2$  is 242.6 kJ per mole of Cl—Cl bonds. The standard heat of formation of  $\text{CaCl}_2$  is -795 kJ mol<sup>-1</sup>.

**9.113** Use an enthalpy diagram and the following data to calculate the electron affinity of bromine. The standard heat of formation of  $\text{NaBr}$  is -360 kJ mol<sup>-1</sup>. The energy needed to vaporize one mole of  $\text{Br}_2(l)$  to give  $\text{Br}_2(g)$  is 31 kJ mol<sup>-1</sup>. The first ionization energy of Na is 495.4 kJ mol<sup>-1</sup>. The bond energy of  $\text{Br}_2$  is 192 kJ per mole of Br—Br bonds. The lattice energy of  $\text{NaBr}$  is -743.3 kJ mol<sup>-1</sup>.

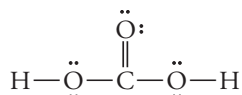
**9.114** In many ways, tin(IV) chloride behaves more like a covalent molecular species than like a typical ionic chloride. Draw the Lewis structure for the tin(IV) chloride molecule.

**9.115** In each pair, choose the one with the more polar bonds. (Use the periodic table to answer the question.)

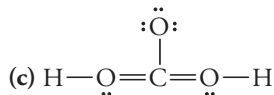
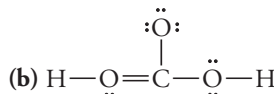
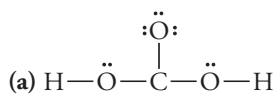
- (a)  $\text{PCl}_3$  or  $\text{AsCl}_3$     (c)  $\text{SiCl}_4$  or  $\text{SCl}_2$   
 (b)  $\text{SF}_2$  or  $\text{GeF}_4$     (d)  $\text{SrO}$  or  $\text{SnO}$

**9.116** How many electrons are in the outer shell of the  $\text{Zn}^{2+}$  ion?

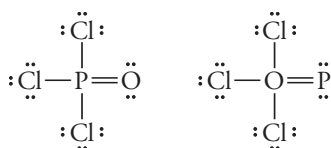
**9.117** The Lewis structure for carbonic acid (formed when  $\text{CO}_2$  dissolves in water) is usually given as



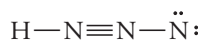
What is wrong with the following structures?



**9.118** Are the following Lewis structures considered to be resonance structures? Explain. Which is the more likely structure for  $\text{POCl}_3$ ?

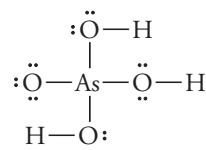


**9.119** Assign formal charges to all the atoms in the following Lewis structure of hydrazoic acid,  $\text{HN}_3$ .



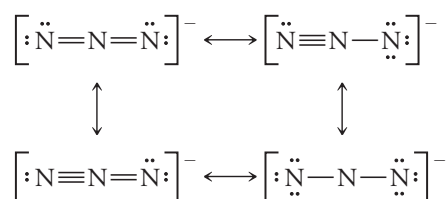
Suggest a lower-energy resonance structure for this molecule.

**9.120** Assign formal charges to all the atoms in the Lewis structure



Suggest a lower-energy Lewis structure for this molecule.

**9.121** The inflation of an “air bag” when a car experiences a collision occurs by the explosive decomposition of sodium azide,  $\text{NaN}_3$ , which yields nitrogen gas that inflates the bag. The following resonance structures can be drawn for the azide ion,  $\text{N}_3^-$ . Identify the best and worst of them.



**9.122** How should the sulfur–oxygen bond lengths compare for the species  $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{SO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ ?

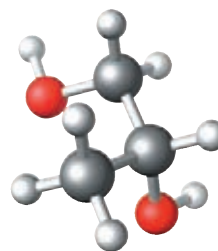
**9.123** What is the most reasonable Lewis structure for  $\text{S}_2\text{Cl}_2$ ?

**\*9.124** There are two acids that have the formula  $\text{HCNO}$ . Which of the following skeletal structures are most likely for them? Justify your answer.



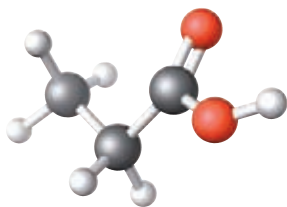
**9.125** In the vapor state, ion pairs of  $\text{KF}$  can be identified. The dipole moment of such a pair is measured to be 8.59 D and the K—F bond length is found to be 217 pm. Is the K—F bond 100% ionic? If not, what percent of full 1+ and 1- charges do the K and F atoms carry, respectively?

**9.126** Below is a ball-and-stick model of a type of alcohol derived from a hydrocarbon. What is the formula for the hydrocarbon and what is its name?

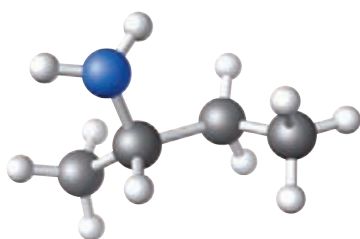


## Multi-Concept Problems

- 9.127** Use Lewis structures to show the ionization of the following organic acid (a weak acid) in water.



- 9.128** The compound below is called an amine. It is a weak base and undergoes ionization in water following a path similar to that of ammonia. Use Lewis structures to diagram the reaction of this amine with water.



- 9.129** Use Lewis structures to diagram the reaction between the acid in Problem 9.127 with the base in Problem 9.128. If

12.5 g of the acid is mixed with 17.4 g of the base, how many grams of which reactant will remain unreacted after the reaction is complete?

- 9.130** How many grams of water could have its temperature raised from 25 °C (room temperature) to 100 °C (the boiling point of water) by the amount of energy released in the formation of 1 mol of H<sub>2</sub> from hydrogen atoms? The bond energy of H<sub>2</sub> is 435 kJ/mol.

- \*9.131** What wavelength of light, if absorbed by a hydrogen molecule, could cause the molecule to split into the ions H<sup>+</sup> and H<sup>-</sup>? (The data required are available in this and previous chapters.)

- \*9.132** A 38.40 mg sample of an organic acid composed of just carbon, hydrogen, and oxygen was burned in pure oxygen to give 37.54 mg CO<sub>2</sub> and 7.684 mg H<sub>2</sub>O in a combustion analysis. In a separate experiment, the molecular mass was determined to be 90. In a titration, 40.2 mg of the acid dissolved in 50 mL of water required 14.28 mL of 0.0625 M NaOH for complete neutralization. Use these data to draw a reasonable Lewis structure for the compound.

## Exercises in Critical Thinking

- 9.133** What is the average bond energy of a C—C covalent bond? What wavelength of light provides enough energy to break such a bond? Using this information, explain why unfiltered sunlight is damaging to the skin.
- 9.134** One way of estimating the electronegativity of an atom is to use an average of its ionization energy and electron affinity. Why would these two quantities, taken together, be related to electronegativity?
- 9.135** The attractions between molecules of a substance can be associated with the size of the molecule's dipole moment. Explain why this is so.
- 9.136** The positive end of the dipole in a water molecule is not located on an atom. Explain why this happens and suggest other simple molecules that show the same effect.
- 9.137** In describing the structures of molecules, we use Lewis structures, formal charges, and experimental evidence. Rank these in terms of importance in deciding on the true structure of a molecule, and defend your choice.