9.1 Lewis Dot Symbols

The development of the periodic table and concept of electron configuration gave chemists a rationale for molecule and compound formation. This explanation, formulated by the American chemist Gilbert Lewis, is that atoms combine to achieve a more stable electron configuration. Maximum stability results when an atom is isoelectronic with a noble gas.

When atoms interact to form a chemical bond, only their outer regions are in contact. For this reason, when we study chemical bonding, we are concerned primarily with the valence electrons of the atoms. To keep track of valence electrons in a chemical reaction, and to make sure that the total number of electrons does not change, chemists use a system of dots devised by Lewis and called Lewis dot symbols. A ***Lewis dot symbol*** *consists of the symbol of an element and one dot for each valence electron in an atom of the element.* Figure 9.1 shows the Lewis dot symbols for the representative elements and the noble gases. Note that, except for helium, the number of valence electrons each atom has is the same as the group number of the element. For example, Li is a Group 1A element and has one dot for one valence electron; Be, a Group 2A element, has two valence electrons (two dots); and so on. Elements in the same group have similar outer electron configurations and hence similar Lewis dot symbols. The transition metals, lanthanides, and actinides all have incompletely filled inner shells, and in general, we cannot write simple Lewis dot symbols for them.

In this chapter we will learn to use electron configurations and the periodic table to predict the type of bond atoms will form, as well as the number of bonds an atom of a particular element can form and the stability of the product.

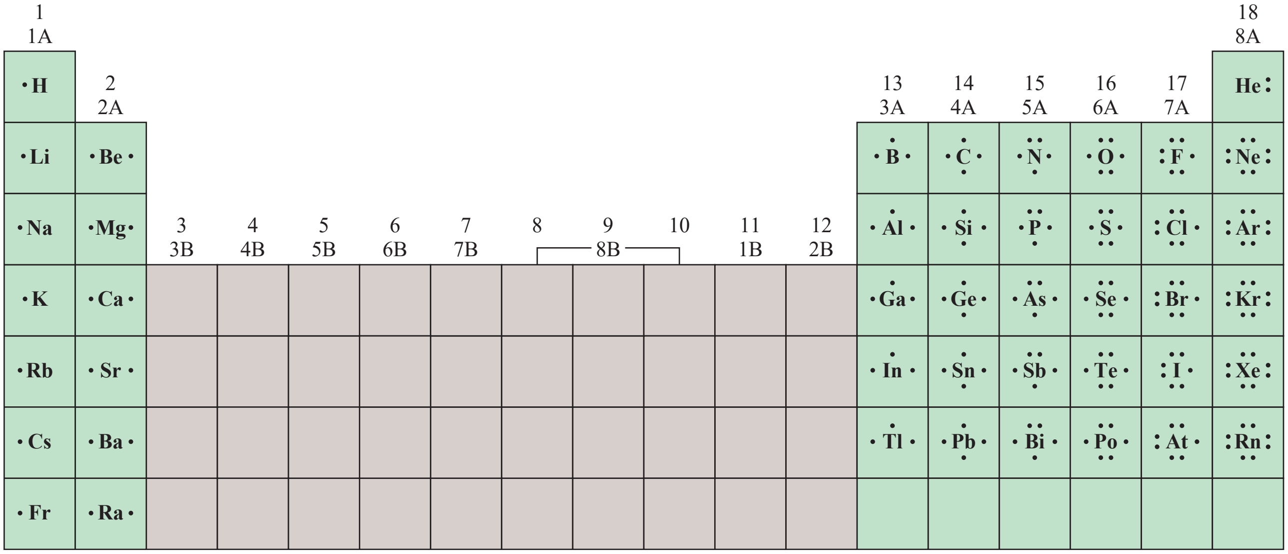


Figure 9.1
Lewis dot symbols for the representative elements and the noble gases. The number of unpaired dots corresponds to the number of bonds an atom of the element can form in a compound.

9.2 The Ionic Bond

Interactivity:
Ionic Bonds
ARIS, Interactives

In Chapter 8 we saw that atoms of elements with low ionization energies tend to form cations, while those with high electron affinities tend to form anions. As a rule, the elements most likely to form cations in ionic compounds are the alkali metals and alkaline earth metals, and the elements most likely to form anions are the halogens and oxygen. Consequently, a wide variety of ionic compounds combine a Group 1A or Group 2A metal with a halogen or oxygen. An ***ionic bond*** is *the electrostatic force that holds ions together in an ionic compound.* Consider, for example, the reaction between lithium and fluorine to form lithium fluoride, a poisonous white powder used in lowering the melting point of solders and in manufacturing ceramics. The electron configuration of lithium is $1s^22s^1$, and that of fluorine is $1s^22s^22p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s^1$ valence electron of lithium is transferred to the fluorine atom. Using Lewis dot symbols, we represent the reaction like this:

$$\begin{array}{ccccccc} \cdot\mathrm{Li} & + & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot & \longrightarrow & \mathrm{Li}^+ & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^- & \text{(or LiF)} \\ 1s^22s^1 & & 1s^22s^22p^5 & & 1s^2 & 1s^22s^22p^6 & \end{array} \tag{9.1}$$


Lithium fluoride. Industrially, LiF (like most other ionic compounds) is obtained by purifying minerals containing the compound.

For convenience, imagine that this reaction occurs in separate steps—first the ionization of Li:

$$\cdot\mathrm{Li} \longrightarrow \mathrm{Li}^+ + e^-$$

and then the acceptance of an electron by F:

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot + e^- \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

Next, imagine the two separate ions joining to form a LiF unit:

$$\mathrm{Li}^+ + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^- \longrightarrow \mathrm{Li}^+ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

Note that the sum of these three equations is

$$\cdot\mathrm{Li} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot \longrightarrow \mathrm{Li}^+ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:^-$$

We normally write the empirical formulas of ionic compounds without showing the charges. The + and − are shown here to emphasize the transfer of electrons.

which is the same as Equation (9.1). The ionic bond in LiF is the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.

Many other common reactions lead to the formation of ionic bonds. For instance, calcium burns in oxygen to form calcium oxide:

$$2\mathrm{Ca}(s) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{CaO}(s)$$

Assuming that the diatomic O_2 molecule first splits into separate oxygen atoms (we will look at the energetics of this step later), we can represent the reaction with Lewis symbols:

$$\begin{array}{cccccc} \cdot\mathrm{Ca}\cdot & + & \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot & \longrightarrow & \mathrm{Ca}^{2+} & :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-} \\ [\mathrm{Ar}]4s^2 & & 1s^22s^22p^4 & & [\mathrm{Ar}] & [\mathrm{Ne}] \end{array}$$

There is a transfer of two electrons from the calcium atom to the oxygen atom. Note that the resulting calcium ion (Ca^{2+}) has the argon electron configuration, the oxide ion (O^{2-}) is isoelectronic with neon, and the compound (CaO) is electrically neutral.

In many cases, the cation and the anion in a compound do not carry the same charges. For instance, when lithium burns in air to form lithium oxide (Li_2O), the balanced equation is

$$4\text{Li}(s) + \text{O}_2(g) \longrightarrow 2\text{Li}_2\text{O}(s)$$

Using Lewis dot symbols, we write

$$\begin{array}{ccccccc} 2\ \cdot\text{Li} & + & \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}\cdot & \longrightarrow & 2\text{Li}^{+} & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}:^{2-} & (\text{or Li}_2\text{O}) \\ 1s^22s^1 & & 1s^22s^22p^4 & & [\text{He}] & [\text{Ne}] & \end{array}$$

In this process, the oxygen atom receives two electrons (one from each of the two lithium atoms) to form the oxide ion. The Li^+ ion is isoelectronic with helium.

When magnesium reacts with nitrogen at elevated temperatures, a white solid compound, magnesium nitride (Mg_3N_2), forms:

$$3\text{Mg}(s) + \text{N}_2(g) \longrightarrow \text{Mg}_3\text{N}_2(s)$$

or

$$\begin{array}{ccccccc} 3\ \cdot\text{Mg}\cdot & + & 2\ \cdot\underset{\cdot}{\overset{\cdot\cdot}{\text{N}}}\cdot & \longrightarrow & 3\text{Mg}^{2+} & 2\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{N}}}:^{3-} & (\text{or Mg}_3\text{N}_2) \\ [\text{Ne}]3s^2 & & 1s^22s^22p^3 & & [\text{Ne}] & [\text{Ne}] & \end{array}$$

The reaction involves the transfer of six electrons (two from each Mg atom) to two nitrogen atoms. The resulting magnesium ion (Mg^{2+}) and the nitride ion (N^{3-}) are both isoelectronic with neon. Because there are three $+2$ ions and two -3 ions, the charges balance and the compound is electrically neutral.


The mineral corundum (Al_2O_3).

Example 9.1

Use Lewis dot symbols to show the formation of aluminum oxide (Al_2O_3).

Strategy We use electroneutrality as our guide in writing formulas for ionic compounds, that is, the total positive charges on the cations must be equal to the total negative charges on the anions.

Solution According to Figure 9.1, the Lewis dot symbols of Al and O are

$$\cdot\overset{\cdot}{\text{Al}}\cdot \qquad \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}\cdot$$

Because aluminum tends to form the cation (Al^{3+}) and oxygen the anion (O^{2-}) in ionic compounds, the transfer of electrons is from Al to O. There are three valence electrons in each Al atom; each O atom needs two electrons to form the O^{2-} ion, which is isoelectronic with neon. Thus, the simplest neutralizing ratio of Al^{3+} to O^{2-} is 2:3; two Al^{3+} ions have a total charge of $+6$, and three O^{2-} ions have a total charge of -6. So the empirical formula of aluminum oxide is Al_2O_3, and the reaction is

$$\begin{array}{ccccccc} 2\ \cdot\overset{\cdot}{\text{Al}}\cdot & + & 3\ \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}\cdot & \longrightarrow & 2\text{Al}^{3+} & 3\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{O}}}:^{2-} & (\text{or Al}_2\text{O}_3) \\ [\text{Ne}]3s^23p^1 & & 1s^22s^22p^4 & & [\text{Ne}] & [\text{Ne}] & \end{array}$$

Check Make sure that the number of valence electrons (24) is the same on both sides of the equation. Are the subscripts in Al_2O_3 reduced to the smallest possible whole numbers?

9.3 Lattice Energy of Ionic Compounds

We can predict which elements are likely to form ionic compounds based on ionization energy and electron affinity, but how do we evaluate the stability of an ionic compound? Ionization energy and electron affinity are defined for processes occurring in the gas phase, but at 1 atm and 25°C all ionic compounds are solids. The solid state is a very different environment because each cation in a solid is surrounded by a specific number of anions, and vice versa. Thus, the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion. A quantitative measure of the stability of any ionic solid is its ***lattice energy,*** defined as *the energy required to completely separate one mole of a solid ionic compound into gaseous ions.*

The Born-Haber Cycle for Determining Lattice Energies

Lattice energy cannot be measured directly. However, if we know the structure and composition of an ionic compound, we can calculate the compound's lattice energy by using ***Coulomb's law,*** which states that *the potential energy (E) between two ions is directly proportional to the product of their charges and inversely proportional to the distance of separation between them.*

We can also determine lattice energy indirectly, by assuming that the formation of an ionic compound takes place in a series of steps. This procedure, known as the ***Born-Haber cycle,*** *relates lattice energies of ionic compounds to ionization energies, electron affinities, and other atomic and molecular properties.* It is based on Hess's law. Developed by the German physicist Max Born and the German chemist Fritz Haber, the Born-Haber cycle defines the various steps that precede the formation of an ionic solid. We will illustrate its use to find the lattice energy of lithium fluoride.

Consider the reaction between lithium and fluorine:

$$\mathrm{Li}(s) + \tfrac{1}{2}\mathrm{F}_2(g) \longrightarrow \mathrm{LiF}(s)$$

The standard enthalpy change for this reaction is −594.1 kJ/mol. (Because the reactants and product are in their standard states, that is, at 1 atm, the enthalpy change is also the standard enthalpy of formation for LiF.) Keeping in mind that the sum of enthalpy changes for the steps is equal to the enthalpy change for the overall reaction (−594.1 kJ/mol), we can trace the formation of LiF from its elements through five separate steps. The process may not occur exactly this way, but this pathway enables us to analyze the energy changes of ionic compound formation, with the application of Hess's law.

1. Convert solid lithium to lithium vapor (the direct conversion of a solid to a gas is called sublimation):

   $$\mathrm{Li}(s) \longrightarrow \mathrm{Li}(g) \qquad \Delta H_1^\circ = 155.2\ \mathrm{kJ/mol}$$

   The energy of sublimation for lithium is 155.2 kJ/mol.
2. Dissociate $\frac{1}{2}$ mole of F_2 gas into separate gaseous F atoms:

   $$\tfrac{1}{2}\mathrm{F}_2(g) \longrightarrow \mathrm{F}(g) \qquad \Delta H_2^\circ = 75.3\ \mathrm{kJ/mol}$$

   The energy needed to break the bonds in 1 mole of F_2 molecules is 150.6 kJ. Here we are breaking the bonds in half a mole of F_2, so the enthalpy change is 150.6/2, or 75.3, kJ.
3. Ionize 1 mole of gaseous Li atoms (see Table 8.3):

   $$\mathrm{Li}(g) \longrightarrow \mathrm{Li}^+(g) + e^- \qquad \Delta H_3^\circ = 520\ \mathrm{kJ/mol}$$

   This process corresponds to the first ionization of lithium.
4. Add 1 mole of electrons to 1 mole of gaseous F atoms. As discussed on page 259, the energy change for this process is just the opposite of electron affinity:

   $$\mathrm{F}(g) + e^- \longrightarrow \mathrm{F}^-(g) \qquad \Delta H_4^\circ = -328\ \mathrm{kJ/mol}$$

5. Combine 1 mole of gaseous Li^+ and 1 mole of F^- to form 1 mole of solid LiF:

   $$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \longrightarrow \mathrm{LiF}(s) \qquad \Delta H_5^\circ = ?$$

The reverse of step 5,

$$\text{energy} + \mathrm{LiF}(s) \longrightarrow \mathrm{Li}^+(g) + \mathrm{F}^-(g)$$

defines the lattice energy of LiF. Thus, the lattice energy must have the same magnitude as ΔH_5° but an opposite sign. Although we cannot determine ΔH_5° directly, we can calculate its value by the following procedure:

$$\begin{array}{lrll}
1. & \mathrm{Li}(s) \longrightarrow & \mathrm{Li}(g) & \Delta H_1^\circ = 155.2\ \mathrm{kJ/mol} \\
2. & \frac{1}{2}\mathrm{F}_2(g) \longrightarrow & \mathrm{F}(g) & \Delta H_2^\circ = 75.3\ \mathrm{kJ/mol} \\
3. & \mathrm{Li}(g) \longrightarrow & \mathrm{Li}^+(g) + e^- & \Delta H_3^\circ = 520\ \mathrm{kJ/mol} \\
4. & \mathrm{F}(g) + e^- \longrightarrow & \mathrm{F}^-(g) & \Delta H_4^\circ = -328\ \mathrm{kJ/mol} \\
5. & \mathrm{Li}^+(g) + \mathrm{F}^-(g) \longrightarrow & \mathrm{LiF}(s) & \Delta H_5^\circ = ? \\
\hline
 & \mathrm{Li}(s) + \frac{1}{2}\mathrm{F}_2(g) \longrightarrow & \mathrm{LiF}(s) & \Delta H_{\mathrm{overall}}^\circ = -594.1\ \mathrm{kJ/mol}
\end{array}$$

According to Hess's law, we can write

$$\Delta H_{\mathrm{overall}}^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ + \Delta H_4^\circ + \Delta H_5^\circ$$

or

$$-594.1\ \mathrm{kJ/mol} = 155.2\ \mathrm{kJ/mol} + 75.3\ \mathrm{kJ/mol} + 520\ \mathrm{kJ/mol} - 328\ \mathrm{kJ/mol} + \Delta H_5^\circ$$

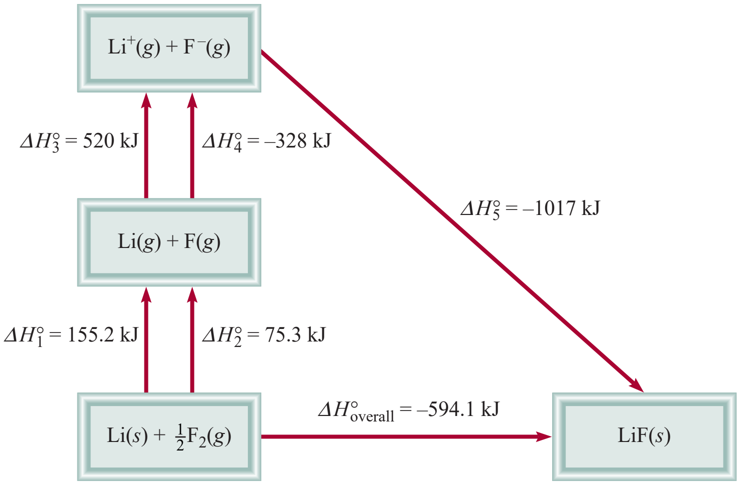


Figure 9.2
The Born-Haber cycle for the formation of 1 mole of solid LiF.

Hence,

$$\Delta H_5^\circ = -1017 \text{ kJ/mol}$$

and the lattice energy of LiF is +1017 kJ/mol.

Figure 9.2 summarizes the Born-Haber cycle for LiF. Steps 1, 2, and 3 all require the input of energy. On the other hand, steps 4 and 5 release energy. Because ΔH_5° is a large negative quantity, the lattice energy of LiF is a large positive quantity, which accounts for the stability of solid LiF. The greater the lattice energy, the more stable the ionic compound. Keep in mind that lattice energy is *always* a positive quantity because the separation of ions in a solid into ions in the gas phase is, by Coulomb's law, an endothermic process.

Table 9.1 lists the lattice energies and the melting points of several common ionic compounds. There is a rough correlation between lattice energy and melting point. The larger the lattice energy, the more stable the solid and the more tightly held the ions. It takes more energy to melt such a solid, and so the solid has a higher melting point than one with a smaller lattice energy. Note that $MgCl_2$, MgO, and CaO have unusually high lattice energies. The first of these ionic compounds has a doubly charged cation (Mg^{2+}) and in the second and third compounds there is an interaction between two doubly charged species (Mg^{2+} or Ca^{2+} and O^{2-}). The coulombic attractions between two doubly charged species, or between a doubly charged ion and a singly charged ion, are much stronger than those between singly charged anions and cations.

TABLE 9.1

Lattice Energies and Melting Points of Some Ionic Compounds

	Lattice Energy (kJ/mol)	Melting Point (°C)
LiF	1017	845
LiCl	828	610
NaCl	788	801
NaBr	736	750
$MgCl_2$	2527	714
MgO	3890	2800
CaO	3414	2580

9.4 The Covalent Bond

Although the concept of molecules goes back to the seventeenth century, it was not until early in the twentieth century that chemists began to understand how and why molecules form. The first major breakthrough was Gilbert Lewis's suggestion that a chemical bond involves electron sharing by atoms. He depicted the formation of a chemical bond in H_2 as

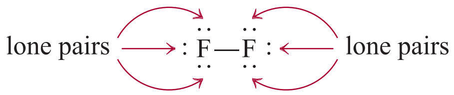
$$\mathrm{H}\cdot \;+\; \cdot\mathrm{H} \longrightarrow \mathrm{H}:\mathrm{H}$$

This type of electron pairing is an example of a ***covalent bond,*** *a bond in which two electrons are shared by two atoms.* ***Covalent compounds*** are *compounds that contain* *only covalent bonds.* For the sake of simplicity, the shared pair of electrons is often represented by a single line. Thus, the covalent bond in the hydrogen molecule can be written as H—H. In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in H_2 together and is responsible for the formation of covalent bonds in other molecules.

Covalent bonding between many-electron atoms involves only the valence electrons. Consider the fluorine molecule, F_2. The electron configuration of F is $1s^22s^22p^5$. The $1s$ electrons are low in energy and stay near the nucleus most of the time. For this reason they do not participate in bond formation. Thus, each F atom has seven valence electrons (the $2s$ and $2p$ electrons). According to Figure 9.1, there is only one unpaired electron on F, so the formation of the F_2 molecule can be represented as follows:

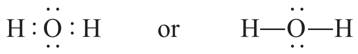
$$:\underset{..}{\ddot{F}}\cdot + \cdot\underset{..}{\ddot{F}}: \longrightarrow :\underset{..}{\ddot{F}}:\underset{..}{\ddot{F}}: \quad \text{or} \quad :\underset{..}{\ddot{F}}-\underset{..}{\ddot{F}}:$$

Note that only two valence electrons participate in the formation of F_2. The other, nonbonding electrons, are called ***lone pairs***—*pairs of valence electrons that are not involved in covalent bond formation.* Thus, each F in F_2 has three lone pairs of electrons:



The structures we use to represent covalent compounds, such as H_2 and F_2, are called Lewis structures. A ***Lewis structure*** is *a representation of covalent bonding in which shared electron pairs are shown either as lines or as pairs of dots between two atoms, and lone pairs are shown as pairs of dots on individual atoms.* Only valence electrons are shown in a Lewis structure.

Let us consider the Lewis structure of the water molecule. Figure 9.1 shows the Lewis dot symbol for oxygen with two unpaired dots or two unpaired electrons, as we expect that O might form two covalent bonds. Because hydrogen has only one electron, it can form only one covalent bond. Thus, the Lewis structure for water is



$$H:\underset{..}{\ddot{O}}:H \quad \text{or} \quad H-\underset{..}{\ddot{O}}-H$$

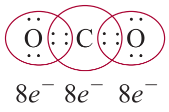
In this case, the O atom has two lone pairs. The hydrogen atom has no lone pairs because its only electron is used to form a covalent bond.

In the F_2 and H_2O molecules, the F and O atoms achieve the stable noble gas configuration by sharing electrons:

The formation of these molecules illustrates the ***octet rule,*** formulated by Lewis: *An atom other than hydrogen tends to form bonds until it is surrounded by eight valence electrons.* In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electron configuration of helium, or a total of two electrons.

The octet rule works mainly for elements in the second period of the periodic table. These elements have only 2*s* and 2*p* subshells, which can hold a total of eight electrons. When an atom of one of these elements forms a covalent compound, it can attain the noble gas electron configuration [Ne] by sharing electrons with other atoms in the same compound. Later, we will discuss a number of important exceptions to the octet rule that give us further insight into the nature of chemical bonding.

Atoms can form different types of covalent bonds. In a ***single bond,*** *two atoms are held together by one electron pair.* Many compounds are held together by ***multiple bonds,*** that is, bonds formed when *two atoms share two or more pairs of electrons.* If *two atoms share two pairs of electrons,* the covalent bond is called a ***double bond.*** Double bonds are found in molecules of carbon dioxide (CO_2) and ethylene (C_2H_4):



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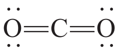
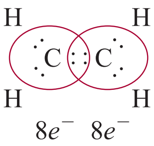


$\ddot{\underset{..}{O}}=C=\ddot{\underset{..}{O}}$



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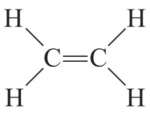
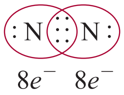


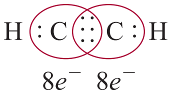
A ***triple bond*** arises when *two atoms share three pairs of electrons,* as in the nitrogen molecule (N_2):



or

$:N\equiv N:$

The acetylene molecule (C_2H_2) also contains a triple bond, in this case between two carbon atoms:



or

$H—C\equiv C—H$

Note that in ethylene and acetylene all the valence electrons are used in bonding; there are no lone pairs on the carbon atoms. In fact, with the exception of carbon monoxide, the vast majority of stable molecules containing carbon do not have lone pairs on the carbon atoms.

Multiple bonds are shorter than single covalent bonds. ***Bond length*** is defined as the *distance between the nuclei of two covalently bonded atoms in a molecule* (Figure 9.3). Table 9.2 shows some experimentally determined bond lengths. For a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds. The shorter multiple bonds are also more stable than single bonds, as we will see later.

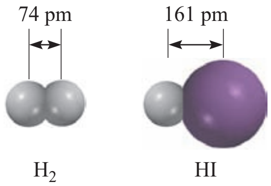


Figure 9.3
Bond length (in pm) in H_2 and HI.

TABLE 9.2

Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C═O	121
C—C	154
C═C	133
C≡C	120
C—N	143
C═N	138
C≡N	116
N—O	136
N═O	122
O—H	96

9.5 Electronegativity

A covalent bond, as we have said, is the sharing of an electron pair by two atoms. In a molecule like H_2, in which the atoms are identical, we expect the electrons to be equally shared—that is, the electrons spend the same amount of time in the vicinity of each atom. However, in the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally because H and F are different atoms:

$H—\ddot{\underset{..}{F}}:$

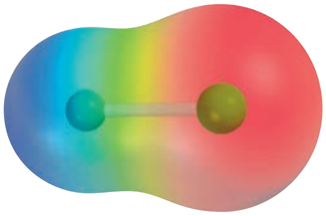


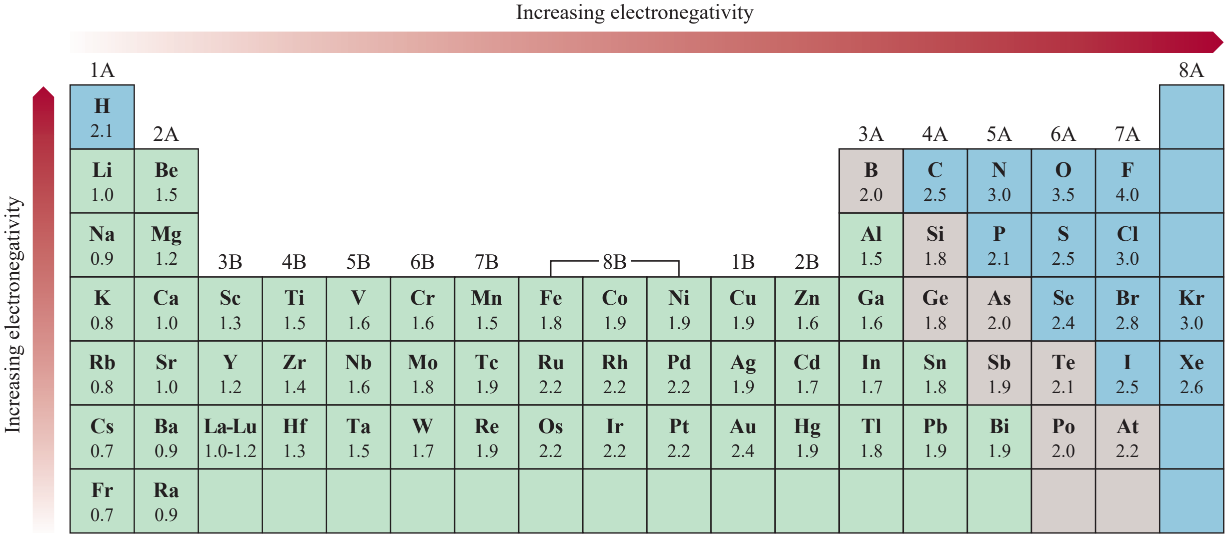
Figure 9.4
Electrostatic potential map of the HF molecule. The distribution varies according to the colors of the rainbow. The most electron-rich region is red; the most electron-poor region is blue.

The bond in HF is called a ***polar covalent bond,*** or simply a *polar bond,* because *the electrons spend more time in the vicinity of one atom than the other.* Experimental evidence indicates that in the HF molecule the electrons spend more time near the F atom. We can think of this unequal sharing of electrons as a partial electron transfer or a shift in electron density, as it is more commonly described, from H to F (Figure 9.4). This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. The HF bond and other polar bonds can be thought of as being intermediate between a (nonpolar) covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the transfer of the electron(s) is nearly complete.

A property that helps us distinguish a nonpolar covalent bond from a polar covalent bond is ***electronegativity,*** *the ability of an atom to attract toward itself the electrons in a chemical bond.* Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity. As we might expect, electronegativity is related to electron affinity and ionization energy. Thus, an atom such as fluorine, which has a high electron affinity (tends to pick up electrons easily) and a high ionization energy (does not lose electrons easily), has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

Electronegativity values have no units.

Electronegativity is a relative concept, meaning that an element's electronegativity can be measured only in relation to the electronegativity of other elements. The American chemist Linus Pauling devised a method for calculating *relative* electronegativities of most elements. These values are shown in Figure 9.5. A careful examination of this chart reveals trends and relationships among electronegativity values of different elements. In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character. Note that the transition metals do not follow



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	
K 0.8	**Ca** 1.0	**Sc** 1.3	**Ti** 1.5	**V** 1.6	**Cr** 1.6	**Mn** 1.5	**Fe** 1.8	**Co** 1.9	**Ni** 1.9	**Cu** 1.9	**Zn** 1.6	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8	**Kr** 3.0
Rb 0.8	**Sr** 1.0	**Y** 1.2	**Zr** 1.4	**Nb** 1.6	**Mo** 1.8	**Tc** 1.9	**Ru** 2.2	**Rh** 2.2	**Pd** 2.2	**Ag** 1.9	**Cd** 1.7	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5	**Xe** 2.6
Cs 0.7	**Ba** 0.9	**La-Lu** 1.0-1.2	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.9	**Bi** 1.9	**Po** 2.0	**At** 2.2	
Fr 0.7	**Ra** 0.9																

Figure 9.5
The electronegativities of common elements.

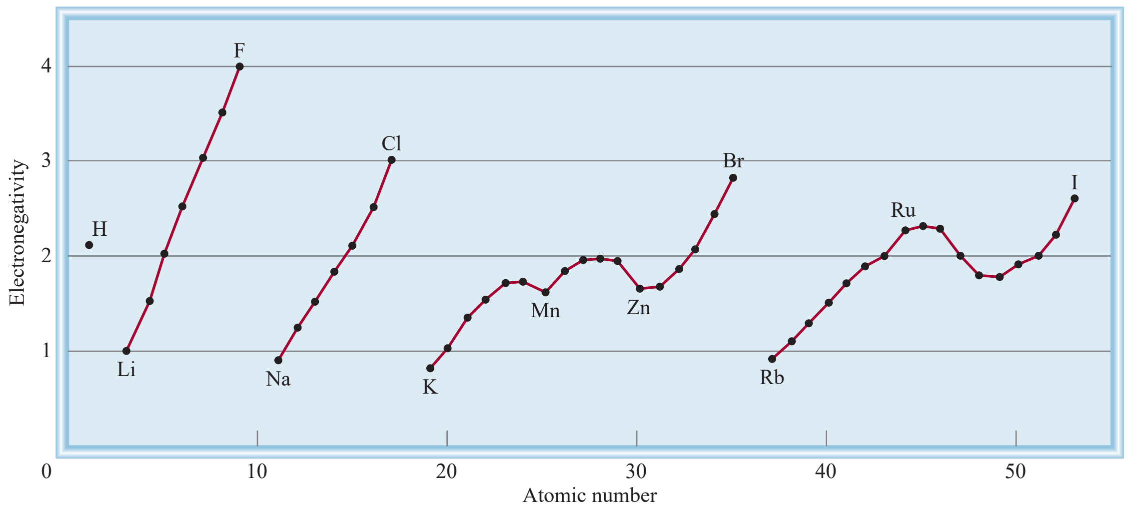


Figure 9.6

Variation of electronegativity with atomic number. The halogens have the highest electronegativities, and the alkali metals the lowest.

these trends. The most electronegative elements—the halogens, oxygen, nitrogen, and sulfur—are found in the upper right-hand corner of the periodic table, and the least electronegative elements (the alkali and alkaline earth metals) are clustered near the lower left-hand corner. These trends are readily apparent on a graph, as shown in Figure 9.6.

Atoms of elements with widely different electronegativities tend to form ionic bonds (such as those that exist in NaCl and CaO compounds) with each other because the atom of the less electronegative element gives up its electron(s) to the atom of the more electronegative element. An ionic bond generally joins an atom of a metallic element and an atom of a nonmetallic element. Atoms of elements with comparable electronegativities tend to form polar covalent bonds with each other because the shift in electron density is usually small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same element, which have the same electronegativity, can be joined by a pure covalent bond. These trends and characteristics are what we would expect, given our knowledge of ionization energies and electron affinities.

There is no sharp distinction between a polar covalent bond and an ionic bond, but the following rules are helpful as a rough guide. An ionic bond forms when the electronegativity difference between the two bonding atoms is 2.0 or more. This rule applies to most but not all ionic compounds. A polar covalent bond forms when the electronegativity difference between the atoms is in the range of 0.5–1.6. If the electronegativity difference is below 0.3, the bond is normally classified as a covalent bond, with little or no polarity. Sometimes chemists use the quantity *percent ionic character* to describe the nature of a bond. A purely ionic bond would have 100 percent ionic character, although no such bond is known, whereas a purely covalent bond (such as that in H_2) has 0 percent ionic character. As Figure 9.7 shows, there is a correlation between the percent ionic character of a bond and the electronegativity difference between the bonding atoms.

Electronegativity and electron affinity are related but different concepts. Both indicate the tendency of an atom to attract electrons. However, electron affinity

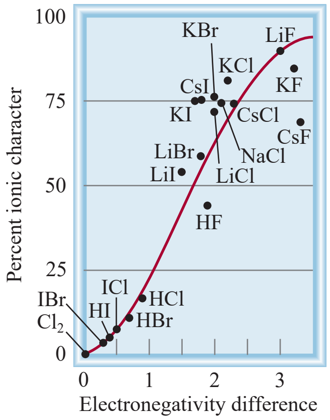
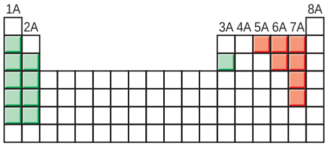


Figure 9.7

Relation between percent ionic character and electronegativity difference.

refers to an isolated atom's attraction for an additional electron, whereas electronegativity signifies the ability of an atom in a chemical bond (with another atom) to attract the shared electrons. Furthermore, electron affinity is an experimentally measurable quantity, whereas electronegativity is an estimated number that cannot be measured.



The most electronegative elements are the nonmetals (Groups 5A–7A) and the least electronegative elements are the alkali and alkaline earth metals (Groups 1A–2A) and aluminum. Beryllium, the first member of Group 2A, forms mostly covalent compounds.

Example 9.2

Classify the following bonds as ionic, polar covalent, or covalent: (a) the bond in HCl, (b) the bond in KF, and (c) the CC bond in H_3CCH_3.

Strategy We follow the 2.0 rule of electronegativity difference and look up the values in Figure 9.5.

Solution (a) The electronegativity difference between H and Cl is 0.9, which is appreciable but not large enough (by the 2.0 rule) to qualify HCl as an ionic compound. Therefore, the bond between H and Cl is polar covalent.

(b) The electronegativity difference between K and F is 3.2, which is well above the 2.0 mark; therefore, the bond between K and F is ionic.

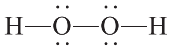
(c) The two C atoms are identical in every respect—they are bonded to each other and each is bonded to three other H atoms. Therefore, the bond between them is purely covalent.

Electronegativity and Oxidation Number

In Chapter 4 we introduced the rules for assigning oxidation numbers of elements in their compounds. The concept of electronegativity is the basis for these rules. In essence, oxidation number refers to the number of charges an atom would have if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Consider the NH_3 molecule, in which the N atom forms three single bonds with the H atoms. Because N is more electronegative than H, electron density will be shifted from H to N. If the transfer were complete, each H would donate an electron to N, which would have a total charge of -3 while each H would have a charge of $+1$. Thus, we assign an oxidation number of -3 to N and an oxidation number of $+1$ to H in NH_3.

Oxygen usually has an oxidation number of -2 in its compounds, except in hydrogen peroxide (H_2O_2), whose Lewis structure is



$$\mathrm{H{-}\underset{..}{\ddot{O}}{-}\underset{..}{\ddot{O}}{-}H}$$

A bond between identical atoms makes no contribution to the oxidation number of those atoms because the electron pair of that bond is *equally* shared. Because H has an oxidation number of $+1$, each O atom has an oxidation number of -1.

Can you see now why fluorine always has an oxidation number of -1? It is the most electronegative element known, and it *usually* forms a single bond in its compounds. Therefore, it would bear a -1 charge if electron transfer were complete.

9.6 Writing Lewis Structures

Interactivity:
Lewis Dot Structure
ARIS, Interactives

Although the octet rule and Lewis structures do not present a complete picture of covalent bonding, they do help to explain the bonding scheme in many compounds and account for the properties and reactions of molecules. For this reason, you should practice writing Lewis structures of compounds. The basic steps are as follows:

1. Write the skeletal structure of the compound, using chemical symbols and placing bonded atoms next to one another. For simple compounds, this task is fairly easy. For more complex compounds, we must either be given the information or make an intelligent guess about it. In general, the least electronegative atom occupies the central position. Hydrogen and fluorine usually occupy the terminal (end) positions in the Lewis structure.
2. Count the total number of valence electrons present, referring, if necessary, to Figure 9.1. For polyatomic anions, add the number of negative charges to that total. (For example, for the CO_3^{2-} ion we add two electrons because the 2− charge indicates that there are two more electrons than are provided by the atoms.) For polyatomic cations, we subtract the number of positive charges from this total. (Thus, for NH_4^+ we subtract one electron because the 1+ charge indicates a loss of one electron from the group of atoms.)
3. Draw a single covalent bond between the central atom and each of the surrounding atoms. Complete the octets of the atoms bonded to the central atom. (Remember that the valence shell of a hydrogen atom is complete with only two electrons.) Electrons belonging to the central or surrounding atoms must be shown as lone pairs if they are not involved in bonding. The total number of electrons to be used is that determined in step 2.
4. After completing steps 1–3, if the central atom has fewer than eight electrons, try adding double or triple bonds between the surrounding atoms and the central atom, using lone pairs from the surrounding atoms to complete the octet of the central atom.

Example 9.3

Write the Lewis structure for nitrogen trifluoride (NF_3) in which all three F atoms are bonded to the N atom.

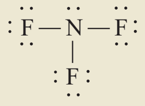
Solution We follow the preceding procedure for writing Lewis structure.

Step 1: The N atom is less electronegative than F, so the skeletal structure of NF_3 is

F N F
F

Step 2: The outer-shell electron configurations of N and F are $2s^22p^3$ and $2s^22p^5$, respectively. Thus, there are 5 + (3 × 7), or 26, valence electrons to account for in NF_3.

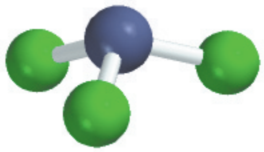
Step 3: We draw a single covalent bond between N and each F, and complete the octets for the F atoms. We place the remaining two electrons on N:



$$\begin{array}{c} :\underset{..}{\ddot{F}}-\ddot{N}-\underset{..}{\ddot{F}}: \\ | \\ :\underset{..}{F}: \end{array}$$

Because this structure satisfies the octet rule for all the atoms, step 4 is not required.

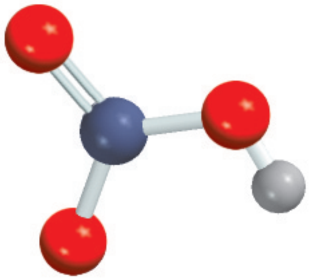
(Continued)



NF_3 is a colorless, odorless, unreactive gas.

Check Count the valence electrons in NF_3 (in bonds and in lone pairs). The result is 26, the same as the total number of valence electrons on three F atoms ($3 \times 7 = 21$) and one N atom (5).

Similar problem: 9.41.



HNO_3 is a strong electrolyte.

Example 9.4

Write the Lewis structure for nitric acid (HNO_3) in which the three O atoms are bonded to the central N atom and the ionizable H atom is bonded to one of the O atoms.

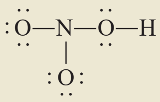
Solution We follow the procedure already outlined for writing Lewis structure.

Step 1: The skeletal structure of HNO_3 is

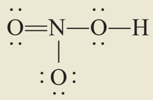
O N O H
O

Step 2: The outer-shell electron configurations of N, O, and H are $2s^22p^3$, $2s^22p^4$, and $1s^1$, respectively. Thus, there are $5 + (3 \times 6) + 1$, or 24, valence electrons to account for in HNO_3.

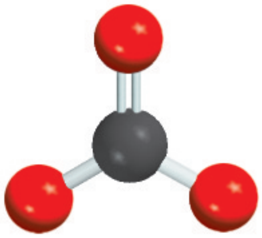
Step 3: We draw a single covalent bond between N and each of the three O atoms and between one O atom and the H atom. Then we fill in electrons to comply with the octet rule for the O atoms:



Step 4: We see that this structure satisfies the octet rule for all the O atoms but not for the N atom. The N atom has only six electrons. Therefore, we move a lone pair from one of the end O atoms to form another bond with N. Now the octet rule is also satisfied for the N atom:



Check Make sure that all the atoms (except H) satisfy the octet rule. Count the valence electrons in HNO_3 (in bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ($3 \times 6 = 18$), one N atom (5), and one H atom (1).



CO_3^{2-}

Example 9.5

Write the Lewis structure for the carbonate ion (CO_3^{2-}).

Solution We follow the preceding procedure for writing Lewis structures and note that this is an anion with two negative charges.

(Continued)

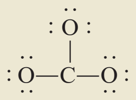
Step 1: We can deduce the skeletal structure of the carbonate ion by recognizing that C is less electronegative than O. Therefore, it is most likely to occupy a central position as follows:

O

O C O

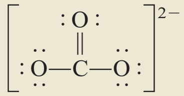
Step 2: The outer-shell electron configurations of C and O are $2s^22p^2$ and $2s^22p^4$, respectively, and the ion itself has two negative charges. Thus, the total number of electrons is $4 + (3 \times 6) + 2$, or 24.

Step 3: We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms:



This structure shows all 24 electrons.

Step 4: Although the octet rule is satisfied for the O atoms, it is not for the C atom. Therefore, we move a lone pair from one of the O atoms to form another bond with C. Now the octet rule is also satisfied for the C atom:



We use the brackets to indicate that the −2 charge is on the whole molecule.

Check Make sure that all the atoms satisfy the octet rule. Count the valence electrons in CO_3^{2-} (in chemical bonds and in lone pairs). The result is 24, the same as the total number of valence electrons on three O atoms ($3 \times 6 = 18$), one C atom (4), and two negative charges (2).

Similar problem: 9.42.

$\overline{2}$

9.7 Formal Charge and Lewis Structure

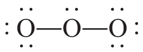
By comparing the number of electrons in an isolated atom with the number of electrons that are associated with the same atom in a Lewis structure, we can determine the distribution of electrons in the molecule and draw the most plausible Lewis structure. The bookkeeping procedure is as follows: In an isolated atom, the number of electrons associated with the atom is simply the number of valence electrons. (As usual, we need not be concerned with the inner electrons.) In a molecule, electrons associated with the atom are the nonbonding electrons plus the electrons in the bonding pair(s) between the atom and other atom(s). However, because electrons are shared in a bond, we must divide the electrons in a bonding pair equally between the atoms forming the bond. An atom's ***formal charge*** is *the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.*

To assign the number of electrons on an atom in a Lewis structure, we proceed as follows:

- All the atom's nonbonding electrons are assigned to the atom.
- We break the bond(s) between the atom and other atom(s) and assign half of the bonding electrons to the atom.

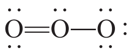
Liquid ozone below its boiling point (−111.3°C). Ozone is a toxic, light-blue gas with a pungent odor.

Let us illustrate the concept of formal charge using the ozone molecule (O_3). Proceeding by steps, as we did in Examples 9.3 and 9.4, we draw the skeletal structure of O_3 and then add bonds and electrons to satisfy the octet rule for the two end atoms:



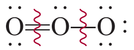
$$:\overset{..}{\underset{..}{O}}-\overset{..}{O}-\overset{..}{\underset{..}{O}}:$$

You can see that although all available electrons are used, the octet rule is not satisfied for the central atom. To remedy this, we convert a lone pair on one of the end atoms to a second bond between that end atom and the central atom, as follows:



$$\overset{..}{\underset{..}{O}}=\overset{..}{O}-\overset{..}{\underset{..}{O}}:$$

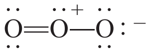
The formal charge on each atom in O_3 can now be calculated according to the following scheme:



Valence e^-	6	6	6
e^- assigned to atom	6	5	7
Difference (formal charge)	0	+1	−1

where the wavy red lines denote the breaking of the bonds. Note that the breaking of a single bond results in the transfer of an electron, the breaking of a double bond results in a transfer of two electrons to each of the bonding atoms, and so on. Thus, the formal charges of the atoms in O_3 are

By the same token, the breaking of a triple bond transfers three electrons to each of the bonding atoms.



$$\overset{..}{\underset{..}{O}}=\overset{..+}{O}-\overset{..}{\underset{..}{O}}:^{-}$$

For single positive and negative charges, we normally omit the numeral 1.

When you write formal charges, these rules are helpful:

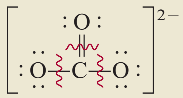
1. For molecules, the sum of the formal charges must add up to zero because molecules are electrically neutral species. (This rule applies, for example, to the O_3 molecule.)
2. For cations, the sum of the formal charges must equal the positive charge.
3. For anions, the sum of the formal charges must equal the negative charge.

Keep in mind that formal charges do not represent actual charge separation within the molecule. In the O_3 molecule, for example, there is no evidence that the central atom bears a net +1 charge or that one of the end atoms bears a −1 charge. Writing these charges on the atoms in the Lewis structure merely helps us keep track of the valence electrons in the molecule.

Example 9.6

Write formal charges for the carbonate ion.

Solution The Lewis structure for the carbonate ion was developed in Example 9.5:



The formal charges on the atoms can be calculated using the given procedure.

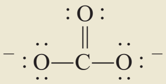
(Continued)

The C atom: The C atom has four valence electrons and there are no nonbonding electrons on the atom in the Lewis structure. The breaking of the double bond and two single bonds results in the transfer of four electrons to the C atom. Therefore, the formal charge is $4 - 4 = 0$.

The O atom in C═O: The O atom has six valence electrons and there are four nonbonding electrons on the atom. The breaking of the double bond results in the transfer of two electrons to the O atom. Here the formal charge is $6 - 4 - 2 = 0$.

The O atom in C—O: This atom has six nonbonding electrons and the breaking of the single bond transfers another electron to it. Therefore, the formal charge is $6 - 6 - 1 = -1$.

Thus, the Lewis structure for CO_3^{2-} with formal charges is



$$\begin{array}{c} :\!\mathrm{O}\!: \\ \| \\ {}^{-}:\!\ddot{\underset{..}{\mathrm{O}}}\!-\!\mathrm{C}\!-\!\ddot{\underset{..}{\mathrm{O}}}\!:{}^{-} \end{array}$$

Check Note that the sum of the formal charges is -2, the same as the charge on the carbonate ion.

$\overline{2}$

Similar problem: 9.42.

Sometimes there is more than one acceptable Lewis structure for a given species. In such cases, we can often select the most plausible Lewis structure by using formal charges and the following guidelines:

- For molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
- Lewis structures with large formal charges (+2, +3, and/or −2, −3, and so on) are less plausible than those with small formal charges.
- Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Example 9.7

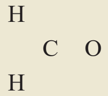
Formaldehyde (CH_2O), a liquid with a disagreeable odor, traditionally has been used to preserve laboratory specimens. Draw the most likely Lewis structure for the compound.

Strategy A plausible Lewis structure should satisfy the octet rule for all the elements, except H, and have the formal charges (if any) distributed according to electronegativity guidelines.

Solution The two possible skeletal structures are

H C O H

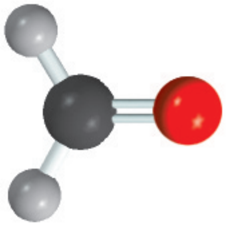
(a)



$$\begin{array}{ll} \mathrm{H} & \\ & \mathrm{C} \quad \mathrm{O} \\ \mathrm{H} & \end{array}$$

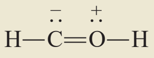
(b)

(*Continued*)

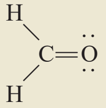


CH_2O

First we draw the Lewis structures for each of these possibilities


$H{-}\overset{-}{C}{=}\overset{+}{O}{-}H$

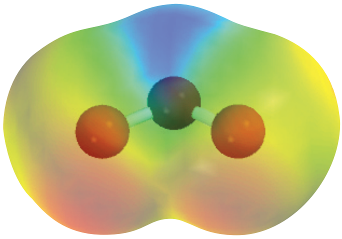
(a)



(b)

To show the formal charges, we follow the procedure given in Example 9.6. In (a), the C atom has a total of five electrons (one lone pair plus three electrons from the breaking of a single and a double bond). Because C has four valence electrons, the formal charge on the atom is $4 - 5 = -1$. The O atom has a total of five electrons (one lone pair and three electrons from the breaking of a single and a double bond). Because O has six valence electrons, the formal charge on the atom is $6 - 5 = +1$. In (b) the C atom has a total of four electrons from the breaking of two single bonds and a double bond, so its formal charge is $4 - 4 = 0$. The O atom has a total of six electrons (two lone pairs and two electrons from the breaking of the double bond). Therefore, the formal charge on the atom is $6 - 6 = 0$. Although both structures satisfy the octet rule, (b) is the more likely structure because it carries no formal charges.

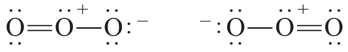
Check In each case, make sure that the total number of valence electrons is 12. Can you suggest two other reasons why (a) is less plausible?



Electrostatic potential map of O_3. The electron density is evenly distributed between the two end O atoms.

9.8 The Concept of Resonance

Our drawing of the Lewis structure for ozone (O_3) satisfied the octet rule for the central atom because we placed a double bond between it and one of the two end O atoms. In fact, we can put the double bond at either end of the molecule, as shown by these two equivalent Lewis structures:


$$O{=}\overset{+}{O}{-}O^{-} \qquad {}^{-}O{-}\overset{+}{O}{=}O$$

However, neither one of these two Lewis structures accounts for the known bond lengths in O_3.

We would expect the O—O bond in O_3 to be longer than the O═O bond because double bonds are known to be shorter than single bonds. Yet experimental evidence shows that both oxygen-to-oxygen bonds are equal in length (128 pm). We resolve this discrepancy by using *both* Lewis structures to represent the ozone molecule:

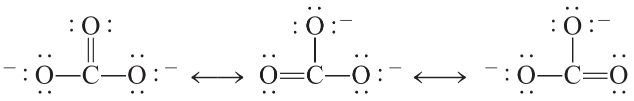

$$O{=}\overset{+}{O}{-}O^{-} \longleftrightarrow {}^{-}O{-}\overset{+}{O}{=}O$$

Each of these structures is called a resonance structure. A ***resonance structure,*** then, is *one of two or more Lewis structures for a single molecule that cannot be represented accurately by only one Lewis structure.* The double-headed arrow indicates that the structures shown are resonance structures.

The term ***resonance*** itself means *the use of two or more Lewis structures to represent a particular molecule.* Like the medieval European traveler to Africa who described a rhinoceros as a cross between a griffin and a unicorn, two familiar but imaginary animals, we describe ozone, a real molecule, in terms of two familiar but nonexistent structures.

A common misconception about resonance is the notion that a molecule such as ozone somehow shifts quickly back and forth from one resonance structure to the other. Keep in mind that *neither* resonance structure adequately represents the actual molecule, which has its own unique, stable structure. "Resonance" is a human invention, designed to address the limitations in these simple bonding models. To extend the animal analogy, a rhinoceros is a distinct creature, not some oscillation between mythical griffin and unicorn!

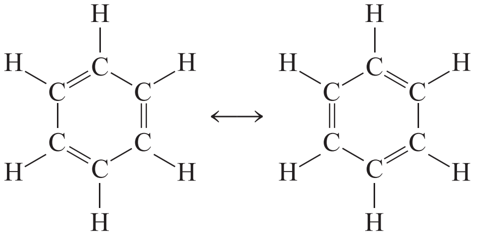
The carbonate ion provides another example of resonance:

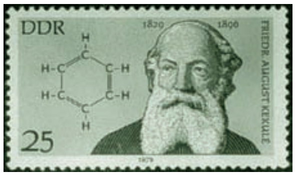


$$^{-}:\ddot{\underset{\cdot\cdot}{O}}-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}:^{-} \longleftrightarrow \ddot{\underset{\cdot\cdot}{O}}=\overset{\overset{:\ddot{O}:^{-}}{|}}{C}-\ddot{\underset{\cdot\cdot}{O}}:^{-} \longleftrightarrow {}^{-}:\ddot{\underset{\cdot\cdot}{O}}-\overset{\overset{:\ddot{O}:^{-}}{|}}{C}=\underset{\cdot\cdot}{O}$$

According to experimental evidence, all carbon-to-oxygen bonds in CO_3^{2-} are equivalent. Therefore, the properties of the carbonate ion are best explained by considering its resonance structures together.

The concept of resonance applies equally well to organic systems. A good example is the benzene molecule (C_6H_6):

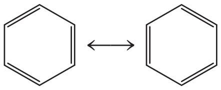




The hexagonal structure of benzene was first proposed by the German chemist August Kekulé (1829–1896).

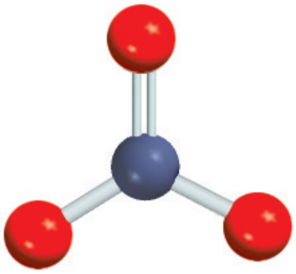
If one of these resonance structures corresponded to the actual structure of benzene, there would be two different bond lengths between adjacent C atoms, one characteristic of the single bond and the other of the double bond. In fact, the distance between all adjacent C atoms in benzene is 140 pm, which is shorter than a C—C bond (154 pm) and longer than a C═C bond (133 pm).

A simpler way of drawing the structure of the benzene molecule and other compounds containing the "benzene ring" is to show only the skeleton and not the carbon and hydrogen atoms. By this convention the resonance structures are represented by



Note that the C atoms at the corners of the hexagon and the H atoms are all omitted, although they are understood to exist. Only the bonds between the C atoms are shown.

Remember this important rule for drawing resonance structures: The positions of electrons (that is, bonds), but not those of atoms, can be rearranged in different resonance structures. In other words, the same atoms must be bonded to one another in all the resonance structures for a given species.



NO_3^-

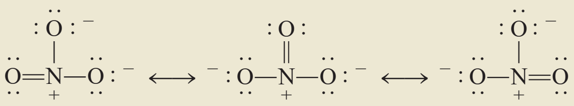
Example 9.8

Draw resonance structures (including formal charges) for the nitrate ion, NO_3^-, which has the following skeletal arrangement:

O
O N O

Strategy We follow the procedure used for drawing Lewis structures and calculating formal charges in Examples 9.5 and 9.6.

Solution Just as in the case of the carbonate ion, we can draw three equivalent resonance structures for the nitrate ion:



$$O=\overset{\overset{O^-}{|}}{N^+}-O^- \longleftrightarrow {}^-O-\overset{\overset{O}{\|}}{N^+}-O^- \longleftrightarrow {}^-O-\overset{\overset{O^-}{|}}{N^+}=O$$

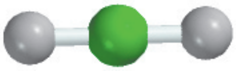
Check Because N has five valence electrons and each O has six valence electrons and there is a net negative charge, the total number of valence electrons is 5 + (3 × 6) + 1 = 24, the same as the number of valence electrons in the NO_3^- ion.

$\overline{2}$

9.9 Exceptions to the Octet Rule

As mentioned earlier, the octet rule applies mainly to the second-period elements. Exceptions to the octet rule fall into three categories characterized by an incomplete octet, an odd number of electrons, or more than eight valence electrons around the central atom.

The Incomplete Octet



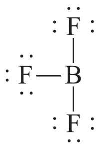
Beryllium, unlike the other Group 2A elements, forms mostly covalent compounds of which BeH_2 is an example.

In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Consider, for example, beryllium, which is a Group 2A (and a second-period) element. The electron configuration of beryllium is $1s^22s^2$; it has two valence electrons in the 2*s* orbital. In the gas phase, beryllium hydride (BeH_2) exists as discrete molecules. The Lewis structure of BeH_2 is

$$H—Be—H$$

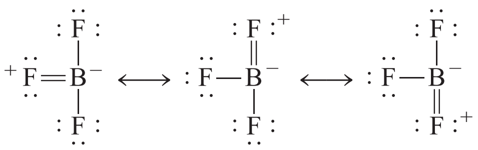
As you can see, only four electrons surround the Be atom, and there is no way to satisfy the octet rule for beryllium in this molecule.

Elements in Group 3A, particularly boron and aluminum, also tend to form compounds in which they are surrounded by fewer than eight electrons. Take boron as an example. Because its electron configuration is $1s^22s^22p^1$, it has a total of three valence electrons. Boron reacts with the halogens to form a class of compounds having the general formula BX_3, where X is a halogen atom. Thus, in boron trifluoride there are only six electrons around the boron atom:



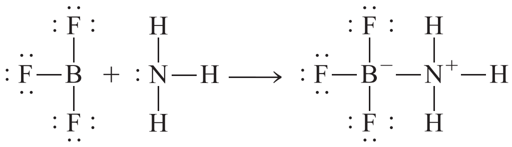
$$F-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{B}}$$

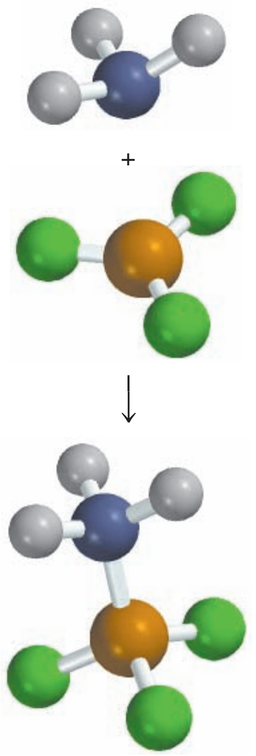
The following resonance structures all contain a double bond between B and F and satisfy the octet rule for boron:



The fact that the B—F bond length in BF_3 (130.9 pm) is shorter than a single bond (137.3 pm) lends support to the resonance structures even though in each case the negative formal charge is placed on the B atom and the positive formal charge on the F atom.

Although boron trifluoride is stable, it readily reacts with ammonia. This reaction is better represented by using the Lewis structure in which boron has only six valence electrons around it:





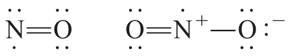
$NH_3 + BF_3 \longrightarrow H_3N—BF_3$

It seems that the properties of the BF_3 molecule are best explained by all four resonance structures.

The B—N bond in the preceding compound is different from the covalent bonds discussed so far in the sense that both electrons are contributed by the N atom. This type of bond is called a ***coordinate covalent bond*** (also referred to as a *dative bond*), defined as *a covalent bond in which one of the atoms donates both electrons.* Although the properties of a coordinate covalent bond do not differ from those of a normal covalent bond (because all electrons are alike no matter what their source), the distinction is useful for keeping track of valence electrons and assigning formal charges.

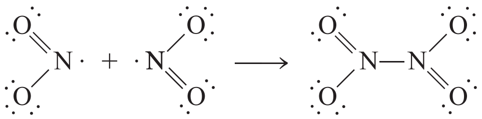
Odd-Electron Molecules

Some molecules contain an *odd* number of electrons. Among them are nitric oxide (NO) and nitrogen dioxide (NO_2):

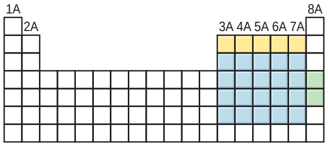


Because we need an even number of electrons for complete pairing (to reach eight), the octet rule clearly cannot be satisfied for all the atoms in any of these molecules.

Odd-electron molecules are sometimes called *radicals*. Many radicals are highly reactive. The reason is that there is a tendency for the unpaired electron to form a covalent bond with an unpaired electron on another molecule. For example, when two nitrogen dioxide molecules collide, they form dinitrogen tetroxide in which the octet rule is satisfied for both the N and O atoms:

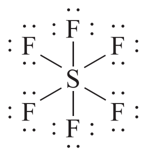


The Expanded Octet



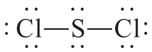
Yellow: second-period elements cannot have an expanded octet. Blue: third-period elements and beyond can have an expanded octet. Green: the noble gases usually only have an expanded octet.

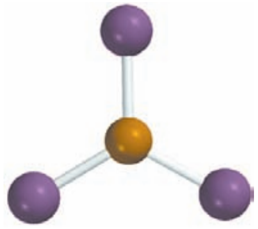
Atoms of the second-period elements cannot have more than eight valence electrons around the central atom, but atoms of elements in and beyond the third period of the periodic table form some compounds in which more than eight electrons surround the central atom. In addition to the 3*s* and 3*p* orbitals, elements in the third period also have 3*d* orbitals that can be used in bonding. These orbitals enable an atom to form an *expanded octet.* One compound in which there is an expanded octet is sulfur hexafluoride, a very stable compound. The electron configuration of sulfur is $[\mathrm{Ne}]3s^23p^4$. In SF_6, each of sulfur's six valence electrons forms a covalent bond with a fluorine atom, so there are twelve electrons around the central sulfur atom:



In Chapter 10 we will see that these 12 electrons, or six bonding pairs, are accommodated in six orbitals that originate from the one 3*s*, the three 3*p*, and two of the five 3*d* orbitals. Sulfur also forms many compounds in which it obeys the octet rule. In sulfur dichloride, for instance, S is surrounded by only eight electrons:

Sulfur dichloride is a toxic, foul-smelling cherry-red liquid (boiling point: 59°C).


$$\mathrm{:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{S}}-\ddot{\underset{..}{Cl}}:}$$



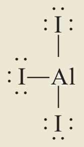
AlI_3 has a tendency to dimerize or form two units as Al_2I_6.

Example 9.9

Draw the Lewis structure for aluminum triiodide (AlI_3).

Strategy We follow the procedures used in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

Solution The outer-shell electron configurations of Al and I are $3s^23p^1$ and $5s^25p^5$, respectively. The total number of valence electrons is $3 + (3 \times 7)$ or 24. Because Al is less electronegative than I, it occupies a central position and forms three bonds with the I atoms:



Note that there are no formal charges on the Al and I atoms.

Check Although the octet rule is satisfied for the I atoms, there are only six valence electrons around the Al atom. Thus, AlI_3 is an example of the incomplete octet.

Similar problem: 9.60.

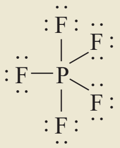
Example 9.10

Draw the Lewis structure for phosphorus pentafluoride (PF_5), in which all five F atoms are bonded to the central P atom.

(Continued)

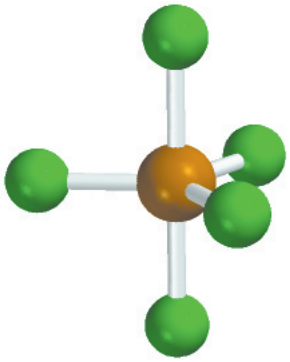
Strategy Note that P is a third-period element. We follow the procedures given in Examples 9.5 and 9.6 to draw the Lewis structure and calculate formal charges.

Solution The outer-shell electron configurations for P and F are $3s^23p^3$ and $2s^22p^5$, respectively, and so the total number of valence electrons is $5 + (5 \times 7)$, or 40. Phosphorus, like sulfur, is a third-period element, and therefore it can have an expanded octet. The Lewis structure of PF_5 is



Note that there are no formal charges on the P and F atoms.

Check Although the octet rule is satisfied for the F atoms, there are 10 valence electrons around the P atom, giving it an expanded octet.



PF_5 is a reactive gaseous compound.

Similar problem: 9.62.

A final note about the expanded octet: In drawing Lewis structures of compounds containing a central atom from the third period and beyond, sometimes we find that the octet rule is satisfied for all the atoms but there are still valence electrons left to place. In such cases, the extra electrons should be placed as lone pairs on the central atom.

Example 9.11

Draw a Lewis structure of the noble gas compound xenon tetrafluoride (XeF_4) in which all F atoms are bonded to the central Xe atom.

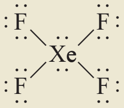
Strategy Note that Xe is a fifth-period element. We follow the procedures in Examples 9.5 and 9.6 for drawing the Lewis structure and calculating formal charges.

Solution *Step 1:* The skeletal structure of XeF_4 is

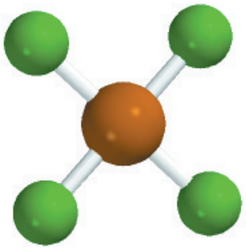
F F
Xe
F F

Step 2: The outer-shell electron configurations of Xe and F are $5s^25p^6$ and $2s^22p^5$, respectively, and so the total number of valence electrons is $8 + (4 \times 7)$ or 36.

Step 3: We draw a single covalent bond between all the bonding atoms. The octet rule is satisfied for the F atoms, each of which has three lone pairs. The sum of the lone pair electrons on the four F atoms (4×6) and the four bonding pairs (4×2) is 32. Therefore, the remaining four electrons are shown as two lone pairs on the Xe atom:



We see that the Xe atom has an expanded octet. There are no formal charges on the Xe and F atoms.



XeF_4

9.10 Bond Enthalpy

A measure of the stability of a molecule is its ***bond enthalpy,*** which is *the enthalpy change required to break a particular bond in 1 mole of gaseous molecules.* (Bond enthalpies in solids and liquids are affected by neighboring molecules.) The experimentally determined bond enthalpy of the diatomic hydrogen molecule, for example, is

$$H_2(g) \longrightarrow H(g) + H(g) \qquad \Delta H^\circ = 436.4 \text{ kJ/mol}$$

This equation tells us that breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436.4 kJ of energy. For the less stable chlorine molecule,

$$Cl_2(g) \longrightarrow Cl(g) + Cl(g) \qquad \Delta H^\circ = 242.7 \text{ kJ/mol}$$

Bond enthalpies can also be directly measured for diatomic molecules containing unlike elements, such as HCl,

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H^\circ = 431.9 \text{ kJ/mol}$$

as well as for molecules containing double and triple bonds:

$$O_2(g) \longrightarrow O(g) + O(g) \qquad \Delta H^\circ = 498.7 \text{ kJ/mol}$$
$$N_2(g) \longrightarrow N(g) + N(g) \qquad \Delta H^\circ = 941.4 \text{ kJ/mol}$$

Measuring the strength of covalent bonds in polyatomic molecules is more complicated. For example, measurements show that the energy needed to break the first O—H bond in H_2O is different from that needed to break the second O—H bond:

$$H_2O(g) \longrightarrow H(g) + OH(g) \qquad \Delta H^\circ = 502 \text{ kJ/mol}$$
$$OH(g) \longrightarrow H(g) + O(g) \qquad \Delta H^\circ = 427 \text{ kJ/mol}$$

In each case, an O—H bond is broken, but the first step is more endothermic than the second. The difference between the two ΔH° values suggests that the second O—H bond itself has undergone change, because of the changes in the chemical environment.

Now we can understand why the bond enthalpy of the same O—H bond in two different molecules such as methanol (CH_3OH) and water (H_2O) will not be the same: their environments are different. Thus, for polyatomic molecules we speak of the *average* bond enthalpy of a particular bond. For example, we can measure the energy of the O—H bond in 10 different polyatomic molecules and obtain the average O—H bond enthalpy by dividing the sum of the bond enthalpies by 10. Table 9.3 lists the average bond enthalpies of a number of diatomic and polyatomic molecules. As stated earlier, triple bonds are stronger than double bonds, which, in turn, are stronger than single bonds.

Use of Bond Enthalpies in Thermochemistry

A comparison of the thermochemical changes that take place during a number of reactions (Chapter 6) reveals a strikingly wide variation in the enthalpies of different reactions. For example, the combustion of hydrogen gas in oxygen gas is fairly exothermic:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ/mol}$$

TABLE 9.3 Some Bond Enthalpies of Diatomic Molecules* and Average Bond Enthalpies for Bonds in Polyatomic Molecules

Bond	Bond Enthalpy (kJ/mol)	Bond	Bond Enthalpy (kJ/mol)
H—H	436.4	C—S	255
H—N	393	C═S	477
H—O	460	N—N	193
H—S	368	N═N	418
H—P	326	N≡N	941.4
H—F	568.2	N—O	176
H—Cl	431.9	N═O	607
H—Br	366.1	O—O	142
H—I	298.3	O═O	498.7
C—H	414	O—P	502
C—C	347	O═S	469
C═C	620	P—P	197
C≡C	812	P═P	489
C—N	276	S—S	268
C═N	615	S═S	352
C≡N	891	F—F	156.9
C—O	351	Cl—Cl	242.7
C═O†	745	Br—Br	192.5
C—P	263	I—I	151.0

*Bond enthalpies for diatomic molecules (in color) have more significant figures than bond enthalpies for bonds in polyatomic molecules because the bond enthalpies of diatomic molecules are directly measurable quantities and not averaged over many compounds.

†The C═O bond enthalpy in CO_2 is 799 kJ/mol.

On the other hand, the formation of glucose ($C_6H_{12}O_6$) from water and carbon dioxide, best achieved by photosynthesis, is highly endothermic:

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g) \qquad \Delta H^\circ = 2801 \text{ kJ/mol}$$

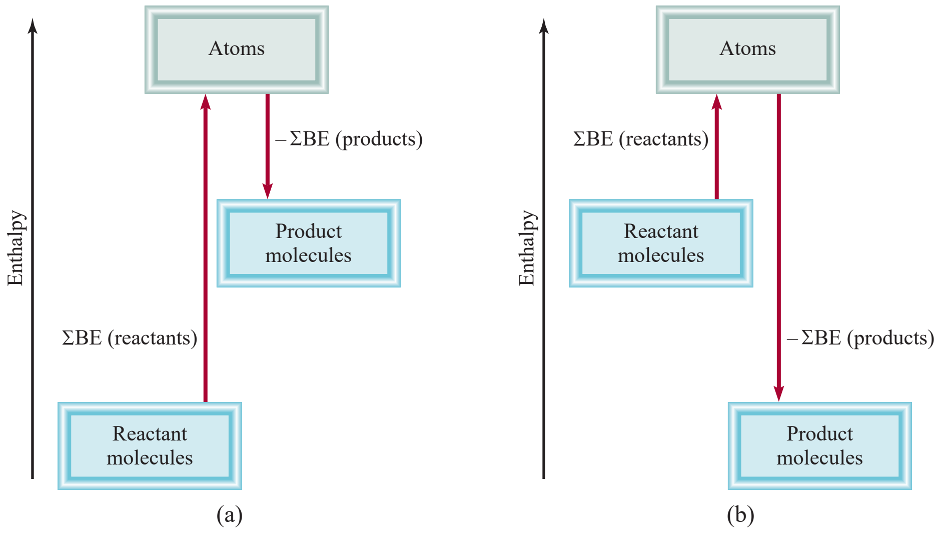
We can account for such variations by looking at the stability of individual reactant and product molecules. After all, most chemical reactions involve the making and breaking of bonds. Therefore, knowing the bond enthalpies and hence the stability of molecules tells us something about the thermochemical nature of reactions that molecules undergo.

In many cases, it is possible to predict the approximate enthalpy of reaction by using the average bond enthalpies. Because energy is always required to break chemical bonds and chemical bond formation is always accompanied by a release of energy, we can estimate the enthalpy of a reaction by counting the total number of bonds broken and formed in the reaction and recording all the corresponding energy changes. The enthalpy of reaction in the *gas phase* is given by

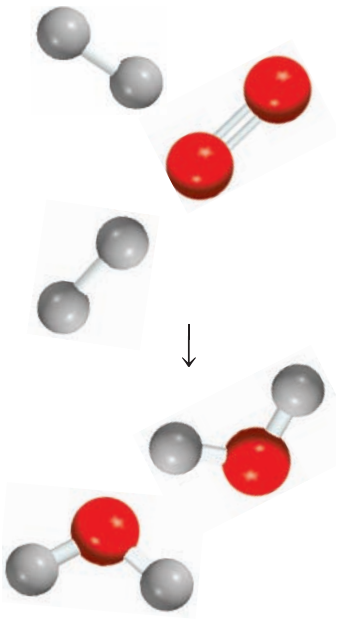
$$\begin{aligned}\Delta H^\circ &= \Sigma \text{BE(reactants)} - \Sigma \text{BE(products)} \\ &= \text{total energy input} - \text{total energy released}\end{aligned} \qquad (9.3)$$

where BE stands for average bond enthalpy and Σ is the summation sign. As written, Equation (9.3) takes care of the sign convention for ΔH°. Thus, if the total energy

Figure 9.8
Bond enthalpy changes in (a) an endothermic reaction and (b) an exothermic reaction.



input is greater than the total energy released, $\Delta H°$ is positive and the reaction is endothermic. On the other hand, if more energy is released than absorbed, $\Delta H°$ is negative and the reaction is exothermic (Figure 9.8). If reactants and products are all diatomic molecules, then Equation (9.3) will yield accurate results because the bond enthalpies of diatomic molecules are accurately known. If some or all of the reactants and products are polyatomic molecules, Equation (9.3) will yield only approximate results because the bond enthalpies used will be averages.



Example 9.12

Estimate the enthalpy change for the combustion of hydrogen gas:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Strategy Note that H_2O is a polyatomic molecule, and so we need to use the average bond enthalpy value for the O—H bond.

Solution We construct the following table:

Type of bonds broken	*Number of bonds broken*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
H—H (H_2)	2	436.4	872.8
O═O (O_2)	2	498.7	498.7

Type of bonds formed	*Number of bonds formed*	*Bond enthalpy (kJ/mol)*	*Energy change (kJ/mol)*
O—H (H_2O)	4	460	1840

Next, we obtain the total energy input and total energy released:

$$\text{total energy input} = 872.8 \text{ kJ/mol} + 498.7 \text{ kJ/mol} = 1371.5 \text{ kJ/mol}$$
$$\text{total energy released} = 1840 \text{ kJ/mol}$$

(*Continued*)

Using Equation (9.3), we write

$$\Delta H^\circ = 1371.5\text{ kJ/mol} - 1840\text{ kJ/mol} = -469\text{ kJ/mol}$$

This result is only an estimate because the bond enthalpy of O—H is an average quantity. Alternatively, we can use Equation (6.18) and the data in Appendix 3 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H^\circ &= 2\Delta H^\circ_f(H_2O) - [2\Delta H^\circ_f(H_2) + \Delta H^\circ_f(O_2)]\\ &= 2(-241.8\text{ kJ/mol}) - 0 - 0\\ &= -483.6\text{ kJ/mol}\end{aligned}$$

Check Note that the estimated value based on average bond enthalpies is quite close to the value calculated using ΔH°_f data. In general, Equation (9.3) works best for reactions that are either quite endothermic or quite exothermic, that is, reactions for which $\Delta H^\circ_{rxn} >$ 100 kJ/mol or for which $\Delta H^\circ_{rxn} < -100$ kJ/mol.

Practice Exercise For the reaction

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

(a) Estimate the enthalpy of reaction, using the bond enthalpy values in Table 9.3.

(b) Calculate the enthalpy of reaction, using standard enthalpies of formation. (ΔH°_f for H_2, C_2H_4, and C_2H_6 are 0, 52.3 kJ/mol, and -84.7 kJ/rom, respectively.)

KEY EQUATION

$\Delta H^\circ = \Sigma\text{BE(reactants)} - \Sigma\text{BE(products)}$ (9.3) Calculating enthalpy change of a reaction from bond enthalpies.

SUMMARY OF FACTS AND CONCEPTS

1. A Lewis dot symbol shows the number of valence electrons possessed by an atom of a given element. Lewis dot symbols are useful mainly for the representative elements.
2. In a covalent bond, two electrons (one pair) are shared by two atoms. In multiple covalent bonds, two or three electron pairs are shared by two atoms. Some bonded atoms possess lone pairs, that is, pairs of valence electrons not involved in bonding. The arrangement of bonding electrons and lone pairs around each atom in a molecule is represented by the Lewis structure.
3. Electronegativity is a measure of the ability of an atom to attract electrons in a chemical bond.
4. The octet rule predicts that atoms form enough covalent bonds to surround themselves with eight electrons each. When one atom in a covalently bonded pair donates two electrons to the bond, the Lewis structure can include the formal charge on each atom as a means of keeping track of the valence electrons. There are exceptions to the octet rule, particularly for covalent beryllium compounds, elements in Group 3A, and elements in the third period and beyond in the periodic table.
5. For some molecules or polyatomic ions, two or more Lewis structures based on the same skeletal structure satisfy the octet rule and appear chemically reasonable. Such resonance structures taken together represent the molecule or ion.
6. The strength of a covalent bond is measured in terms of its bond enthalpy. Bond enthalpies can be used to estimate the enthalpy of reactions.