8 Bonding: General Concepts

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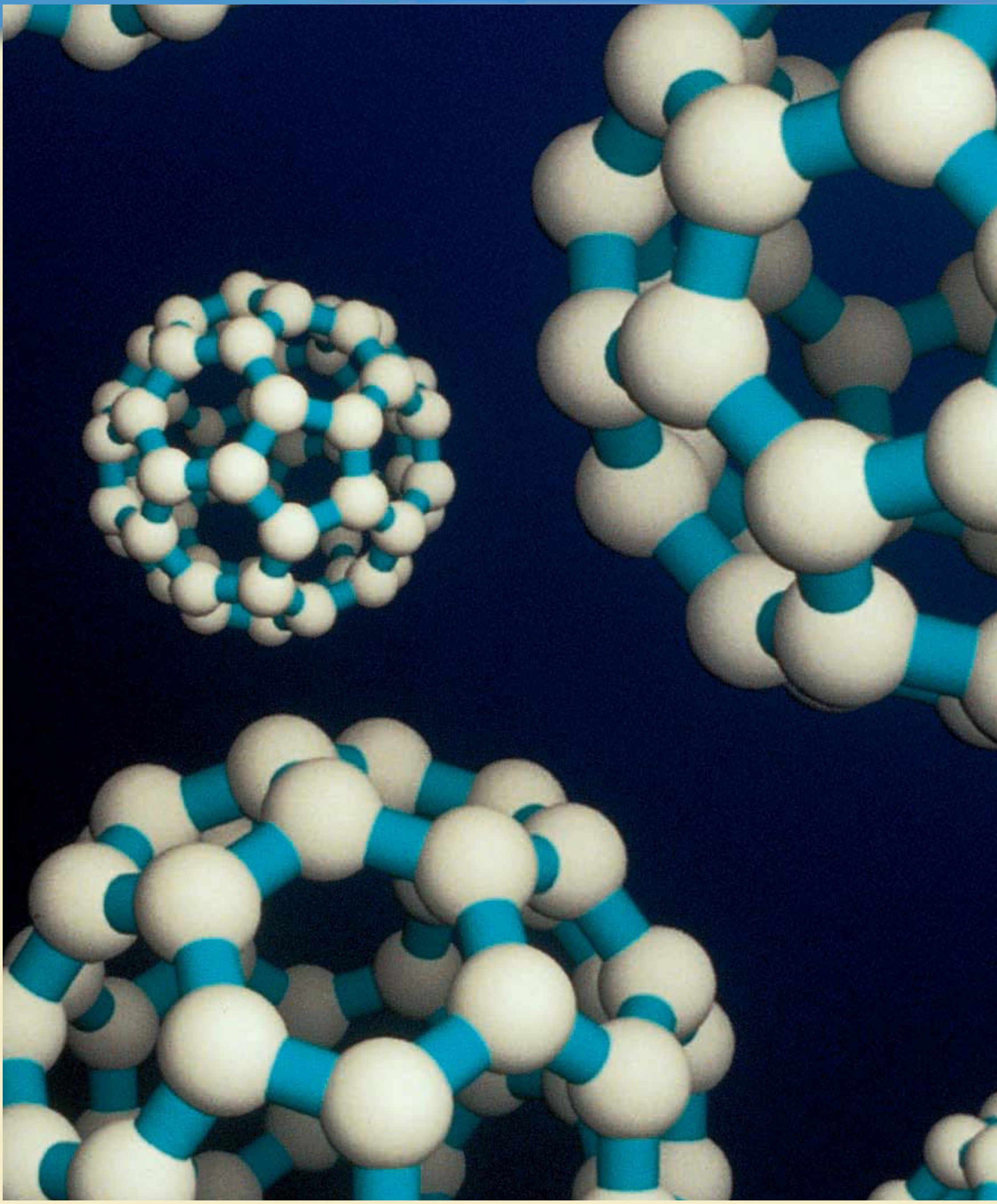


Carbon forms very stable spherical C_{60} molecules.

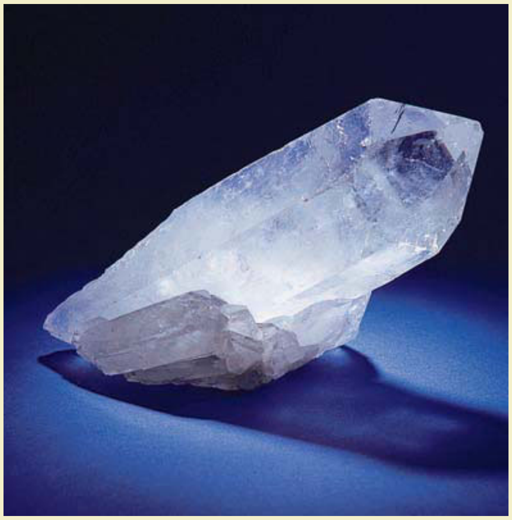
As we examine the world around us, we find it to be composed almost entirely of compounds and mixtures of compounds: Rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together. Substances composed of unbound atoms do exist in nature, but they are very rare. Examples are the argon in the atmosphere and the helium mixed with natural gas reserves.

The manner in which atoms are bound together has a profound effect on chemical and physical properties. For example, graphite is a soft, slippery material used as a lubricant in locks, and diamond is one of the hardest materials known, valuable both as a gemstone and in industrial cutting tools. Why do these materials, both composed solely of carbon atoms, have such different properties? The answer, as we will see, lies in the bonding in these substances.

Silicon and carbon are next to each other in Group 4A of the periodic table. From our knowledge of periodic trends, we might expect SiO_2 and CO_2 to be very similar. But SiO_2 is the empirical formula of silica, which is found in sand and quartz, and carbon dioxide is a gas, a product of respiration. Why are they so different? We will be able to answer this question after we have developed models for bonding.

Molecular bonding and structure play the central role in determining the course of all chemical reactions, many of which are vital to our survival. Later in this book we will demonstrate their importance by showing how enzymes facilitate complex chemical reactions, how genetic characteristics are transferred, and how hemoglobin in the blood carries oxygen throughout the body. All of these fundamental biological reactions hinge on the geometric structures of molecules, sometimes depending on very subtle differences in molecular shape to channel the chemical reaction one way rather than another.

Many of the world's current problems require fundamentally chemical answers: disease and pollution control, the search for new energy sources, the development of new fertilizers to increase crop yields, the improvement of the protein content in various staple grains, and many more. To understand the behavior of natural materials, we must understand the nature of chemical bonding and the factors that control the structures of



Quartz grows in beautiful, regular crystals.

compounds. In this chapter we will present various classes of compounds that illustrate the different types of bonds and then develop models to describe the structure and bonding that characterize materials found in nature. Later these models will be useful in understanding chemical reactions.

8.1 Types of Chemical Bonds

What is a chemical bond? There is no simple and yet complete answer to this question. In Chapter 2 we defined bonds as forces that hold groups of atoms together and make them function as a unit.

There are many types of experiments we can perform to determine the fundamental nature of materials. For example, we can study physical properties such as melting point, hardness, and electrical and thermal conductivity. We can also study solubility characteristics and the properties of the resulting solutions. To determine the charge distribution in a molecule, we can study its behavior in an electric field. We can obtain information about the strength of a bonding interaction by measuring the **bond energy,** which is the energy required to break the bond.

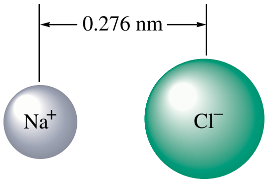
There are several ways in which atoms can interact with one another to form aggregates. We will consider several specific examples to illustrate the various types of chemical bonds.

Earlier, we saw that when solid sodium chloride is dissolved in water, the resulting solution conducts electricity, a fact that helps to convince us that sodium chloride is composed of Na^+ and Cl^- ions. Therefore, when sodium and chlorine react to form sodium chloride, electrons are transferred from the sodium atoms to the chlorine atoms to form Na^+ and Cl^- ions, which then aggregate to form solid sodium chloride. Why does this happen? The best simple answer is that *the system can achieve the lowest possible energy by behaving in this way.* The attraction of a chlorine atom for the extra electron and the very strong mutual attractions of the oppositely charged ions provide the driving forces for the process. The resulting solid sodium chloride is a very sturdy material; it has a melting point of approximately 800°C. The bonding forces that produce this great thermal stability result from the electrostatic attractions of the closely packed, oppositely charged ions. This is an example of **ionic bonding.** Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons. That is, an **ionic compound** results when a metal reacts with a nonmetal.

The energy of interaction between a pair of ions can be calculated using **Coulomb's law** in the form

$$E = (2.31 \times 10^{-19}\ \text{J} \cdot \text{nm})\left(\frac{Q_1Q_2}{r}\right)$$

where E has units of joules, r is the distance between the ion centers in nanometers, and Q_1 and Q_2 are the numerical ion charges.



For example, in solid sodium chloride the distance between the centers of the Na^+ and Cl^- ions is 2.76 Å (0.276 nm), and the ionic energy per pair of ions is

$$E = (2.31 \times 10^{-19}\ \text{J} \cdot \text{nm})\left[\frac{(+1)(-1)}{0.276\ \text{nm}}\right] = -8.37 \times 10^{-19}\ \text{J}$$

where the negative sign indicates an attractive force. That is, the *ion pair has lower energy than the separated ions.*

Coulomb's law also can be used to calculate the repulsive energy when two like-charged ions are brought together. In this case the calculated value of the energy will have a positive sign.

We have seen that a bonding force develops when two different types of atoms react to form oppositely charged ions. But how does a bonding force develop between two

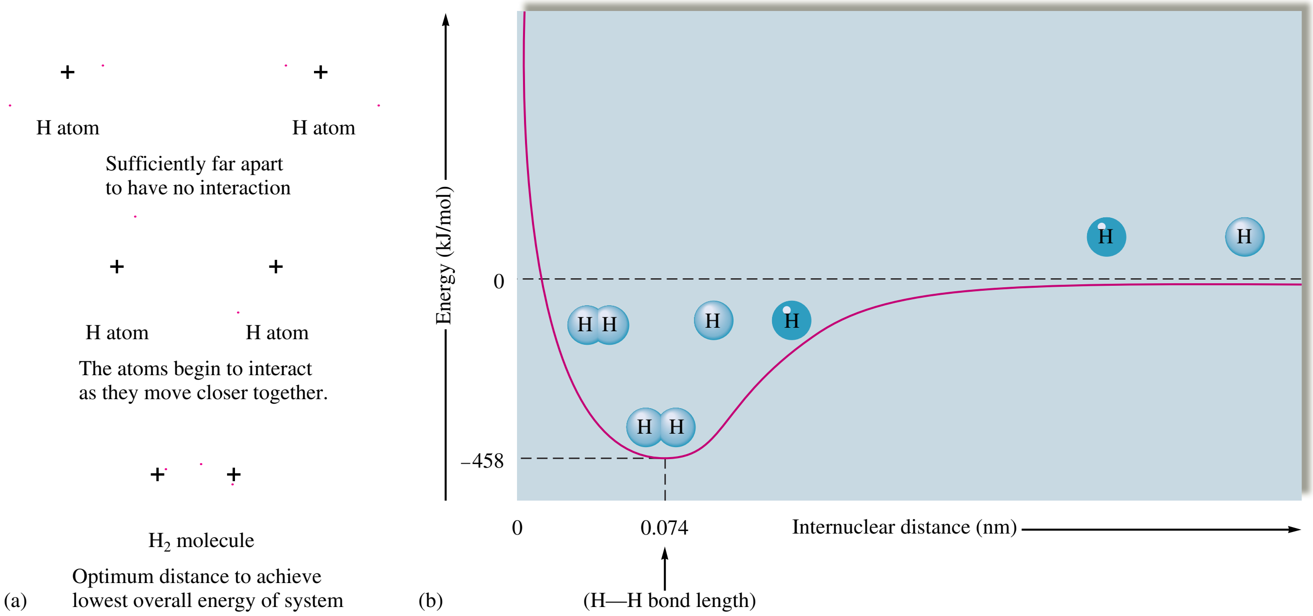


FIGURE 8.1

(a) The interaction of two hydrogen atoms. (b) Energy profile as a function of the distance between the nuclei of the hydrogen atoms. As the atoms approach each other (right side of graph), the energy decreases until the distance reaches 0.074 nm (0.74 Å) and then begins to increase again due to repulsions.

identical atoms? Let's explore this situation from a very simple point of view by considering the energy terms that result when two hydrogen atoms are brought close together, as shown in Fig. 8.1(a). When hydrogen atoms are brought close together, there are two unfavorable potential energy terms, proton–proton repulsion and electron–electron repulsion, and one favorable term, proton–electron attraction. Under what conditions will the H_2 molecule be favored over the separated hydrogen atoms? That is, what conditions will favor bond formation? The answer lies in the strong tendency in nature for any system to achieve the lowest possible energy. A bond will form (that is, the two hydrogen atoms will exist as a molecular unit) if the system can lower its total energy in the process.

A bond will form if the energy of the aggregate is lower than that of the separated atoms.

In this case, then, the hydrogen atoms will position themselves so that the system will achieve the lowest possible energy; the system will act to minimize the sum of the positive (repulsive) energy terms and the negative (attractive) energy term. The distance where the energy is minimal is called the **bond length.** The total energy of this system as a function of distance between the hydrogen nuclei is shown in Fig. 8.1(b). Note several important features of this diagram:

Potential energy was discussed in Chapter 6.

The energy terms involved are the net potential energy that results from the attractions and repulsions among the charged particles and the kinetic energy due to the motions of the electrons.

The zero point of energy is defined with the atoms at infinite separation.

At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together.

The bond length is the distance at which the system has minimum energy.

In the H_2 molecule, the electrons reside primarily in the space between the two nuclei, where they are attracted simultaneously by both protons. This positioning is precisely what leads to the stability of the H_2 molecule compared with two separated hydrogen

CHEMICAL IMPACT

No Lead Pencils

Did you ever wonder why the part of a pencil that makes the mark is called the "lead"? Pencils have no lead in them now—and they never have. Apparently the association between writing and the element lead arose during the Roman Empire, when lead rods were used as writing utensils because they leave a gray mark on paper. Many centuries later, in 1564, a deposit of a black substance found to be very useful for writing was discovered in Borrowdale, England. This substance, originally called "black lead," was shown in 1879 by Swedish chemist Carl Scheele to be a form of carbon and was subsequently named graphite (after the Greek *graphein,* meaning "to write").

Originally, chunks of graphite from Borrowdale, called marking stones, were used as writing instruments. Later, sticks of graphite were used. Because graphite is brittle, the sticks needed reinforcement. At first they were wrapped in string, which was unwound as the core wore down. Eventually, graphite rods were tied between two wooden slats or inserted into hollowed-out wooden sticks to form the first crude pencils.

Although Borrowdale graphite was pure enough to use directly, most graphite must be mixed with other materials to be useful for writing instruments. In 1795, the French chemist Nicolas-Jaques Conté invented a process in which graphite is mixed with clay and water to produce pencil "lead," a recipe that is still used today. In modern pencil manufacture, graphite and clay are mixed and crushed into a fine powder to which water is added. After the gray sludge

atoms. The potential energy of each electron is lowered because of the increased attractive forces in this area. When we say that a bond is formed between the hydrogen atoms, we mean that the H_2 molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy).

We can also think of a bond in terms of forces. The simultaneous attraction of each electron by the protons generates a force that pulls the protons toward each other and that just balances the proton–proton and electron–electron repulsive forces at the distance corresponding to the bond length.

The type of bonding we encounter in the hydrogen molecule and in many other molecules in which *electrons are shared by nuclei* is called **covalent bonding.**

Ionic and covalent bonds are the extreme bond types.

So far we have considered two extreme types of bonding. In ionic bonding the participating atoms are so different that one or more electrons are transferred to form oppositely charged ions, which then attract each other. In covalent bonding two identical atoms share electrons equally. The bonding results from the mutual attraction of the two nuclei for the shared electrons. Between these extremes are intermediate cases in which the atoms are not so different that electrons are completely transferred but are different enough that unequal sharing results, forming what is called a **polar covalent bond.** An example of this type of bond occurs in the hydrogen fluoride (HF) molecule. When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves as shown in Fig. 8.2, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole. This result implies that the HF molecule has the following charge distribution:

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

where δ (lowercase delta) is used to indicate a fractional charge. This same effect was noted in Chapter 4, where many of water's unusual properties were attributed to the polar O—H bonds in the H_2O molecule.

Visualization: Polar Molecules

The most logical explanation for the development of the partial positive and negative charges on the atoms (bond polarity) in such molecules as HF and H_2O is that the is blended for several days, it is dried, ground up again, and mixed with more water to give a gray paste. The paste is extruded through a metal tube to form thin rods, which are then cut into pencil-length pieces called "leads." These leads are heated in an oven to 1000°C until they are smooth and hard. The ratio of clay to graphite is adjusted to vary the hardness of the lead—the more clay in the mix, the harder the lead and the lighter the line it makes.

Pencils are made from a slat of wood with several grooves cut in it to hold the leads. A similar grooved slat is then placed on top and glued to form a "sandwich" from which individual pencils are cut, sanded smooth, and painted. Although many types of wood have been used over the years to make pencils, the current favorite is incense cedar from the Sierra Nevada Mountains of California.

Modern pencils are simple but amazing instruments. The average pencil can write approximately 45,000 words, which is equivalent to a line 35 miles long. The graphite in a pencil is easily transferred to paper because graphite contains layers of carbon atoms bound together in a "chicken-wire" structure. Although the bonding *within* each layer is very strong, the bonding *between* layers is weak, giving graphite its slippery, soft nature. In this way, graphite is much different from diamond, the other common elemental form of carbon. In diamond the carbon atoms are bound tightly in all three dimensions, making it extremely hard—the hardest natural substance.

Pencils are very useful—especially for doing chemistry problems—because we can erase our mistakes. Most pencils used in the United States have erasers (first attached to pencils in 1858), although most European pencils do not. Laid end-to end, the number of pencils made in the United States each year would circle the earth about 15 times. Pencils illustrate how useful a simple substance like graphite can be.

electrons in the bonds are not shared equally. For example, we can account for the polarity of the HF molecule by assuming that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom. Likewise, in the H_2O molecule the oxygen atom appears to attract the shared electrons more strongly than the hydrogen atoms do. Because bond polarity has important chemical implications, we find it useful to quantify the ability of an atom to attract shared electrons. In the next section we show how this is done.

8.2 Electronegativity

The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity:** *the ability of an atom in a molecule to attract shared electrons to itself.*

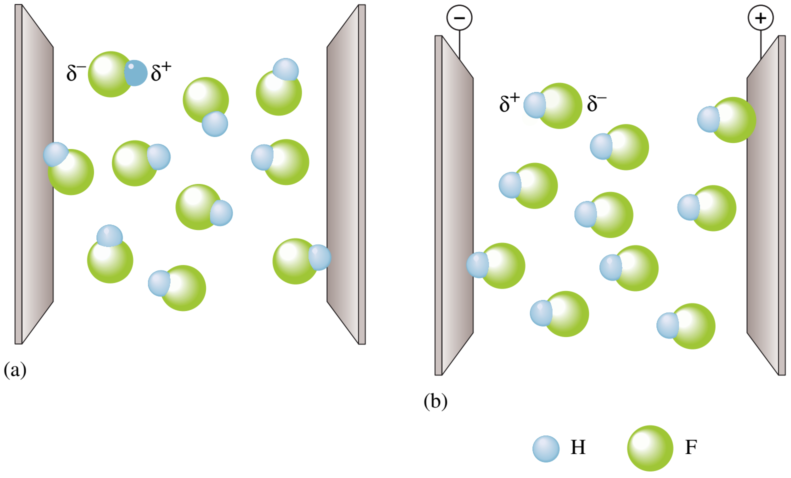


FIGURE 8.2
The effect of an electric field on hydrogen fluoride molecules. (a) When no electric field is present, the molecules are randomly oriented. (b) When the field is turned on, the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.

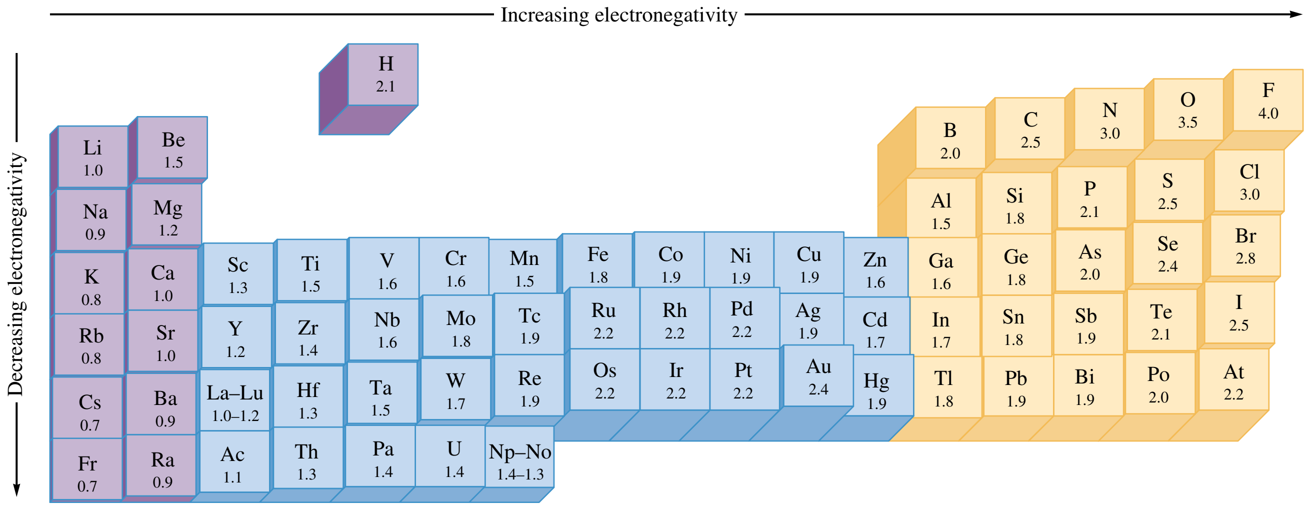


FIGURE 8.3

The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.

The most widely accepted method for determining values of electronegativity is that of Linus Pauling (1901–1995), an American scientist who won the Nobel Prizes for both chemistry and peace. To understand Pauling's model, consider a hypothetical molecule HX. The relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy with the "expected" H—X bond energy, which is an average of the H—H and X—X bond energies:

$$\text{Expected H—X bond energy} = \frac{\text{H—H bond energy} + \text{X—X bond energy}}{2}$$

The difference (Δ) between the actual (measured) and expected bond energies is

$$\Delta = (\text{H—X})_{\text{act}} - (\text{H—X})_{\text{exp}}$$

If H and X have identical electronegativities, $(\text{H—X})_{\text{act}}$ and $(\text{H—X})_{\text{exp}}$ are the same, and Δ is 0. On the other hand, if X has a greater electronegativity than H, the shared electron(s) will tend to be closer to the X atom. The molecule will be polar, with the following charge distribution:

$$\underset{\delta+}{\text{H}}\text{—}\underset{\delta-}{\text{X}}$$

Note that this bond can be viewed as having an ionic as well as a covalent component. The attraction between the partially (and oppositely) charged H and X atoms will lead to a greater bond strength. Thus $(\text{H—X})_{\text{act}}$ will be larger than $(\text{H—X})_{\text{exp}}$. The greater is the difference in the electronegativities of the atoms, the greater is the ionic component of the bond and the greater is the value of Δ. Thus the relative electronegativities of H and X can be assigned from the Δ values.

Electronegativity values have been determined by this process for virtually all the elements; the results are given in Fig. 8.3. Note that electronegativity generally increases going from left to right across a period and decreases going down a group for the representative elements. The range of electronegativity values is from 4.0 for fluorine to 0.7 for cesium.

The relationship between electronegativity and bond type is shown in Table 8.1. For identical atoms (an electronegativity difference of zero), the electrons in the bond are shared equally, and no polarity develops. When two atoms with very different electronegativities

TABLE 8.1 The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type	
Zero	Covalent	Covalent character
Intermediate	Polar covalent	
Large	Ionic	Ionic character

interact, electron transfer can occur to form the ions that make up an ionic substance. Intermediate cases give polar covalent bonds with unequal electron sharing.

Sample Exercise 8.1

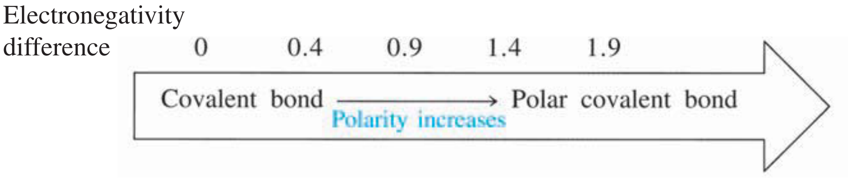
Relative Bond Polarities

Order the following bonds according to polarity: H—H, O—H, Cl—H, S—H, and F—H.

Solution

The polarity of the bond increases as the difference in electronegativity increases. From the electronegativity values in Fig. 8.3, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):

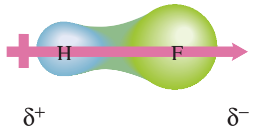
$$\underset{(2.1)(2.1)}{\text{H—H}} < \underset{(2.5)(2.1)}{\text{S—H}} < \underset{(3.0)(2.1)}{\text{Cl—H}} < \underset{(3.5)(2.1)}{\text{O—H}} < \underset{(4.0)(2.1)}{\text{F—H}}$$



See Exercises 8.31 and 8.32.

8.3 Bond Polarity and Dipole Moments

We have seen that when hydrogen fluoride is placed in an electric field, the molecules have a preferential orientation (see Fig. 8.2). This follows from the charge distribution in the HF molecule, which has a positive end and a negative end. A molecule such as HF that has a center of positive charge and a center of negative charge is said to be **dipolar,** or to have a **dipole moment.** The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge:



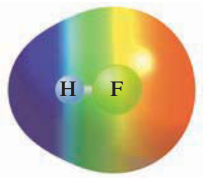
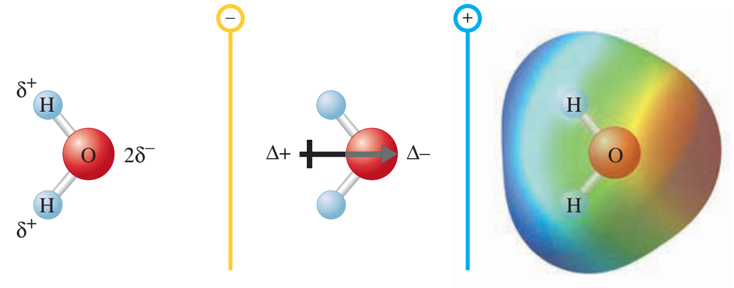


FIGURE 8.4
An electrostatic potential map of HF. Red indicates the most electron-rich area (the fluorine atom) and blue indicates the most electron-poor region (the hydrogen atom).

Another way to represent the charge distribution in HF is by an electrostatic potential diagram (see Fig. 8.4). For this representation the colors of visible light are used to show the variation in charge distribution. Red indicates the most electron-rich region of the molecule and blue indicates the most electron-poor region.

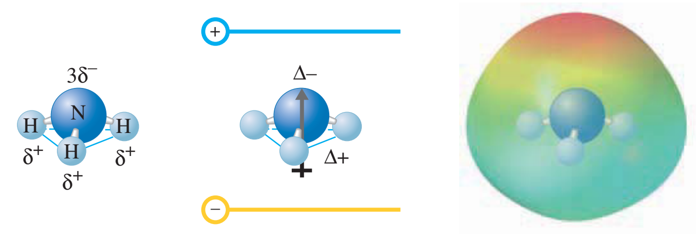
Of course, any diatomic (two-atom) molecule that has a polar bond also will show a molecular dipole moment. Polyatomic molecules also can exhibit dipolar behavior. For example, because the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms, the molecular charge distribution is that shown in Fig. 8.5(a). Because of this charge distribution, the water molecule behaves in an electric field as if it had two centers of charge—one positive and one negative—as shown in Fig. 8.5(b). The water molecule has a dipole moment. The same type of behavior is observed for the NH_3 molecule (Fig. 8.6). Some molecules have polar bonds but do not have a dipole moment. This occurs when the individual bond polarities are arranged in such a way that they cancel each other out. An example is the CO_2 molecule, which is a linear molecule that has the charge distribution shown in Fig. 8.7. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment. There is no preferential way for this molecule to line up in an electric field. (Try to find a preferred orientation to make sure you understand this concept.)

There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are shown in Table 8.2.



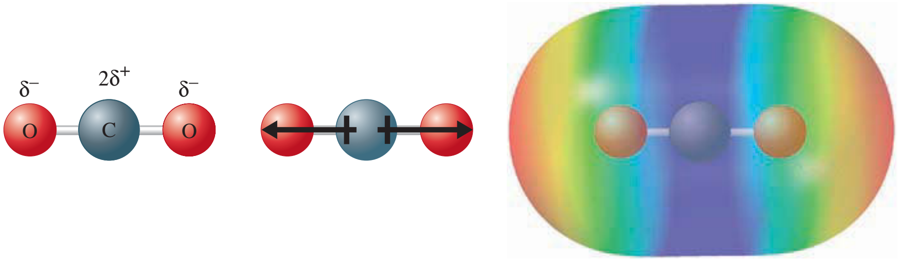
(a) (b) (c)

FIGURE 8.5
(a) The charge distribution in the water molecule. (b) The water molecule in an electric field. (c) The electrostatic potential diagram of the water molecule.



(a) (b) (c)

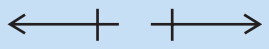
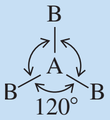
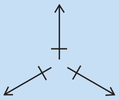
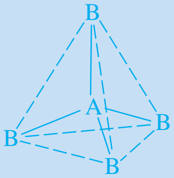
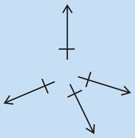
FIGURE 8.6
(a) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen.
(b) The dipole moment of the ammonia molecule oriented in an electric field.
(c) The electrostatic potential diagram for ammonia.



(a) (b) (c)

FIGURE 8.7
(a) The carbon dioxide molecule. (b) The opposed bond polarities cancel out, and the carbon dioxide molecule has no dipole moment. (c) The electrostatic potential diagram for carbon dioxide.

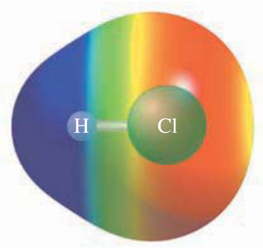
TABLE 8.2 Types of Molecules with Polar Bonds but No Resulting Dipole Moment

Type			Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B	CO_2			
Planar molecules with three identical bonds 120 degrees apart				SO_3	
Tetrahedral molecules with four identical bonds 109.5 degrees apart				CCl_4	

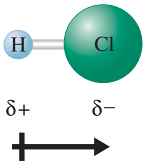
Sample Exercise 8.2 Bond Polarity and Dipole Moment

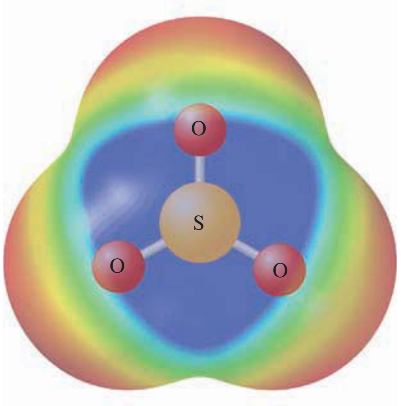
For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCl, Cl_2, SO_3 (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH_4 [tetrahedral (see Table 8.2) with the carbon atom at the center], and H_2S (V-shaped with the sulfur atom at the point).

Solution



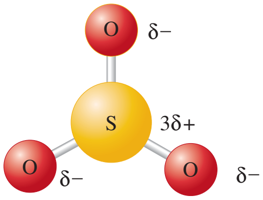
The HCl molecule: In Fig. 8.3, we see that the electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1). Thus the chlorine will be partially negative, and the hydrogen will be partially positive. The HCl molecule has a dipole moment:





The Cl_2 molecule: The two chlorine atoms share the electrons equally. No bond polarity occurs, and the Cl_2 molecule has no dipole moment.

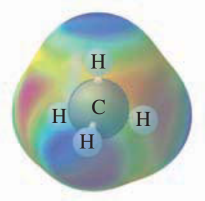
The SO_3 molecule: The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5). This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge:

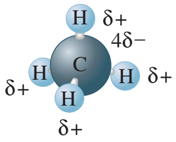


The presence of polar bonds does not always yield a polar molecule.

The bond polarities arranged symmetrically as shown cancel, and the molecule has no dipole moment. This molecule is the second type shown in Table 8.2.

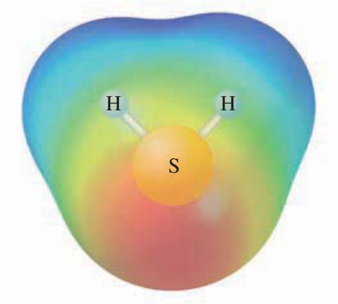
The CH_4 molecule: Carbon has a slightly higher electronegativity (2.5) than does hydrogen (2.1). This leads to small partial positive charges on the hydrogen atoms and a small partial negative charge on the carbon:

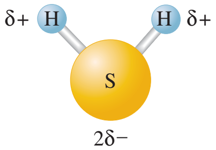




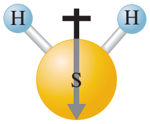
This case is similar to the third type in Table 8.2, and the bond polarities cancel. The molecule has no dipole moment.

The H_2S molecule: Since the electronegativity of sulfur (2.5) is slightly greater than that of hydrogen (2.1), the sulfur will have a partial negative charge, and the hydrogen atoms will have a partial positive charge, which can be represented as





This case is analogous to the water molecule, and the polar bonds result in a dipole moment oriented as shown:



See Exercise 8.114.

8.4 Ions: Electron Configurations and Sizes

Atoms in stable compounds usually have a noble gas electron configuration.

The description of the electron arrangements in atoms that emerged from the quantum mechanical model has helped a great deal in our understanding of what constitutes a stable compound. In virtually every case the atoms in a stable compound have a noble gas arrangement of electrons. Nonmetallic elements achieve a noble gas electron configuration either by sharing electrons with other nonmetals to form covalent bonds or by taking electrons from metals to form ions. In the second case, the nonmetals form anions, and the metals form cations. The generalizations that apply to electron configurations in stable compounds are as follows:

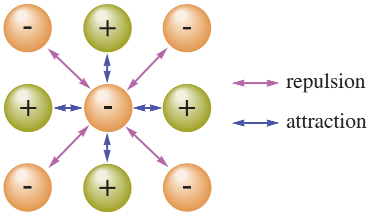
- When *two nonmetals* react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations.

- When *a nonmetal and a representative-group metal* react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied. In this way both ions achieve noble gas electron configurations.

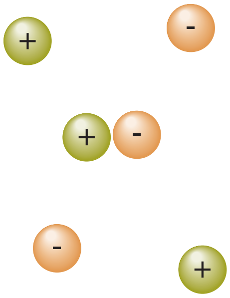
These generalizations apply to the vast majority of compounds and are important to remember. We will deal with covalent bonds more thoroughly later, but now we will consider what implications these rules hold for ionic compounds.

Predicting Formulas of Ionic Compounds

In the solid state of an ionic compound the ions are relatively close together, and many ions are simultaneously interacting:



In the gas phase of an ionic substance the ions would be relatively far apart and would not contain large groups of ions:



At the beginning of this discussion it should be emphasized that when chemists use the term *ionic compound,* they are usually referring to the solid state of that compound. In the solid state the ions are close together. That is, solid ionic compounds contain a large collection of positive and negative ions packed together in a way that minimizes the ⊖··⊖ and ⊕··⊕ repulsions and maximizes the ⊕··⊖ attractions. This situation stands in contrast to the gas phase of an ionic substance, where the ions are quite far apart on average. In the gas phase, a pair of ions may get close enough to interact, but large collections of ions do not exist. Thus, when we speak in this text of the stability of an ionic compound, we are referring to the solid state, where the large attractive forces present among oppositely charged ions tend to stabilize (favor the formation of) the ions. For example, as we mentioned in the preceding chapter, the O^{2-} ion is not stable as an isolated, gas-phase species but, of course, is very stable in many solid ionic compounds. That is, $MgO(s)$, which contains Mg^{2+} and O^{2-} ions, is very stable, but the isolated, gas-phase ion pair $Mg^{2+} \cdot\cdot O^{2-}$ is not energetically favorable in comparison with the separate neutral gaseous atoms. Thus you should keep in mind that in this section, and in most other cases where we are describing the nature of ionic compounds, the discussion usually refers to the solid state, where many ions are simultaneously interacting.

To illustrate the principles of electron configurations in stable, solid ionic compounds, we will consider the formation of an ionic compound from calcium and oxygen. We can predict what compound will form by considering the valence electron configurations of the two atoms:

$$\text{Ca:} \quad [\mathrm{Ar}]4s^2$$
$$\text{O:} \quad [\mathrm{He}]2s^2 2p^4$$

From Fig. 8.3 we see that the electronegativity of oxygen (3.5) is much greater than that of calcium (1.0). Because of this large difference, electrons will be transferred from calcium to oxygen to form oxygen anions and calcium cations in the compound. How many electrons are transferred? We can base our prediction on the observation that noble gas configurations are generally the most stable. Note that oxygen needs two electrons to fill its 2*s* and 2*p* valence orbitals and to achieve the configuration of neon ($1s^2 2s^2 2p^6$). And by losing two electrons, calcium can achieve the configuration of argon. Two electrons are therefore transferred:

$$\underset{\underset{2e^-}{\curvearrowright}}{\mathrm{Ca} + \mathrm{O}} \longrightarrow \mathrm{Ca}^{2+} + \mathrm{O}^{2-}$$

Visualization: Formation of Ionic Compounds

To predict the formula of the ionic compound, we simply recognize that chemical compounds are always electrically neutral—they have the same quantities of positive and negative charges. In this case we have equal numbers of Ca^{2+} and O^{2-} ions, and the empirical formula of the compound is CaO.

The same principles can be applied to many other cases. For example, consider the compound formed between aluminum and oxygen. Because aluminum has the configuration $[\mathrm{Ne}]3s^2 3p^1$, it loses three electrons to form the Al^{3+} ion and thus achieves the neon

A bauxite mine. Bauxite contains Al_2O_3, the main source of aluminum.

configuration. Therefore, the Al^{3+} and O^{2-} ions form in this case. Since the compound must be electrically neutral, there must be three O^{2-} ions for every two Al^{3+} ions, and the compound has the empirical formula Al_2O_3.

Table 8.3 shows common elements that form ions with noble gas electron configurations in ionic compounds. In losing electrons to form cations, metals in Group 1A lose one electron, those in Group 2A lose two electrons, and those in Group 3A lose three electrons. In gaining electrons to form anions, nonmetals in Group 7A (the halogens) gain one electron, and those in Group 6A gain two electrons. Hydrogen typically behaves as a nonmetal and can gain one electron to form the hydride ion (H^-), which has the electron configuration of helium.

There are some important exceptions to the rules discussed here. For example, tin forms both Sn^{2+} and Sn^{4+} ions, and lead forms both Pb^{2+} and Pb^{4+} ions. Also, bismuth forms Bi^{3+} and Bi^{5+} ions, and thallium forms Tl^+ and Tl^{3+} ions. There are no simple explanations for the behavior of these ions. For now, just note them as exceptions to the very useful rule that ions generally adopt noble gas electron configurations in ionic compounds. Our discussion here refers to representative metals. The transition metals exhibit more complicated behavior, forming a variety of ions that will be considered in Chapter 21.

Sizes of Ions

Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biologic effects of ions. As with atoms, it is impossible to define precisely the sizes of ions. Most often, ionic radii are determined

TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

from the measured distances between ion centers in ionic compounds. This method, of course, involves an assumption about how the distance should be divided up between the two ions. Thus you will note considerable disagreement among ionic sizes given in various sources. Here we are mainly interested in trends and will be less concerned with absolute ion sizes.

Visualization: Ionic Radii

Various factors influence ionic size. We will first consider the relative sizes of an ion and its parent atom. Since a positive ion is formed by removing one or more electrons from a neutral atom, the resulting cation is smaller than its parent atom. The opposite is true for negative ions; the addition of electrons to a neutral atom produces an anion significantly larger than its parent atom.

It is also important to know how the sizes of ions vary depending on the positions of the parent elements in the periodic table. Figure 8.8 shows the sizes of the most important ions (each with a noble gas configuration) and their position in the periodic table. Note that ion size increases down a group. The changes that occur horizontally are complicated because of the change from predominantly metals on the left-hand side of the periodic table to nonmetals on the right-hand side. A given period thus contains both elements that give up electrons to form cations and ones that accept electrons to form anions.

One trend worth noting involves the relative sizes of a set of **isoelectronic ions**—*ions containing the same number of electrons.* Consider the ions O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+}. Each of these ions has the neon electron configuration. How do the sizes of these ions vary? In general, there are two important facts to consider in predicting the relative sizes of ions: the number of electrons and the number of protons. Since these ions are isoelectronic, the number of electrons is 10 in each case. Electron repulsions therefore should be about the same in all cases. However, the number of protons increases from 8 to 13 as we go from the O^{2-} ion to the Al^{3+} ion. Thus, in going from O^{2-} to Al^{3+}, the 10 electrons experience a greater attraction as the positive charge on the nucleus increases. This causes the ions to become smaller. You can confirm this by looking at Fig. 8.8. In general, for a series of isoelectronic ions, the size decreases as the nuclear charge Z increases.

For isoelectronic ions, size decreases as Z increases.

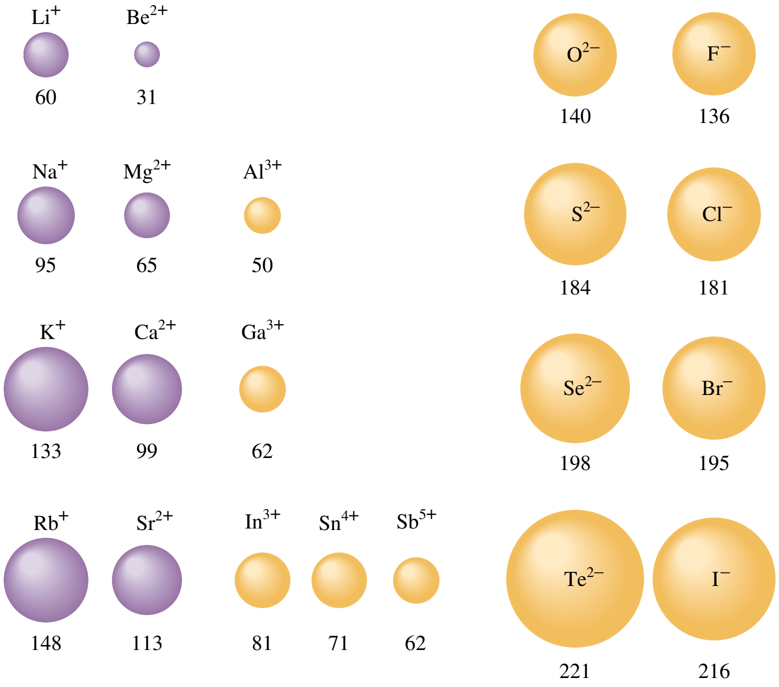


FIGURE 8.8
Sizes of ions related to positions of the elements on the periodic table. Note that size generally increases down a group. Also note that in a series of isoelectronic ions, size decreases with increasing atomic number. The ionic radii are given in units of picometers.

Sample Exercise 8.3 Relative Ion Size I

Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{2+} in order of decreasing size.

Solution

This is an isoelectronic series of ions with the krypton electron configuration. Since these ions all have the same number of electrons, their sizes will depend on the nuclear charge. The Z values are 34 for Se^{2-}, 35 for Br^-, 37 for Rb^+, and 38 for Sr^{2+}. Since the nuclear charge is greatest for Sr^{2+}, it is the smallest of these ions. The Se^{2-} ion is largest:

$$\underset{\text{Largest}}{\underset{\uparrow}{Se^{2-}}} > Br^- > Rb^+ > \underset{\text{Smallest}}{\underset{\uparrow}{Sr^{2+}}}$$

See Exercises 8.37 and 8.38.

Sample Exercise 8.4 Relative Ion Size II

Choose the largest ion in each of the following groups.

a. Li^+, Na^+, K^+, Rb^+, Cs^+
b. Ba^{2+}, Cs^+, I^-, Te^{2-}

Solution

a. The ions are all from Group 1A elements. Since size increases down a group (the ion with the greatest number of electrons is largest), Cs^+ is the largest ion.

b. This is an isoelectronic series of ions, all of which have the xenon electron configuration. The ion with the smallest nuclear charge is largest:

$$\begin{array}{ccccccc} Te^{2-} & > & I^- & > & Cs^+ & > & Ba^{2+} \\ Z = 52 & & Z = 53 & & Z = 55 & & Z = 56 \end{array}$$

See Exercises 8.39 and 8.40.

8.5 Energy Effects in Binary Ionic Compounds

In this section we will introduce the factors that influence the stability and the structures of solid binary ionic compounds. We know that metals and nonmetals react by transferring electrons to form cations and anions that are mutually attractive. The resulting ionic solid forms because the aggregated oppositely charged ions have a lower energy than the original elements. Just how strongly the ions attract each other in the solid state is indicated by the **lattice energy**—*the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid:*

$$M^+(g) + X^-(g) \longrightarrow MX(s)$$

The structures of ionic solids will be discussed in detail in Chapter 10.

The lattice energy is often defined as the energy *released* when an ionic solid forms from its ions. However, in this book the sign of an energy term is always determined from the system's point of view: negative if the process is exothermic, positive if endothermic. Thus, using this convention, the lattice energy has a negative sign.

We can illustrate the energy changes involved in the formation of an ionic solid by considering the formation of solid lithium fluoride from its elements:

$$Li(s) + \tfrac{1}{2}F_2(g) \longrightarrow LiF(s)$$

To see the energy terms associated with this process, we take advantage of the fact that energy is a state function and break this reaction into steps, the sum of which gives the overall reaction.

➥ **1** Sublimation of solid lithium. Sublimation involves taking a substance from the solid state to the gaseous state:

$$\mathrm{Li}(s) \longrightarrow \mathrm{Li}(g)$$

Lithium fluoride.

The enthalpy of sublimation for Li(s) is 161 kJ/mol.

➥ **2** Ionization of lithium atoms to form Li^+ ions in the gas phase:

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

This process corresponds to the first ionization energy for lithium, which is 520 kJ/mol.

➥ **3** Dissociation of fluorine molecules. We need to form a mole of fluorine atoms by breaking the F—F bonds in a half mole of F_2 molecules:

$$\tfrac{1}{2}\mathrm{F}_2(g) \longrightarrow \mathrm{F}(g)$$

The energy required to break this bond is 154 kJ/mol. In this case we are breaking the bonds in a half mole of fluorine, so the energy required for this step is (154 kJ)/2, or 77 kJ.

➥ **4** Formation of F^- ions from fluorine atoms in the gas phase:

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

The energy change for this process corresponds to the electron affinity of fluorine, which is −328 kJ/mol.

➥ **5** Formation of solid lithium fluoride from the gaseous Li^+ and F^- ions:

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

This corresponds to the lattice energy for LiF, which is −1047 kJ/mol.

Since the sum of these five processes yields the desired overall reaction, the sum of the individual energy changes gives the overall energy change:

Process	Energy Change (kJ)
$\mathrm{Li}(s) \rightarrow \mathrm{Li}(g)$	161
$\mathrm{Li}(g) \rightarrow \mathrm{Li}^+(g) + e^-$	520
$\tfrac{1}{2}\mathrm{F}_2(g) \rightarrow \mathrm{F}(g)$	77
$\mathrm{F}(g) + e^- \rightarrow \mathrm{F}^-(g)$	−328
$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \rightarrow \mathrm{LiF}(s)$	−1047
Overall: $\mathrm{Li}(s) + \tfrac{1}{2}\mathrm{F}_2(g) \rightarrow \mathrm{LiF}(s)$	−617 kJ (per mole of LiF)

In doing this calculation, we have ignored the small difference between ΔH_{sub} and ΔE_{sub}.

This process is summarized by the energy diagram in Fig. 8.9. Note that the formation of solid lithium fluoride from its elements is highly exothermic, mainly because of the very large negative lattice energy. A great deal of energy is released when the ions combine to form the solid. In fact, note that the energy released when an electron is added to a fluorine atom to form the F^- ion (328 kJ/mol) is not enough to remove an electron from lithium (520 kJ/mol). That is, when a metallic lithium atom reacts with a nonmetallic fluorine atom to form *separated* ions,

$$\mathrm{Li}(g) + \mathrm{F}(g) \longrightarrow \mathrm{Li}^+(g) + \mathrm{F}^-(g)$$

the process is endothermic and thus unfavorable. Clearly, then, the main impetus for the formation of an ionic compound rather than a covalent compound results from the strong mutual attractions among the Li^+ and F^- ions in the solid. The lattice energy is the dominant energy term.

Visualization: Born–Haber Cycle for NaCl(s)

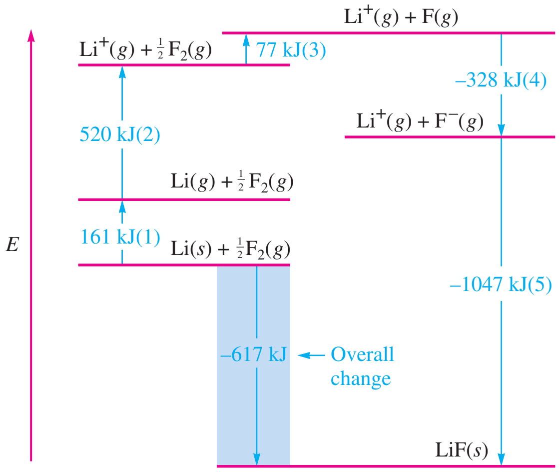
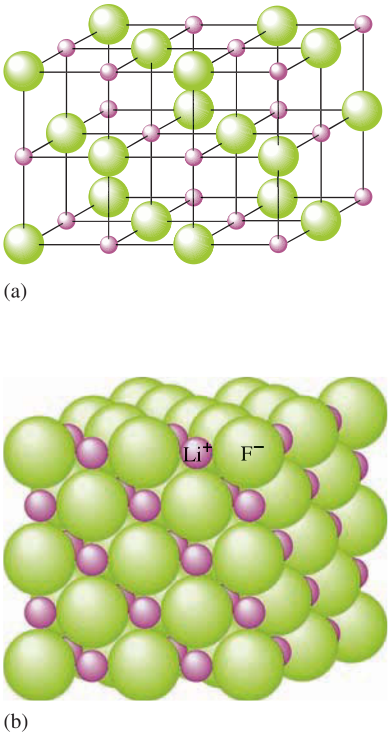


FIGURE 8.9
The energy changes involved in the formation of solid lithium fluoride from its elements. The numbers in parentheses refer to the reaction steps discussed in the text.

The structure of solid lithium fluoride is represented in Fig. 8.10. Note the alternating arrangement of the Li^+ and F^- ions. Also note that each Li^+ is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions. This structure can be rationalized by assuming that the ions behave as hard spheres that pack together in a way that both maximizes the attractions among the oppositely charged ions and minimizes the repulsions among the identically charged ions.

All the binary ionic compounds formed by an alkali metal and a halogen have the structure shown in Fig. 8.10, except for the cesium salts. The arrangement of ions shown in Fig. 8.10 is often called the *sodium chloride structure,* after the most common substance that possesses it.


(a)

(b)

FIGURE 8.10
The structure of lithium fluoride. (a) Represented by ball-and-stick model. Note that each Li^+ ion is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions. (b) Represented with the ions shown as spheres. The structure is determined by packing the spherical ions in a way that both maximizes the ionic attractions and minimizes the ionic repulsions.

Lattice Energy Calculations

In discussing the energetics of the formation of solid lithium fluoride, we emphasized the importance of lattice energy in contributing to the stability of the ionic solid. Lattice energy can be represented by a modified form of Coulomb's law:

$$\text{Lattice energy} = k\left(\frac{Q_1Q_2}{r}\right)$$

where k is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions, Q_1 and Q_2 are the charges on the ions, and r is the shortest distance between the centers of the cations and anions. Note that the lattice energy has a negative sign when Q_1 and Q_2 have opposite signs. This result is expected, since bringing cations and anions together is an exothermic process. Also note that the process becomes more exothermic as the ionic charges increase and as the distances between the ions in the solid decrease.

The importance of the charges in ionic solids can be illustrated by comparing the energies involved in the formation of NaF(s) and MgO(s). These solids contain the isoelectronic ions Na^+, F^-, Mg^{2+}, and O^{2-}. The energy diagram for the formation of the two solids is given in Fig. 8.11. Note several important features:

> The energy released when the gaseous Mg^{2+} and O^{2-} ions combine to form solid MgO is much greater (more than four times greater) than that released when the gaseous Na^+ and F^- ions combine to form solid NaF.

> The energy required to remove two electrons from the magnesium atom (735 kJ/mol for the first and 1445 kJ/mol for the second, yielding a total of 2180 kJ/mol) is much greater than the energy required to remove one electron from a sodium atom (495 kJ/mol).

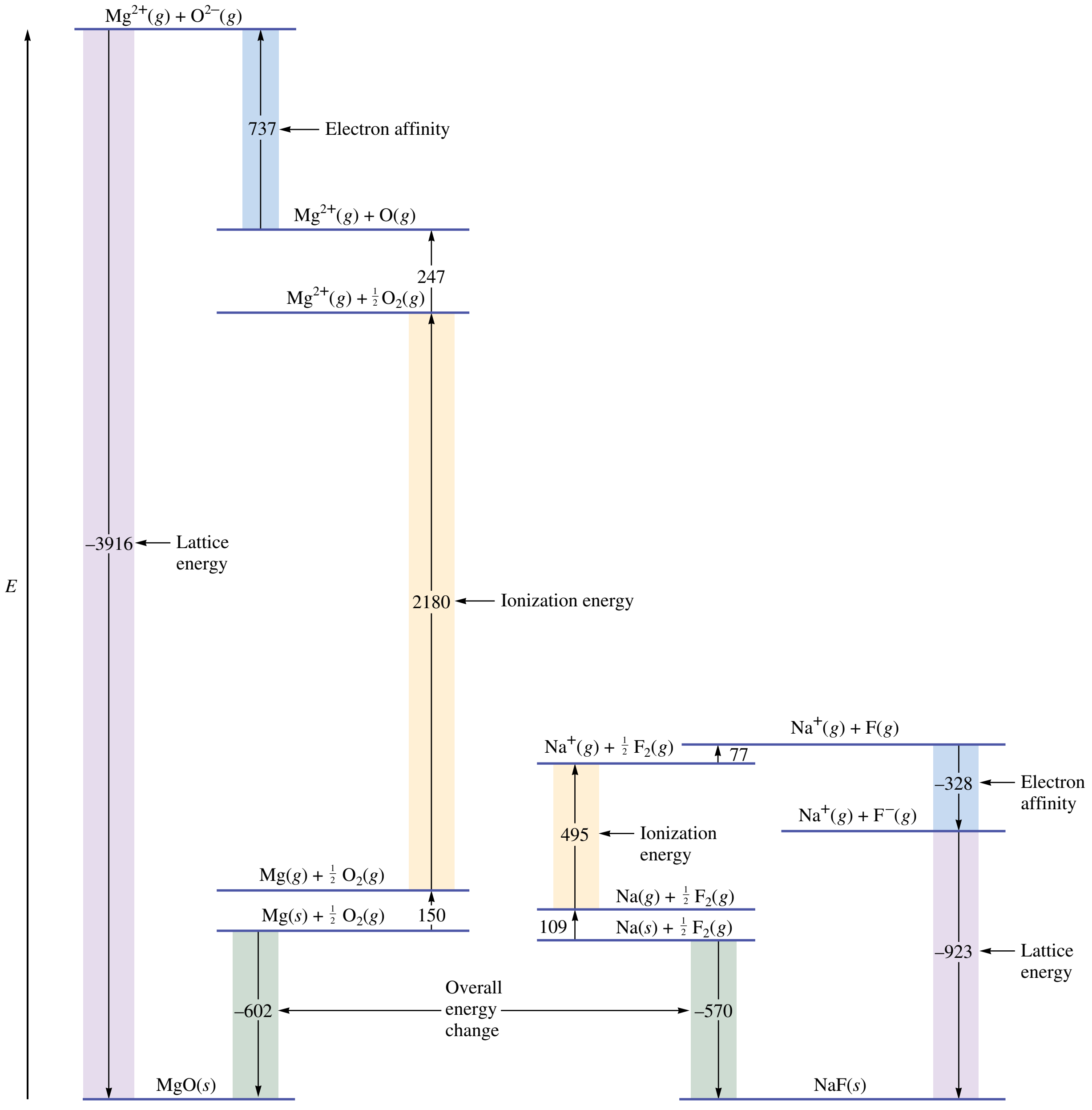


FIGURE 8.11
Comparison of the energy changes involved in the formation of solid sodium fluoride and solid magnesium oxide. Note the large lattice energy for magnesium oxide (where doubly charged ions are combining) compared with that for sodium fluoride (where singly charged ions are combining).

Energy (737 kJ/mol) is required to add two electrons to the oxygen atom in the gas phase. Addition of the first electron is exothermic (−141 kJ/mol), but addition of the second electron is quite endothermic (878 kJ/mol). This latter energy must be obtained indirectly, since the $O^{2-}(g)$ ion is not stable.

In view of the facts that twice as much energy is required to remove the second electron from magnesium as to remove the first and that addition of an electron to the gaseous O^- ion is quite endothermic, it seems puzzling that magnesium oxide contains Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions. The answer lies in the lattice energy. Note that the lattice energy for combining gaseous Mg^{2+} and O^{2-} ions to form MgO(s) is 3000 kJ/mol more negative than that for combining gaseous Na^+ and F^- ions to form NaF(*s*). Thus the energy released in forming a solid containing Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions more than compensates for the energies required for the processes that produce the Mg^{2+} and O^{2-} ions.

Since the equation for lattice energy contains the product Q_1Q_2, the lattice energy for a solid with 2+ and 2− ions should be four times that for a solid with 1+ and 1− ions. That is,

$$\frac{(+2)(-2)}{(+1)(-1)} = 4$$

For MgO and NaF, the observed ratio of lattice energies (see Fig. 8.11) is

$$\frac{-3916\text{ kJ}}{-923\text{ kJ}} = 4.24$$

If there is so much lattice energy to be gained in going from singly charged to doubly charged ions in the case of magnesium oxide, why then does solid sodium fluoride contain Na^+ and F^- ions rather than Na^{2+} and F^{2-} ions? We can answer this question by recognizing that both Na^+ and F^- ions have the neon electron configuration. Removal of an electron from Na^+ requires an extremely large quantity of energy (4560 kJ/mol) because a 2*p* electron must be removed. Conversely, the addition of an electron to F^- would require use of the relatively high-energy 3*s* orbital, which is also an unfavorable process. Thus we can say that for sodium fluoride the extra energy required to form the doubly charged ions is greater than the gain in lattice energy that would result.

This discussion of the energies involved in the formation of solid ionic compounds illustrates that a variety of factors operate to determine the composition and structure of these compounds. The most important of these factors involve the balancing of the energies required to form highly charged ions and the energy released when highly charged ions combine to form the solid.

8.6 Partial Ionic Character of Covalent Bonds

Recall that when atoms with different electronegativities react to form molecules, the electrons are not shared equally. The possible result is a polar covalent bond or, in the case of a large electronegativity difference, a complete transfer of one or more electrons to form ions. The cases are summarized in Fig. 8.12.

How well can we tell the difference between an ionic bond and a polar covalent bond? The only honest answer to this question is that there are probably no totally ionic bonds between *discrete pairs of atoms.* The evidence for this statement comes from calculations of the percent ionic character for the bonds of various binary compounds in the gas phase. These calculations are based on comparisons of the measured dipole moments for molecules of the type X—Y with the calculated dipole moments for the completely ionic case, X^+Y^-. The percent ionic character of a bond can be defined as

$$\text{Percent ionic character of a bond} = \left(\frac{\text{measured dipole moment of X—Y}}{\text{calculated dipole moment of }X^+Y^-}\right) \times 100\%$$

Application of this definition to various compounds (in the gas phase) gives the results shown in Fig. 8.13, where percent ionic character is plotted versus the difference in the electronegativity values of X and Y. Note from this plot that ionic character increases with electronegativity difference, as expected. However, none of the bonds reaches 100% ionic character, even though compounds with the maximum possible electronegativity differences are considered. Thus, according to this definition, no individual bonds are completely ionic. This conclusion is in contrast to the usual classification of many of these compounds (as ionic solids). All the compounds shown in Fig. 8.13 with more than 50% ionic character are normally considered to be ionic solids. Recall, however, the results in Fig. 8.13 are for the gas phase, where individual XY molecules exist. These results cannot necessarily be assumed to apply to the solid state, where the existence of ions is favored by the multiple ion interactions.

Another complication in identifying ionic compounds is that many substances contain polyatomic ions. For example, NH_4Cl contains NH_4^+ and Cl^- ions, and Na_2SO_4 contains Na^+ and SO_4^{2-} ions. The ammonium and sulfate ions are held together by covalent bonds. Thus, calling NH_4Cl and Na_2SO_4 ionic compounds is somewhat ambiguous.

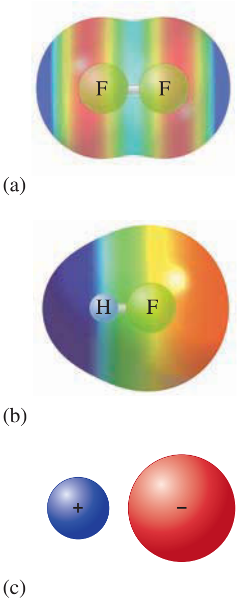


FIGURE 8.12
The three possible types of bonds: (a) a covalent bond formed between identical F atoms; (b) the polar covalent bond of HF, with both ionic and covalent components; and (c) an ionic bond with no electron sharing.

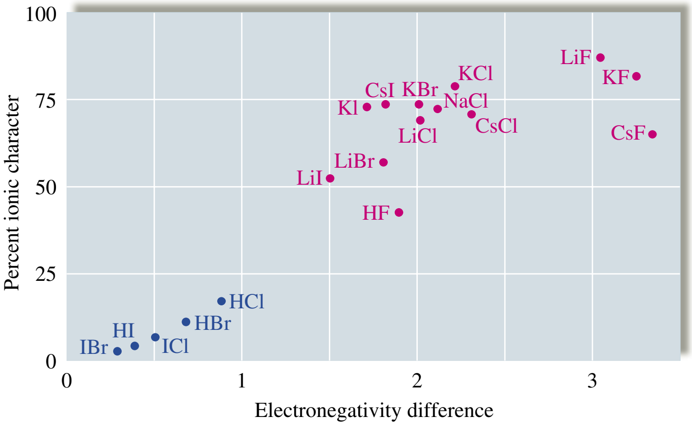


FIGURE 8.13
The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms. Note that the compounds with ionic character greater than 50% are normally considered to be ionic compounds.

We will avoid these problems by adopting an operational definition of ionic compounds: *Any compound that conducts an electric current when melted will be classified as ionic.*

8.7 The Covalent Chemical Bond: A Model

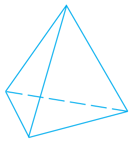
Before we develop specific models for covalent chemical bonding, it will be helpful to summarize some of the concepts introduced in this chapter.

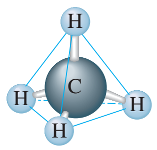
What is a chemical bond? Chemical bonds can be viewed as forces that cause a group of atoms to behave as a unit.

Why do chemical bonds occur? There is no principle of nature that states that bonds are favored or disfavored. Bonds are neither inherently “good” nor inherently “bad” as far as nature is concerned; *bonds result from the tendency of a system to seek its lowest possible energy.* From a simplistic point of view, bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms. For example, approximately 1652 kJ of energy is required to break a mole of methane (CH_4) molecules into separate C and H atoms. Or, taking the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms. Thus we can say that 1 mole of CH_4 molecules in the gas phase is 1652 kJ lower in energy than 1 mole of carbon atoms plus 4 moles of hydrogen atoms. Methane is therefore a stable molecule relative to its separated atoms.

A tetrahedron has four equal triangular faces.

We find it useful to interpret molecular stability in terms of a model called a *chemical bond.* To understand why this model was invented, let’s continue with methane, which consists of four hydrogen atoms arranged at the corners of a tetrahedron around a carbon atom:



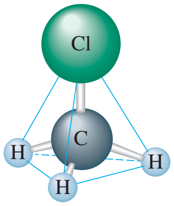


Given this structure, it is natural to envision four individual C—H interactions (we call them *bonds*). The energy of stabilization of CH_4 is divided equally among the four bonds to give an average C—H bond energy per mole of C—H bonds:

$$\frac{1652\ \text{kJ/mol}}{4} = 413\ \text{kJ/mol}$$

Molten NaCl conducts an electric current, indicating the presence of mobile Na^+ and Cl^- ions.

Next, consider methyl chloride, which consists of CH_3Cl molecules having the structure



Experiments have shown that approximately 1578 kJ of energy is required to break down 1 mole of gaseous CH_3Cl molecules into gaseous carbon, chlorine, and hydrogen atoms. The reverse process can be represented as

$$C(g) + Cl(g) + 3H(g) \longrightarrow CH_3Cl(g) + 1578 \text{ kJ/mol}$$

A mole of gaseous methyl chloride is lower in energy by 1578 kJ than its separate gaseous atoms. Thus a mole of methyl chloride is held together by 1578 kJ of energy. Again, it is very useful to divide this energy into individual bonds. Methyl chloride can be visualized as containing one C—Cl bond and three C—H bonds. If we assume arbitrarily that a C—H interaction represents the same quantity of energy in any situation (that is, that the strength of a C—H bond is independent of its molecular environment), we can do the following bookkeeping:

$$\begin{aligned} 1 \text{ mol C—Cl bonds plus 3 mol C—H bonds} &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} + 3(\text{average C—H bond energy}) &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} + 3(413 \text{ kJ/mol}) &= 1578 \text{ kJ} \\ \text{C—Cl bond energy} = 1578 - 1239 &= 339 \text{ kJ/mol} \end{aligned}$$

These assumptions allow us to associate given quantities of energy with C—H and C—Cl bonds.

It is important to note that the bond concept is a human invention. Bonds provide a method for dividing up the energy evolved when a stable molecule is formed from its component atoms. Thus in this context a bond represents a quantity of energy obtained from the overall molecular energy of stabilization in a rather arbitrary way. This is not to say that the concept of individual bonds is a bad idea. In fact, the modern concept of the chemical bond, conceived by the American chemists G. N. Lewis and Linus Pauling, is one of the most useful ideas chemists have ever developed.

Models: An Overview

The framework of chemistry, like that of any science, consists of *models*—attempts to explain how nature operates on the microscopic level based on experiences in the macroscopic world. To understand chemistry, one must understand its models and how they are used. We will use the concept of bonding to reemphasize the important characteristics of models, including their origin, structure, and uses.

Bonding is a model proposed to explain molecular stability.

Models originate from our observations of the properties of nature. For example, the concept of bonds arose from the observations that most chemical processes involve collections of atoms and that chemical reactions involve rearrangements of the ways the atoms are grouped. Therefore, to understand reactions, we must understand the forces that bind atoms together.

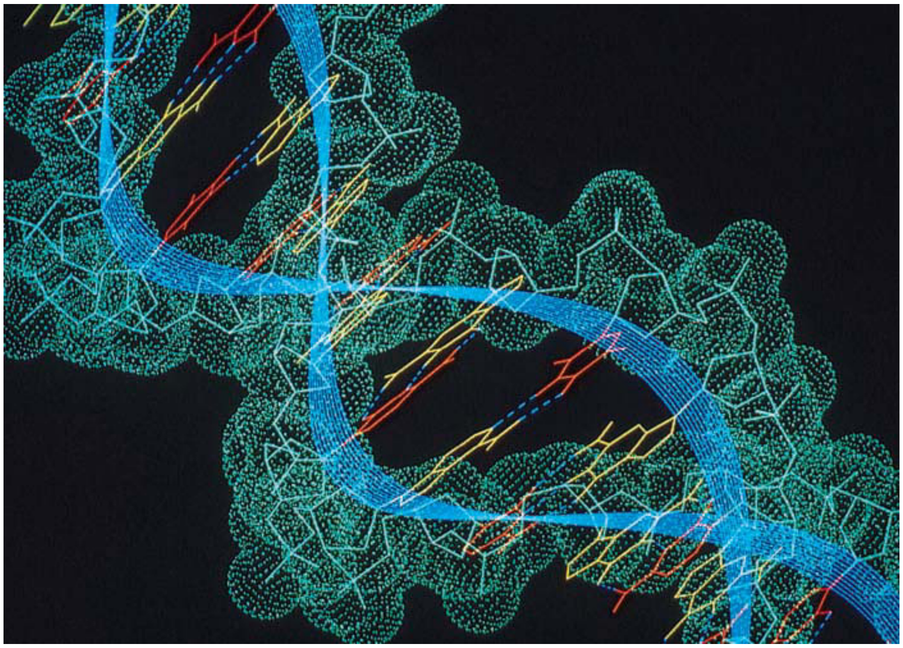
In natural processes there is a tendency toward lower energy. Collections of atoms therefore occur because the aggregated state has lower energy than the separated atoms. Why? As we saw earlier in this chapter, the best explanations for the energy change involve atoms sharing electrons or atoms transferring electrons to become ions. In the case of electron sharing, we find it convenient to assume that individual bonds occur between pairs of atoms. Let's explore the validity of this assumption and see how it is useful.

In a diatomic molecule such as H_2, it is natural to assume that a bond exists between the atoms, holding them together. It is also useful to assume that individual bonds are present in polyatomic molecules such as CH_4. Therefore, instead of thinking of CH_4 as a unit with a stabilization energy of 1652 kJ per mole, we choose to think of CH_4 as containing four C—H bonds, each worth 413 kJ of energy per mole of bonds. Without this concept of individual bonds in molecules, chemistry would be hopelessly complicated. There are millions of different chemical compounds, and if each of these compounds had to be considered as an entirely new entity, the task of understanding chemical behavior would be overwhelming.

The bonding model provides a framework to systematize chemical behavior by enabling us to think of molecules as collections of common fundamental components. For example, a typical biomolecule, such as a protein, contains hundreds of atoms and might seem discouragingly complex. However, if we think of a protein as constructed of individual bonds, C—C, C—H, C—N, C—O, N—H, and so on, it helps tremendously in predicting and understanding the protein's behavior. The essential idea is that we expect a given bond to behave about the same in any molecular environment. Used in this way, the model of the chemical bond has helped chemists to systematize the reactions of the millions of existing compounds.

In addition to being useful, the bonding model is physically sensible. It makes sense that atoms can form stable groups by sharing electrons; shared electrons give a lower energy state because they are simultaneously attracted by two nuclei.

Also, as we will see in the next section, bond energy data support the existence of discrete bonds that are relatively independent of the molecular environment. It is very important to remember, however, that the chemical bond is only a model. Although our concept of discrete bonds in molecules agrees with many of our observations, some molecular properties require that we think of a molecule as a whole, with the electrons free to move through the entire molecule. This is called *delocalization* of the electrons, a concept that will be discussed more completely in the next chapter.



The concept of individual bonds makes it much easier to deal with complex molecules such as DNA. A small segment of a DNA molecule is shown here.

Fundamental Properties of Models

- Models are human inventions, always based on an incomplete understanding of how nature works. *A model does not equal reality*.
- Models are often wrong. This property derives from the first property. Models are based on speculation and are always oversimplifications.
- Models tend to become more complicated as they age. As flaws are discovered in our models, we “patch” them and thus add more detail.
- It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can be expected to yield only qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.

  For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple aufbau principle used to account for the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper, for example, do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the simple model. However, this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we must apply it with caution and not expect it to be correct in every case.
- When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes. (Try to remember this when you get back your next chemistry test.)

8.8 Covalent Bond Energies and Chemical Reactions

In this section we will consider the energies associated with various types of bonds and see how the bonding concept is useful in dealing with the energies of chemical reactions. One important consideration is to establish the sensitivity of a particular type of bond to its molecular environment. For example, consider the stepwise decomposition of methane:

Process	**Energy Required (kJ/mol)**
$CH_4(g) \rightarrow CH_3(g) + H(g)$	435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	453
$CH_2(g) \rightarrow CH(g) + H(g)$	425
$CH(g) \rightarrow C(g) + H(g)$	339
	Total = 1652
	Average = $\frac{1652}{4}$ = 413

Although a C—H bond is broken in each case, the energy required varies in a nonsystematic way. This example shows that the C—H bond is somewhat sensitive to its environment. We use the *average* of these individual bond dissociation energies even though this quantity only approximates the energy associated with a C—H bond in a particular molecule. The degree of sensitivity of a bond to its environment also can be seen

TABLE 8.4 Average Bond Energies (kJ/mol)

Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190	S—S	266	C≡N	891
C—O	358	O—Cl	203			C=N	615
C—F	485	O—I	234	Si—Si	340		
C—Cl	339			Si—H	393		
C—Br	276	F—F	154	Si—C	360		
C—I	240	F—Cl	253	Si—O	452		
C—S	259	F—Br	237				
		Cl—Cl	239				
		Cl—Br	218				
		Br—Br	193				

*C=O(CO_2) = 799

from experimental measurements of the energy required to break the C—H bond in the following molecules:

Molecule	Measured C—H Bond Energy (kJ/mol)
$HCBr_3$	380
$HCCl_3$	380
HCF_3	430
C_2H_6	410

These data show that the C—H bond strength varies significantly with its environment, but the concept of an average C—H bond strength remains useful to chemists. The average values of bond energies for various types of bonds are listed in Table 8.4.

So far we have discussed bonds in which one pair of electrons is shared. This type of bond is called a **single bond.** As we will see in more detail later, atoms sometimes share two pairs of electrons, forming a **double bond,** or share three pairs of electrons, forming a **triple bond.** The bond energies for these *multiple bonds* are also given in Table 8.4.

A relationship also exists between the number of shared electron pairs and the bond length. As the number of shared electrons increases, the bond length shortens. This relationship is shown for selected bonds in Table 8.5.

Bond Energy and Enthalpy

Bond energy values can be used to calculate approximate energies for reactions. To illustrate how this is done, we will calculate the change in energy that accompanies the following reaction:

$$H_2(g) + F_2(g) \longrightarrow 2HF(g)$$

This reaction involves breaking one H—H and one F—F bond and forming two H—F bonds. For bonds to be broken, energy must be *added* to the system—-an endothermic

TABLE 8.5 Bond Lengths for Selected Bonds

Bond	Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	Single	154	347
C=C	Double	134	614
C≡C	Triple	120	839
C—O	Single	143	358
C=O	Double	123	745
C—N	Single	143	305
C=N	Double	138	615
C≡N	Triple	116	891

process. Consequently, the energy terms associated with bond breaking have *positive* signs. The formation of a bond *releases* energy, an exothermic process, so the energy terms associated with bond making carry a *negative* sign. We can write the enthalpy change for a reaction as follows:

ΔH = sum of the energies required to break old bonds (positive signs)
plus the sum of the energies released in the formation of new
bonds (negative signs)

This leads to the expression

$$\Delta H = \underbrace{\Sigma D\,(\text{bonds broken})}_{\text{Energy required}} - \underbrace{\Sigma D\,(\text{bonds formed})}_{\text{Energy released}}$$

where Σ represents the sum of terms, and D represents the bond energy per mole of bonds. (D *always* has a positive sign.)

In the case of the formation of HF,

$$\begin{aligned}\Delta H &= D_{\text{H—H}} + D_{\text{F—F}} - 2D_{\text{H—F}} \\ &= 1\text{ mol} \times \frac{432\text{ kJ}}{\text{mol}} + 1\text{ mol} \times \frac{154\text{ kJ}}{\text{mol}} - 2\text{ mol} \times \frac{565\text{ kJ}}{\text{mol}} \\ &= -544\text{ kJ}\end{aligned}$$

Thus, when 1 mol $H_2(g)$ and 1 mol $F_2(g)$ react to form 2 mol HF(g), 544 kJ of energy should be released.

This result can be compared with the calculation of ΔH for this reaction from the standard enthalpy of formation for HF (−271 kJ/mol):

$$\Delta H^\circ = 2\text{ mol} \times (-271\text{ kJ/mol}) = -542\text{ kJ}$$

Thus the use of bond energies to calculate ΔH works quite well in this case.

Sample Exercise 8.5

ΔH from Bond Energies

Using the bond energies listed in Table 8.4, calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2).

$$CH_4(g) + 2Cl_2(g) + 2F_2(g) \longrightarrow CF_2Cl_2(g) + 2HF(g) + 2HCl(g)$$

Solution

The idea here is to break the bonds in the gaseous reactants to give individual atoms and then assemble these atoms into the gaseous products by forming new bonds:

$$\text{Reactants} \xrightarrow[\text{required}]{\text{Energy}} \text{atoms} \xrightarrow[\text{released}]{\text{Energy}} \text{products}$$

We then combine the energy changes to calculate ΔH:

$$\Delta H = \text{energy required to break bonds} - \text{energy released when bonds form}$$

where the minus sign gives the correct sign to the energy terms for the exothermic processes.

Reactant Bonds Broken:

$$CH_4: \quad 4 \text{ mol C—H} \qquad 4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$$

$$2Cl_2: \quad 2 \text{ mol Cl—Cl} \qquad 2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$$

$$2F_2: \quad 2 \text{ mol F—F} \qquad 2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = \underline{308 \text{ kJ}}$$

$$\text{Total energy required} = 2438 \text{ kJ}$$

Product Bonds Formed:

$$CF_2Cl_2: \quad 2 \text{ mol C—F} \qquad 2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = 970 \text{ kJ}$$

and

$$2 \text{ mol C—Cl} \qquad 2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = 3678 \text{ kJ}$$

$$HF: \quad 2 \text{ mol H—F} \qquad 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = 1130 \text{ kJ}$$

$$HCl: \quad 2 \text{ mol H—Cl} \qquad 2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = \underline{3854 \text{ kJ}}$$

$$\text{Total energy released} = 3632 \text{ kJ}$$

We now can calculate ΔH:

$$\begin{aligned} \Delta H &= \text{energy required to break bonds} - \text{energy released when bonds form} \\ &= 2438 \text{ kJ} - 3632 \text{ kJ} \\ &= -1194 \text{ kJ} \end{aligned}$$

Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of CF_2Cl_2 formed.

See Exercises 8.53 through 8.60.

8.9 The Localized Electron Bonding Model

So far we have discussed the general characteristics of the chemical bonding model and have seen that properties such as bond strength and polarity can be assigned to individual bonds. In this section we introduce a specific model used to describe covalent bonds. We need a simple model that can be applied easily even to very complicated molecules and that can be used routinely by chemists to interpret and organize the wide variety of chemical phenomena. The model that serves this purpose is the **localized electron (LE) model,** which assumes that *a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.* Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called **lone pairs,** and those found in the space between the atoms are called **bonding pairs.**

As we will apply it, the LE model has three parts:

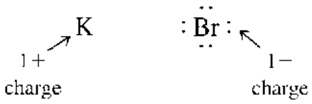
1. Description of the valence electron arrangement in the molecule using Lewis structures (will be discussed in the next section).
2. Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model (will be discussed in Section 8.13).
3. Description of the type of atomic orbitals used by the atoms to share electrons or hold lone pairs (will be discussed in Chapter 9).

8.10 Lewis Structures

The **Lewis structure** of a molecule shows how the valence electrons are arranged among the atoms in the molecule. These representations are named after G. N. Lewis (Fig. 8.14). The rules for writing Lewis structures are based on observations of thousands of molecules. From experiment, chemists have learned that the *most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configurations.*

We have already seen that when metals and nonmetals react to form binary ionic compounds, electrons are transferred and the resulting ions typically have noble gas electron configurations. An example is the formation of KBr, where the K^+ ion has the [Ar] electron configuration and the Br^- ion has the [Kr] electron configuration. In writing Lewis structures, the rule is that *only the valence electrons are included.* Using dots to represent electrons, the Lewis structure for KBr is

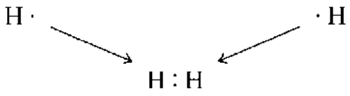
Lewis structures show only valence electrons.



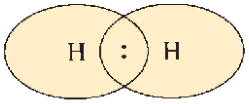
No dots are shown on the K^+ ion because it has no valence electrons. The Br^- ion is shown with eight electrons because it has a filled valence shell.

Next we will consider Lewis structures for molecules with covalent bonds, involving elements in the first and second periods. The principle of achieving a noble gas electron configuration applies to these elements as follows:

- Hydrogen forms stable molecules where it shares two electrons. That is, it follows a **duet rule.** For example, when two hydrogen atoms, each with one electron, combine to form the H_2 molecule, we have



By sharing electrons, each hydrogen in H_2, in effect, has two electrons; that is, each hydrogen has a filled valence shell.



- Helium does not form bonds because its valence orbital is already filled; it is a noble gas. Helium has the electron configuration $1s^2$ and can be represented by the Lewis structure

He :

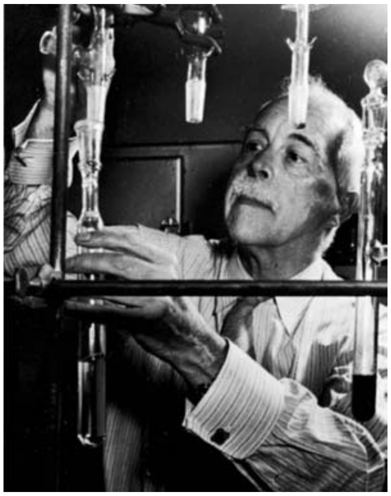
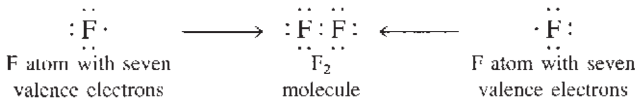


FIGURE 8.14
G. N. Lewis (1875–1946).

- The second-row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the 2*s* and the three 2*p* orbitals. Since eight electrons are required to fill these orbitals, these elements typically obey the **octet rule;** they are surrounded by eight electrons. An example is the F_2 molecule, which has the following Lewis structure:

Carbon, nitrogen, oxygen, and fluorine always obey the octet rule in stable molecules.



Note that each fluorine atom in F_2 is, in effect, surrounded by eight electrons, two of which are shared with the other atom. This is a *bonding pair* of electrons, as discussed earlier. Each fluorine atom also has three pairs of electrons not involved in bonding. These are the *lone pairs.*

- Neon does not form bonds because it already has an octet of valence electrons (it is a noble gas). The Lewis structure is

Note that only the valence electrons of the neon atom ($2s^22p^6$) are represented by the Lewis structure. The $1s^2$ electrons are core electrons and are not shown.

From the preceding discussion we can formulate the following rules for writing the Lewis structures of molecules containing atoms from the first two periods.

Steps for Writing Lewis Structures

➥ 1 **Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.**

➥ 2 **Use a pair of electrons to form a bond between each pair of bound atoms.**

➥ 3 **Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.**

To see how these steps are applied, we will draw the Lewis structures of a few molecules. We will first consider the water molecule and follow the previous steps.

➥ 1 We sum the *valence* electrons for H_2O as shown:

$$\underset{\overset{\nearrow}{\text{H}}}{1} + \underset{\overset{\nearrow}{\text{H}}}{1} + \underset{\overset{\nearrow}{\text{O}}}{6} = 8 \text{ valence electrons}$$

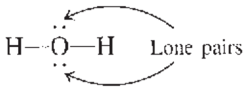
➥ 2 Using a pair of electrons per bond, we draw in the two O—H single bonds:

H—O—H

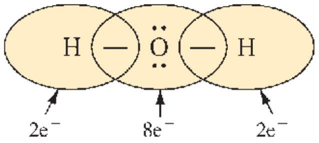
Note that *a line instead of a pair of dots is used to indicate each pair* of *bonding electrons.* This is the standard notation.

➥ 3 We distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons have been used in forming the two bonds, four electrons (8 − 4) remain to be distributed. Hydrogen is satisfied with two electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration. Thus the remaining four electrons are added to oxygen as two lone pairs. Dots are used to represent the lone pairs:

H—O—H represents H:O:H



This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight, as shown below:



As a second example, let's write the Lewis structure for carbon dioxide. Summing the valence electrons gives

$$\underset{\underset{\text{C}}{\nearrow}}{4} + \underset{\underset{\text{O}}{\nearrow}}{6} + \underset{\underset{\text{O}}{\nearrow}}{6} = 16$$

After forming a bond between the carbon and each oxygen,

$$\mathrm{O{-}C{-}O}$$

the remaining electrons are distributed to achieve noble gas configurations on each atom. In this case we have 12 electrons (16 − 4) remaining after the bonds are drawn. The distribution of these electrons is determined by a trial-and-error process. We have 6 pairs of electrons to distribute. Suppose we try 3 pairs on each oxygen to give

$$:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-\mathrm{C}-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:$$

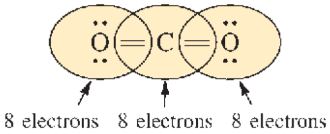
Is this correct? To answer this question, we need to check two things:

1. The total number of electrons. There are 16 valence electrons in this structure, which is the correct number.
2. The octet rule for each atom. Each oxygen has 8 electrons, but the carbon has only 4. This cannot be the correct Lewis structure.

$\ddot{\underset{\cdot\cdot}{\mathrm{O}}}=\mathrm{C}=\ddot{\underset{\cdot\cdot}{\mathrm{O}}}$ represents

$\ddot{\underset{\cdot\cdot}{\mathrm{O}}}::\mathrm{C}::\ddot{\underset{\cdot\cdot}{\mathrm{O}}}$

How can we arrange the 16 available electrons to achieve an octet for each atom? Suppose there are 2 shared pairs between the carbon and each oxygen:



Now each atom is surrounded by 8 electrons, and the total number of electrons is 16, as required. This is the correct Lewis structure for carbon dioxide, which has two double bonds and four lone pairs.

Finally, let's consider the Lewis structure of the $\mathrm{CN^-}$ (cyanide) ion. Summing the valence electrons, we have

$$\underset{\underset{4\ +\ 5\ +\ 1\ =\ 10}{\nearrow\ \ \nearrow\ \uparrow}}{\mathrm{CN^-}}$$

Note that the negative charge means an extra electron is present. After drawing a single bond (C—N), we distribute the remaining electrons to achieve a noble gas configuration for each atom. Eight electrons remain to be distributed. We can try various possibilities, for example:

$$\ddot{\underset{\cdot\cdot}{\text{C}}}\text{—}\ddot{\underset{\cdot\cdot}{\text{N}}}$$

This structure is incorrect because C and N have only six electrons each instead of eight. The correct arrangement is

$$[\,:\text{C}\equiv\text{N}:\,]^-$$

(Satisfy yourself that both carbon and nitrogen have eight electrons.)

Sample Exercise 8.6

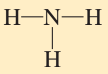
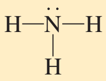
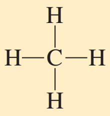
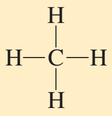
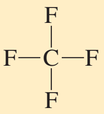
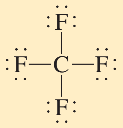
Writing Lewis Structures

Give the Lewis structure for each of the following.

a. HF	**d.** CH_4
b. N_2	**e.** CF_4
c. NH_3	**f.** NO^+

Solution

In each case we apply the three steps for writing Lewis structures. Recall that lines are used to indicate shared electron pairs and that dots are used to indicate nonbonding pairs (lone pairs). We have the following tabulated results:

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	$1 + 7 = 8$	H—F	6	$\text{H—}\ddot{\underset{\cdot\cdot}{\text{F}}}\colon$	H, 2 F, 8
b. N_2	$5 + 5 = 10$	N—N	8	$:\text{N}\equiv\text{N}:$	N, 8
c. NH_3	$5 + 3(1) = 8$	 $\begin{array}{c}\text{H—N—H}\\ \vert\\ \text{H}\end{array}$	2	 $\begin{array}{c}\text{H—}\ddot{\text{N}}\text{—H}\\ \vert\\ \text{H}\end{array}$	H, 2 N, 8
d. CH_4	$4 + 4(1) = 8$	 $\begin{array}{c}\text{H}\\ \vert\\ \text{H—C—H}\\ \vert\\ \text{H}\end{array}$	0	 $\begin{array}{c}\text{H}\\ \vert\\ \text{H—C—H}\\ \vert\\ \text{H}\end{array}$	H, 2 C, 8
e. CF_4	$4 + 4(7) = 32$	 $\begin{array}{c}\text{F}\\ \vert\\ \text{F—C—F}\\ \vert\\ \text{F}\end{array}$	24	 $\begin{array}{c}:\ddot{\text{F}}:\\ \vert\\ :\ddot{\underset{\cdot\cdot}{\text{F}}}\text{—C—}\ddot{\underset{\cdot\cdot}{\text{F}}}:\\ \vert\\ :\underset{\cdot\cdot}{\text{F}}:\end{array}$	F, 8 C, 8
f. NO^+	$5 + 6 - 1 = 10$	N—O	8	$[:\text{N}\equiv\text{O}:]^+$	N, 8 O, 8

See Exercises 8.67 and 8.68.

CHEMICAL IMPACT

Nitrogen Under Pressure

The element nitrogen exists at normal temperatures and pressures as a gas containing N_2, a molecule with a very strong triple bond. In the gas phase the diatomic molecules move around independently with almost no tendency to associate with each other. Under intense pressure, however, nitrogen changes to a dramatically different form. This conclusion was reached at the Carnegie Institution in Washington, D.C., by Mikhail Erements and his colleagues, who subjected nitrogen to a pressure of 2.4 million atmospheres in a special diamond anvil press. Under this tremendous pressure the bonds of the N_2 molecules break and a substance containing an aggregate of nitrogen atoms forms. In other words, under great pressure elemental nitrogen changes from a substance containing diatomic molecules to one containing many nitrogen atoms bonded to each other. Interestingly, this substance remains intact even after the pressure is released—-as long as the temperature remains at 100 K. This new form of nitrogen has a very high potential energy relative to N_2. Thus this substance would be an extraordinarily powerful propellant or explosive if enough of it could be made. This new form of nitrogen is also a semiconductor for electricity; normal nitrogen gas is an insulator.

The newly discovered form of nitrogen is significant for several reasons. For one thing, it may help us understand the nature of the interiors of the giant gas planets such as Jupiter. Also, their success in changing nitrogen to an atomic solid encourages high-pressure scientists who are trying to accomplish the same goal with hydrogen. It is surprising that nitrogen, which has diatomic molecules containing bonds more than twice as strong as those in hydrogen, will form an atomic solid at these pressures but hydrogen does not. Hydrogen remains a molecular solid at far greater pressures than nitrogen can endure.

A diamond anvil cell used to study materials at very high pressures.

When writing Lewis structures, do not worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all the available valence electrons of the atoms to achieve the lowest possible energy.* The valence electrons belong to the molecule, rather than to the individual atoms. Simply distribute all valence electrons so that the various rules are satisfied, without regard for the origin of each particular electron.

8.11 Exceptions to the Octet Rule

The localized electron model is a simple but very successful model, and the rules we have used for Lewis structures apply to most molecules. However, with such a simple model, some exceptions are inevitable. Boron, for example, tends to form compounds in which the boron atom has fewer than eight electrons around it—it does not have a complete octet. Boron trifluoride (BF_3), a gas at normal temperatures and pressures, reacts very

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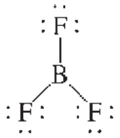
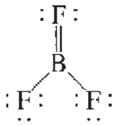
*In a sense this approach corrects for the fact that the localized electron model overemphasizes that a molecule is simply a sum of its parts—that is, that the atoms retain their individual identities in the molecule.

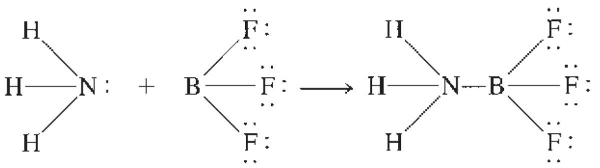
energetically with molecules such as water and ammonia that have available electron pairs (lone pairs). The violent reactivity of BF_3 with electron-rich molecules arises because the boron atom is electron-deficient. Boron trifluoride has 24 valence electrons. The Lewis structure often drawn for BF_3 is



Note that in this structure boron has only 6 electrons around it. The octet rule for boron can be satisfied by drawing a structure with a double bond, such as



Recent studies indicate that double bonding may be important in BF_3. However, the boron atom in BF_3 certainly behaves as if it is electron-deficient, as indicated by the reactivity of BF_3 toward electron-rich molecules, for example, toward NH_3 to form H_3NBF_3:



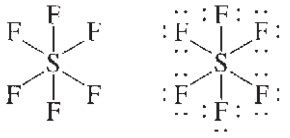
In this stable compound, boron has an octet of electrons.

It is characteristic of boron to form molecules in which the boron atom is electron-deficient. On the other hand, carbon, nitrogen, oxygen, and fluorine can be counted on to obey the octet rule.

Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond. To see how this arises, we will consider the Lewis structure for sulfur hexafluoride (SF_6), a well-known and very stable molecule. The sum of the valence electrons is

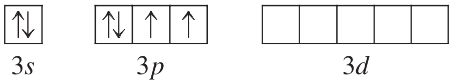
$$6 + 6(7) = 48 \text{ electrons}$$

Indicating the single bonds gives the structure on the left below:



We have used 12 electrons to form the S—F bonds, which leaves 36 electrons. Since fluorine always follows the octet rule, we complete the six fluorine octets to give the structure on the right above. This structure uses all 48 valence electrons for SF_6, but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule. How can this happen?

To answer this question, we need to consider the different types of valence orbitals characteristic of second- and third-period elements. The second-row elements have 2*s* and 2*p* valence orbitals, and the third-row elements have 3*s*, 3*p*, and 3*d* orbitals. The 3*s* and 3*p* orbitals fill with electrons in going from sodium to argon, but the 3*d* orbitals remain empty. For example, the valence orbital diagram for a sulfur atom is



Third-row elements can exceed the octet rule.

The localized electron model assumes that the empty 3*d* orbitals can be used to accommodate extra electrons. Thus the sulfur atom in SF_6 can have 12 electrons around it by using the 3*s* and 3*p* orbitals to hold 8 electrons, with the extra 4 electrons placed in the formerly empty 3*d* orbitals.

Whether the atoms that exceed the octet rule actually place the extra electrons in their *d* orbitals is a matter of controversy among theoretical chemists. We will not consider this issue in this text.

Lewis Structures: Comments About the Octet Rule

- The second-row elements C, N, O, and F should always be assumed to obey the octet rule.
- The second-row elements B and Be often have fewer than eight electrons around them in their compounds. These electron-deficient compounds are very reactive.
- The second-row elements never exceed the octet rule, since their valence orbitals (2*s* and 2*p*) can accommodate only eight electrons.
- Third-row and heavier elements often satisfy the octet rule but can exceed the octet rule by using their empty valence *d* orbitals.
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain after the octet rule has been satisfied, then place them on the elements having available *d* orbitals (elements in Period 3 or beyond).

Sample Exercise 8.7 Lewis Structures for Molecules That Violate the Octet Rule I

Write the Lewis structure for PCl_5.

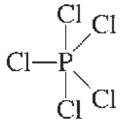
Solution

We can follow the same stepwise procedure we used above for sulfur hexafluoride.

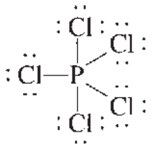
1 Sum the valence electrons.

$$\underset{\substack{\uparrow\\ \text{P}}}{5} + 5\underset{\substack{\uparrow\\ \text{Cl}}}{(7)} = 40 \text{ electrons}$$

2 Indicate single bonds between bound atoms.



3 Distribute the remaining electrons. In this case, 30 electrons (40 − 10) remain. These are used to satisfy the octet rule for each chlorine atom. The final Lewis structure is



Note that phosphorus, which is a third-row element, has exceeded the octet rule by two electrons.

See Exercises 8.71 and 8.72.

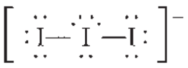
In the PCl_5 and SF_6 molecules, the central atoms (P and S, respectively) must have the extra electrons. However, in molecules having more than one atom that can exceed the octet rule, it is not always clear which atom should have the extra electrons. Consider the Lewis structure for the triiodide ion (I_3^-), which has

$$\underset{\overset{\uparrow}{\text{I}}}{3(7)} + \underset{\overset{\uparrow}{1-\text{ charge}}}{1} = 22 \text{ valence electrons}$$

Indicating the single bonds gives I—I—I. At this point, 18 electrons (22 − 4) remain. Trial and error will convince you that one of the iodine atoms must exceed the octet rule, but *which* one?

The rule we will follow is that *when it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom.*

Thus for I_3^- the Lewis structure is



where the central iodine exceeds the octet rule. This structure agrees with known properties of I_3^-.

Sample Exercise 8.8

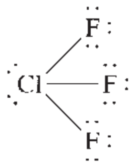
Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structure for each molecule or ion.

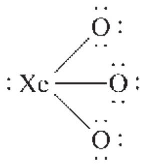
a. ClF_3 **b.** XeO_3 **c.** $RnCl_2$ **d.** $BeCl_2$ **e.** ICl_4^-

Solution

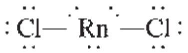
a. The chlorine atom (third row) accepts the extra electrons.



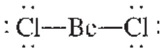
b. All atoms obey the octet rule.



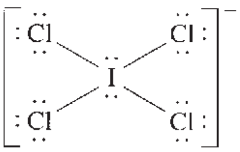
c. Radon, a noble gas in Period 6, accepts the extra electrons.



d. Beryllium is electron-deficient.



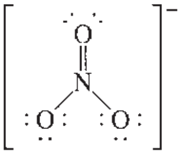
e. Iodine exceeds the octet rule.



See Exercises 8.71 and 8.72.

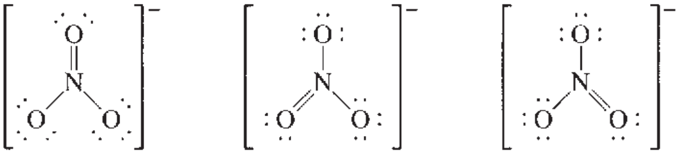
8.12 Resonance

Sometimes more than one valid Lewis structure (one that obeys the rules we have outlined) is possible for a given molecule. Consider the Lewis structure for the nitrate ion (NO_3^-), which has 24 valence electrons. To achieve an octet of electrons around each atom, a structure like this is required:



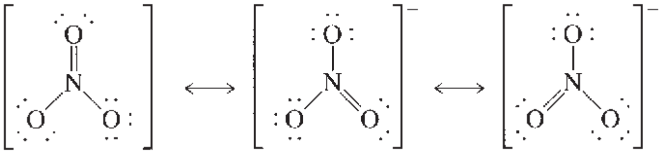
If this structure accurately represents the bonding in NO_3^-, there should be two types of N---O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds). However, experiments clearly show that NO_3^- exhibits only *one* type of N---O bond with a length and strength *between* those expected for a single bond and a double bond. Thus, although the structure we have shown above is a valid Lewis structure, it does *not* correctly represent the bonding in NO_3^-. This is a serious problem, and it means that the model must be modified.

Look again at the proposed Lewis structure for NO_3^-. There is no reason for choosing a particular oxygen atom to have the double bond. There are really three valid Lewis structures:



Is any of these structures a correct description of the bonding in NO_3^-? No, because NO_3^- does not have one double and two single bonds—it has three equivalent bonds. We can solve this problem by making the following assumption: The correct description of NO_3^- is *not given by any one* of the three Lewis structures but is given only by the *superposition of all three.*

The nitrate ion does not exist as any of the three extreme structures but exists as an average of all three. **Resonance** *is invoked when more than one valid Lewis structure can be written for a particular molecule.* The resulting electron structure of the molecule is given by the average of these **resonance structures.** This situation is usually represented by double-headed arrows as follows:



Note that in all these resonance structures the arrangement of the nuclei is the same. Only the placement of the electrons differs. The arrows do not mean that the molecule "flips" from one resonance to another. They simply show that the *actual structure is an average of the three resonance structures.*

The concept of resonance is necessary because the localized electron model postulates that electrons are localized between a given pair of atoms. However, nature does not really operate this way. Electrons are really delocalized—they can move around the entire molecule. The valence electrons in the NO_3^- molecule distribute themselves to provide equivalent N---O bonds. Resonance is necessary to compensate for the defective assumption of the localized electron model. However, this model is so useful that we retain the concept of localized electrons and add resonance to allow the model to treat species such as NO_3^-.

Sample Exercise 8.9 Resonance Structures

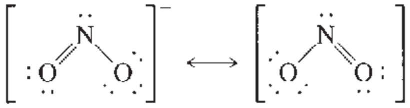
Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model.

Solution

We will follow the usual procedure for obtaining the Lewis structure for the NO_2^- ion. In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons. Indicating the single bonds gives the structure

$$O—N—O$$

The remaining 14 electrons ($18 - 4$) can be distributed to produce these structures:



This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two.* There are two equivalent N---O bonds, each one intermediate between a single and a double bond.

See Exercises 8.73 through 8.78.

Odd-Electron Molecules

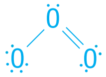
Relatively few molecules formed from nonmetals contain odd numbers of electrons. One common example is nitric oxide (NO), which is formed when nitrogen and oxygen gases react at the high temperatures in automobile engines. Nitric oxide is emitted into the air, where it immediately reacts with oxygen to form gaseous nitrogen dioxide (NO_2), another odd-electron molecule.

Since the localized electron model is based on pairs of electrons, it does not handle odd-electron cases in a natural way. To treat odd-electron molecules, a more sophisticated model is needed.

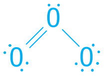
Formal Charge

Molecules or polyatomic ions containing atoms that can exceed the octet rule often have many nonequivalent Lewis structures, all of which obey the rules for writing Lewis structures. For example, as we will see in detail below, the sulfate ion has a Lewis structure with all single bonds and several Lewis structures that contain double bonds. How do we decide which of the many possible Lewis structures best describes the actual bonding in sulfate? One method is to estimate the charge on each atom in the various possible Lewis structures and use these charges to select the most appropriate structure(s). We will see below how this is done, but first we must decide on a method to assign atomic charges in molecules.

Equivalent Lewis structures contain the same numbers of single and multiple bonds. For example, the resonance structures for O_3



and



are equivalent Lewis structures. These are equally important in describing the bonding in O_3. Nonequivalent Lewis structures contain different numbers of single and multiple bonds.

In Chapter 4 we discussed one system for obtaining charges, called *oxidation states.* However, in assigning oxidation states, we always count *both* the shared electrons as belonging to the more electronegative atom in a bond. This practice leads to highly exaggerated estimates of charge. In other words, although oxidation states are useful for bookkeeping electrons in redox reactions, they are not realistic estimates of the actual charges on individual atoms in a molecule, so they are not suitable for judging the appropriateness of Lewis structures. Another definition of the charge on an atom in a molecule, the formal charge, can, however, be used to evaluate Lewis structures. As we will see below, the **formal charge** of an atom in a molecule is *the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.*

Therefore, to determine the formal charge of a given atom in a molecule, we need to know two things:

1. The number of valence electrons on the free neutral atom (which has zero net charge because the number of electrons equals the number of protons)
2. The number of valence electrons "belonging" to the atom in a molecule

We then compare these numbers. If in the molecule the atom has the same number of valence electrons as it does in the free state, the positive and negative charges just balance, and it has a formal charge of zero. If the atom has one more valence electron in a molecule than it has as a free atom, it has a formal charge of -1, and so on. Thus the formal charge on an atom in a molecule is defined as

$$\begin{aligned}\text{Formal charge} = {} & (\text{number of valence electrons on free atom}) \\ & - (\text{number of valence electrons assigned to the atom in the molecule})\end{aligned}$$

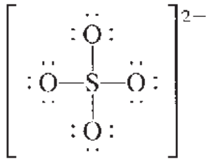
To compute the formal charge of an atom in a molecule, we assign the valence electrons in the molecule to the various atoms, making the following assumptions:

1. Lone pair electrons belong entirely to the atom in question.
2. Shared electrons are *divided equally* between the two sharing atoms.

Thus the number of valence electrons assigned to a given atom is calculated as follows:

$$\begin{aligned}(\text{Valence electrons})_{\text{assigned}} = {} & (\text{number of lone pair electrons}) \\ & + \tfrac{1}{2}(\text{number of shared electrons})\end{aligned}$$

We will illustrate the procedure for calculating formal charges by considering two of the possible Lewis structures for the sulfate ion, which has 32 valence electrons. For the Lewis structure



each oxygen atom has 6 lone pair electrons and shares 2 electrons with the sulfur atom. Thus, using the preceding assumptions, each oxygen is assigned 7 valence electrons.

$$\text{Valence electrons assigned to each oxygen} = \underset{\substack{\uparrow \\ \text{Lone} \\ \text{pair} \\ \text{electrons}}}{6} \textit{ plus } \frac{1}{2}\underset{\substack{\uparrow \\ \text{Shared} \\ \text{electrons}}}{(2)} = 7$$

$$\text{Formal charge on oxygen} = \underset{\substack{\uparrow \\ \text{Valence electrons} \\ \text{on a free O atom}}}{6} \textit{ minus } \underset{\substack{\uparrow \\ \text{Valence electrons} \\ \text{assigned to each O} \\ \text{in } SO_4^{2-}}}{7} = -1$$

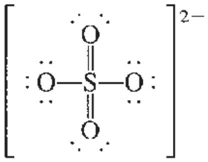
The formal charge on each oxygen is −1.

For the sulfur atom there are no lone pair electrons, and eight electrons are shared with the oxygen atoms. Thus, for sulfur,

$$\text{Valence electrons assigned to sulfur} = \underset{\substack{\uparrow\\ \text{Lone}\\ \text{pair}\\ \text{electrons}}}{0}\ \textit{plus}\ \underset{\substack{\uparrow\\ \text{Shared}\\ \text{electrons}}}{\tfrac{1}{2}(8)} = 4$$

$$\text{Formal charge on sulfur} = \underset{\substack{\uparrow\\ \text{Valence electrons}\\ \text{on a free S atom}}}{6}\ \textit{minus}\ \underset{\substack{\uparrow\\ \text{Valence}\\ \text{electrons}\\ \text{assigned to S}\\ \text{in } SO_4^{2-}}}{4} = 2$$

A second possible Lewis structure is



In this case the formal charges are as follows:

For oxygen atoms with single bonds:

$$\text{Valence electrons assigned} = 6 + \tfrac{1}{2}(2) = 7$$

$$\text{Formal charge} = 6 - 7 = -1$$

For oxygen atoms with double bonds:

$$\text{Valence electrons assigned} = 4 + \underset{\substack{\uparrow\\ \text{Each double}\\ \text{bond has 4}\\ \text{electrons}}}{\tfrac{1}{2}(4)} = 6$$

$$\text{Formal charge} = 6 - 6 = 0$$

For the sulfur atom:

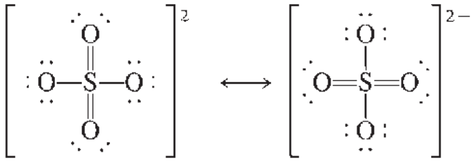
$$\text{Valence electrons assigned} = 0 + \tfrac{1}{2}(12) = 6$$

$$\text{Formal charge} = 6 - 6 = 0$$

We will use two fundamental assumptions about formal charges to evaluate Lewis structures:

1. Atoms in molecules try to achieve formal charges as close to zero as possible.
2. Any negative formal charges are expected to reside on the most electronegative atoms.

We can use these principles to evaluate the two Lewis structures for sulfate given previously. Notice that in the structure with only single bonds, each oxygen has a formal charge of −1, while the sulfur has a formal charge of +2. In contrast, in the structure with two double bonds and two single bonds, the sulfur and two oxygen atoms have a formal charge of 0, while two oxygens have a formal charge of −1. Based on the assumptions given above, the structure with two double bonds is preferred—it has lower formal charges and the −1 formal charges are on electronegative oxygen atoms. Thus, for the sulfate ion, we might expect resonance structures such as



to more closely describe the bonding than the Lewis structure with only single bonds.

Rules Governing Formal Charge

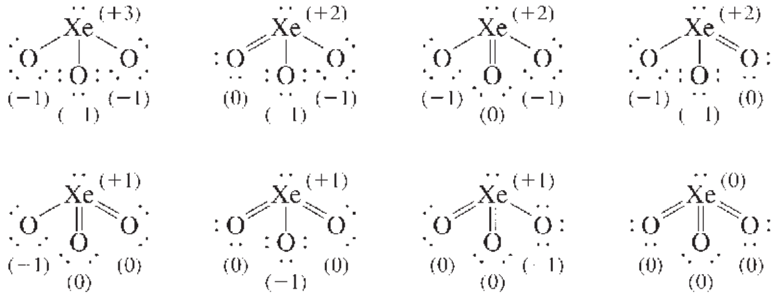
- To calculate the formal charge on an atom:
  1. Take the sum of the lone pair electrons and one-half the shared electrons. This is the number of valence electrons assigned to the atom in the molecule.
  2. Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge.
- The sum of the formal charges of all atoms in a given molecule or ion must equal the overall charge on that species.
- If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion.

Sample Exercise 8.10 Formal Charges

Give possible Lewis structures for XeO_3, an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

Solution

For XeO_3 (26 valence electrons) we can draw the following possible Lewis structures (formal charges are indicated in parentheses):



Based on the ideas of formal charge, we would predict that the Lewis structures with the lower values of formal charge would be most appropriate for describing the bonding in XeO_3.

See Exercises 8.81 through 8.86.

As a final note, there are a couple of cautions about formal charge to keep in mind. First, although formal charges are closer to actual atomic charges in molecules than are oxidation states, formal charges still provide only *estimates* of charge—they should not be taken as actual atomic charges. Second, the evaluation of Lewis structures using formal charge ideas can lead to erroneous predictions. Tests based on experiments must be used to make the final decisions on the correct description of the bonding in a molecule or polyatomic ion.

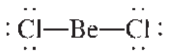
8.13 Molecular Structure: The VSEPR Model

The structures of molecules play a very important role in determining their chemical properties. As we will see later, this is particularly important for biological molecules; a slight change in the structure of a large biomolecule can completely destroy its usefulness to a cell or may even change the cell from a normal one to a cancerous one.

Visualization:VSEPR

Many accurate methods now exist for determining **molecular structure,** the three-dimensional arrangement of the atoms in a molecule. These methods must be used if precise information about structure is required. However, it is often useful to be able to predict the approximate molecular structure of a molecule. In this section we consider a simple model that allows us to do this. This model, called the **valence shell electron-pair repulsion (VSEPR) model,** is useful in predicting the geometries of molecules formed from nonmetals. The main postulate of this model is that *the structure around a given atom is determined principally by minimizing electron-pair repulsions.* The idea here is that the bonding and nonbonding pairs around a given atom will be positioned as far apart as possible. To see how this model works, we will first consider the molecule $BeCl_2$, which has the Lewis structure

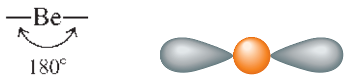
$BeCl_2$ has only four electrons around Be and is expected to be very reactive with electron-pair donors.



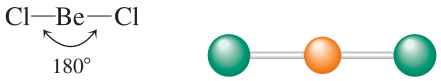
$$:\ddot{\underset{..}{Cl}}-Be-\ddot{\underset{..}{Cl}}:$$

Note that there are two pairs of electrons around the beryllium atom. What arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsions? Clearly, the best arrangement places the pairs on opposite sides of the beryllium atom at 180 degrees from each other:

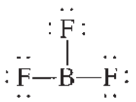
Visualization: VSEPR: Two Electron Pairs



This is the maximum possible separation for two electron pairs. Once we have determined the optimal arrangement of the electron pairs around the central atom, we can specify the molecular structure of $BeCl_2$, that is, the positions of the atoms. Since each electron pair on beryllium is shared with a chlorine atom, the molecule has a **linear structure** with a 180-degree bond angle:

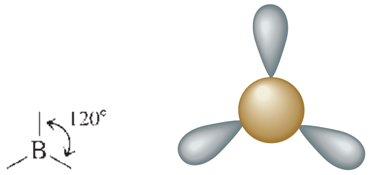


Next, let's consider BF_3, which has the Lewis structure

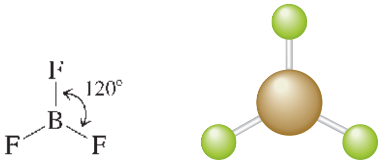


Here the boron atom is surrounded by three pairs of electrons. What arrangement will minimize the repulsions? The electron pairs are farthest apart at angles of 120 degrees:

Visualization: VSEPR: Three Electron Pairs

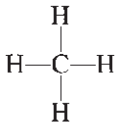


Since each of the electron pairs is shared with a fluorine atom, the molecular structure will be



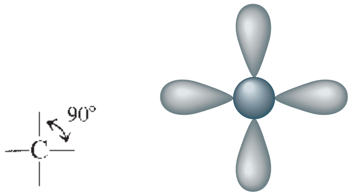
This is a planar (flat) and triangular molecule, which is commonly described as a **trigonal planar structure.**

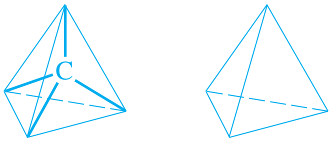
Next, let's consider the methane molecule, which has the Lewis structure



$$\begin{array}{c} \text{H} \\ | \\ \text{H—C—H} \\ | \\ \text{H} \end{array}$$

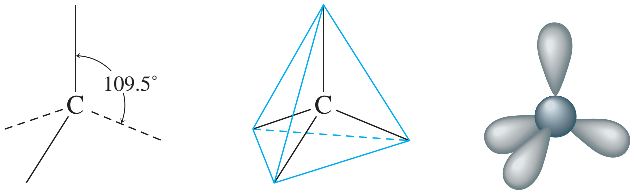
There are four pairs of electrons around the central carbon atom. What arrangement of these electron pairs best minimizes the repulsions? First, let's try a square planar arrangement:





The carbon atom and the electron pairs are centered in the plane of the paper, and the angles between the pairs are all 90 degrees.

Is there another arrangement with angles greater than 90 degrees that would put the electron pairs even farther away from each other? The answer is yes. The **tetrahedral structure** has angles of 109.5 degrees:



Visualization: VSEPR: Four Electron Pairs

It can be shown that this is the maximum possible separation of four pairs around a given atom. This means that *whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally.*

Now that we have the electron-pair arrangement that gives the least repulsion, we can determine the positions of the atoms and thus the molecular structure of CH_4. In methane, each of the four electron pairs is shared between the carbon atom and a hydrogen atom. Thus the hydrogen atoms are placed as in Fig. 8.15, and the molecule has a tetrahedral structure with the carbon atom at the center.

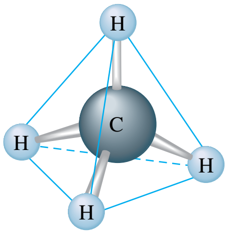


FIGURE 8.15
The molecular structure of methane. The tetrahedral arrangement of electron pairs produces a tetrahedral arrangement of hydrogen atoms.

Recall that the main idea of the VSEPR model is to find the arrangement of electron pairs around the central atom that minimizes the repulsions. Then we can determine the molecular structure from knowing how the electron pairs are shared with the peripheral atoms. Use the following steps to predict the structure of a molecule using the VSEPR model.

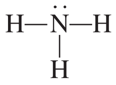
Steps to Apply the VSEPR Model

1. **Draw the Lewis structure for the molecule.**
2. **Count the electron pairs and arrange them in the way that minimizes repulsion (that is, put the pairs as far apart as possible).**
3. **Determine the positions of the atoms from the *way the electron pairs are shared.***
4. **Determine the name of the molecular structure from the *positions of the atoms.***

We will predict the structure of ammonia (NH_3) using this stepwise approach.

When four uniform balloons are tied together, they naturally form a tetrahedral shape.

1 Draw the Lewis structure:



$$\mathrm{H{-}\ddot{N}{-}H}\atop{\mathrm{|}\atop\mathrm{H}}$$

2 Count the pairs of electrons and arrange them to minimize repulsions. The NH_3 molecule has four pairs of electrons: three bonding pairs and one nonbonding pair. From the discussion of the methane molecule, we know that the best arrangement of four electron pairs is a tetrahedral array, as shown in Fig. 8.16(a).

3 Determine the positions of the atoms. The three H atoms share electron pairs, as shown in Fig. 8.16(b).

4 Name the molecular structure. It is very important to recognize that the *name* of the molecular structure is always based on the *positions of the atoms.* The placement of the electron pairs determines the structure, but the name is based on the positions of the atoms. Thus it is incorrect to say that the NH_3 molecule is tetrahedral. It has a tetrahedral arrangement of electron pairs but not a tetrahedral arrangement of atoms. The molecular structure of ammonia is a **trigonal pyramid** (one side is different from the other three) rather than a tetrahedron, as shown in Fig. 8.16(c).

Sample Exercise 8.11

Prediction of Molecular Structure I

Describe the molecular structure of the water molecule.

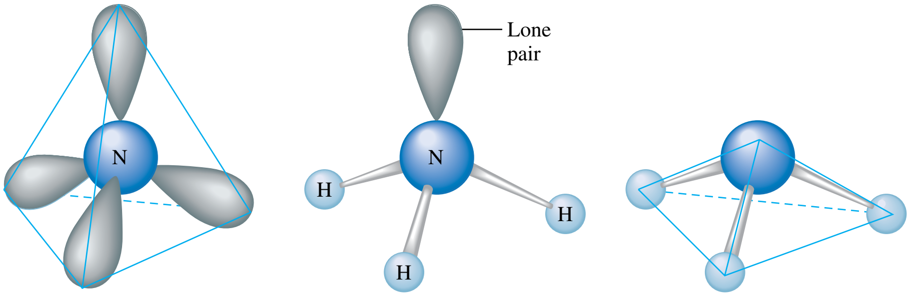
Solution

The Lewis structure for water is

$$\mathrm{H{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{-}H}$$

There are four pairs of electrons: two bonding pairs and two nonbonding pairs. To minimize repulsions, these are best arranged in a tetrahedral array, as shown in Fig. 8.17(a).

FIGURE 8.16
(a) The tetrahedral arrangement of electron pairs around the nitrogen atom in the ammonia molecule. (b) Three of the electron pairs around nitrogen are shared with hydrogen atoms as shown and one is a lone pair. Although the arrangement of *electron pairs* is tetrahedral, as in the methane molecule, the hydrogen atoms in the ammonia molecule occupy only three corners of the tetrahedron. A lone pair occupies the fourth corner. (c) Note that molecular geometry is trigonal pyramidal, not tetrahedral.



(a) (b) (c)

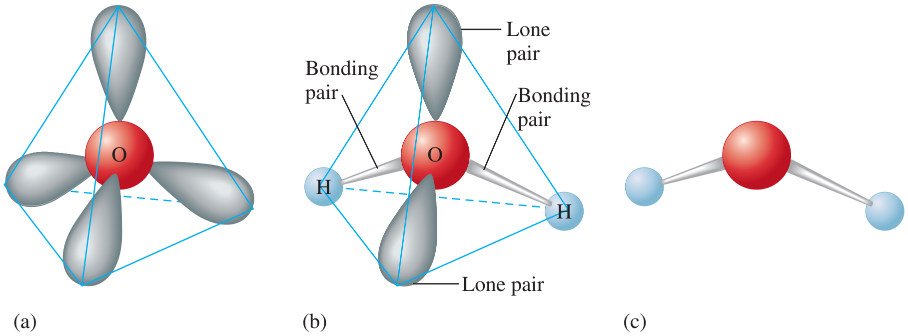


FIGURE 8.17
(a) The tetrahedral arrangement of the four electron pairs around oxygen in the water molecule. (b) Two of the electron pairs are shared between oxygen and the hydrogen atoms and two are lone pairs. (c) The V-shaped molecular structure of the water molecule.

Although H_2O has a tetrahedral arrangement of electron pairs, it is not a tetrahedral molecule. The atoms in the H_2O molecule form a V shape, as shown in Fig. 8.17(b) and (c).

See Exercises 8.91 and 8.92.

From Sample Exercise 8.11 we see that the H_2O molecule is V-shaped, or bent, because of the presence of the lone pairs. If no lone pairs were present, the molecule would be linear, the polar bonds would cancel, and the molecule would have no dipole moment. This would make water very different from the polar substance so familiar to us.

From the previous discussion we would predict that the H—X—H bond angle (where X is the central atom) in CH_4, NH_3, and H_2O should be the tetrahedral angle of 109.5 degrees. Experimental studies, however, show that the actual bond angles are those given in Fig. 8.18. What significance do these results have for the VSEPR model? One possible point of view is that we should be pleased to have the observed angles so close to the tetrahedral angle. The opposite view is that the deviations are significant enough to require modification of the simple model so that it can more accurately handle similar cases. We will take the latter view.

Let us examine the following data:

	CH_4	NH_3	H_2O
Number of Lone Pairs	0	1	2
Bond Angle	109.5°	107°	104.5°

One interpretation of the trend observed here is that lone pairs require more space than bonding pairs; in other words, as the number of lone pairs increases, the bonding pairs are increasingly squeezed together.

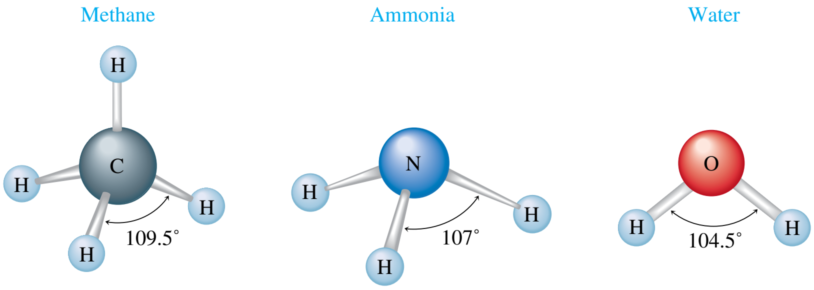
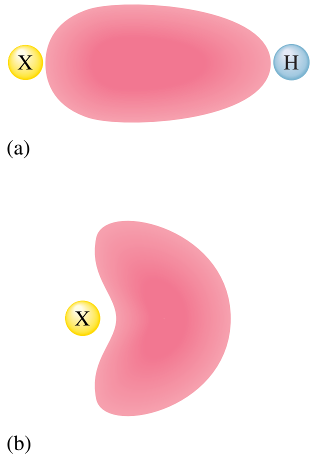


FIGURE 8.18
The bond angles in the CH_4, NH_3, and H_2O molecules. Note that the bond angle between bonding pairs decreases as the number of lone pairs increases. Note that all of the angles in CH_4 are 109.5 degrees and all of the angles in NH_3 are 107 degrees.



(a)

(b)

FIGURE 8.19
(a) In a bonding pair of electrons, the electrons are shared by two nuclei. (b) In a lone pair, both electrons must be close to a single nucleus and tend to take up more of the space around that atom.

This interpretation seems to make physical sense if we think in the following terms. A bonding pair is shared between two nuclei, and the electrons can be close to either nucleus. They are relatively confined between the two nuclei. A lone pair is localized on only one nucleus, and both electrons will be close only to that nucleus, as shown schematically in Fig. 8.19. These pictures help us understand why a lone pair may require more space near an atom than a bonding pair.

As a result of these observations, we make the following addition to the original postulate of the VSEPR model: *Lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs.*

So far we have considered cases with two, three, and four electron pairs around the central atom. These are summarized in Table 8.6.

Table 8.7 summarizes the structures possible for molecules in which there are four electron pairs around the central atom with various numbers of atoms bonded to it. Note that molecules with four pairs of electrons around the central atom can be tetrahedral (AB_4), trigonal pyramidal (AB_3), and V-shaped (AB_2).

For five pairs of electrons, there are several possible choices. The one that produces minimum repulsion is a **trigonal bipyramid.** Note from Table 8.6 that this arrangement

TABLE 8.6 Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

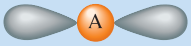
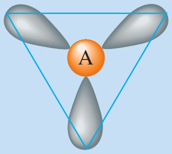
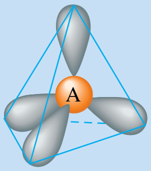
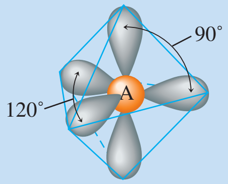
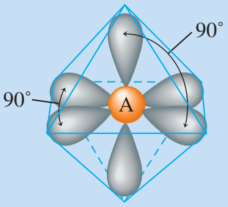
Number of Electron Pairs	Arrangement of Electron Pairs	Example
2	Linear 	
3	Trigonal planar 	
4	Tetrahedral 	
5	Trigonal bipyramidal 	
6	Octahedral 	

TABLE 8.7 Structures of Molecules That Have Four Electron Pairs Around the Central Atom

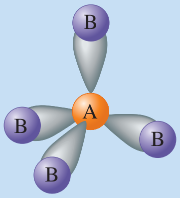
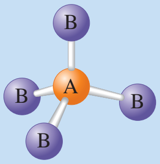
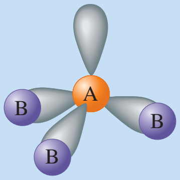
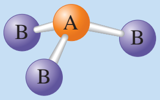
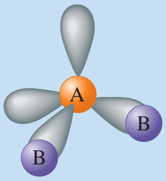
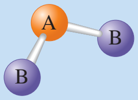
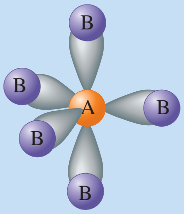
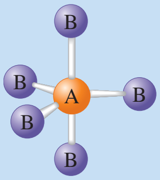
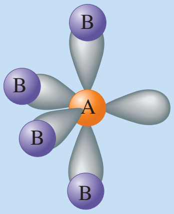
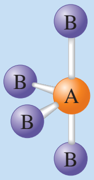
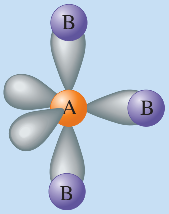
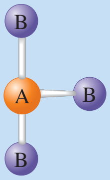
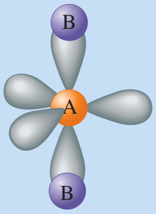
Electron-Pair Arrangement	Molecular Structure
	 Tetrahedral
	 Trigonal pyramid
	 V-shaped (bent)

TABLE 8.8 Structures of Molecules with Five Electron Pairs Around the Central Atom

Electron-Pair Arrangement	Molecular Structure
	 Trigonal bipyramidal
	 “See-saw”
	 T-structure
	 Linear

has two different angles, 90 degrees and 120 degrees. As the name suggests, the structure formed by this arrangement of pairs consists of two trigonal-based pyramids that share a common base. Table 8.8 summarizes the structures possible for molecules in which there are five electron pairs around the central atom with various numbers of atoms bonded to it. Note that molecules with five pairs of electrons around the central atom can be trigonal bipyramidal (AB_5), see-saw (AB_4), T-shaped (AB_3), and linear (AB_2).

Six pairs of electrons can best be arranged around a given atom with 90-degree angles to form an **octahedral structure,** as shown in Table 8.6.

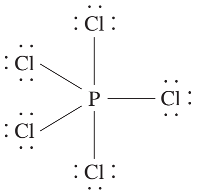
To use the VSEPR model to determine the geometric structures of molecules, you should memorize the relationships between the number of electron pairs and their best arrangement.

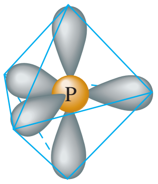
Sample Exercise 8.12 Prediction of Molecular Structure II

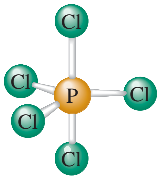
When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed. In the gaseous and liquid states, this substance consists of PCl_5 molecules, but in the solid state it consists of a 1 : 1 mixture of PCl_4^+ and PCl_6^- ions. Predict the geometric structures of PCl_5, PCl_4^+, and PCl_6^-.

Solution

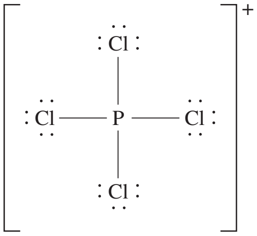
The Lewis structure for PCl_5 is shown. Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement (see Table 8.6). When the chlorine atoms are included, a trigonal bipyramidal molecule results:

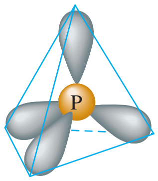


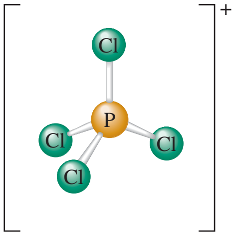




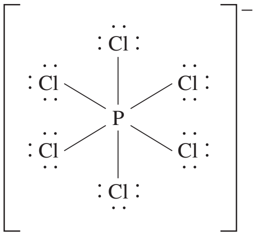
The Lewis structure for the PCl_4^+ ion ($5 + 4(7) - 1 = 32$ valence electrons) is shown below. There are four pairs of electrons surrounding the phosphorus atom in the PCl_4^+ ion, which requires a tetrahedral arrangement of the pairs. Since each pair is shared with a chlorine atom, a tetrahedral PCl_4^+ cation results.

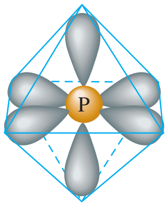


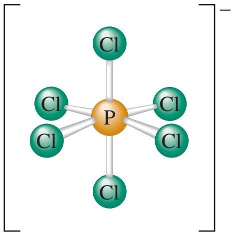




The Lewis structure for PCl_6^- ($5 + 6(7) + 1 = 48$ valence electrons) is shown below. Since phosphorus is surrounded by six pairs of electrons, an octahedral arrangement is required to minimize repulsions, as shown below in the center. Since each electron pair is shared with a chlorine atom, an octahedral PCl_6^- anion is predicted.







See Exercises 8.89, 8.90, 8.93, and 8.94.

Sample Exercise 8.13 Prediction of Molecular Structure III

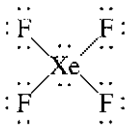
Visualization: VSEPR: Iodine Pentafluoride

Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called *inert gases* because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the

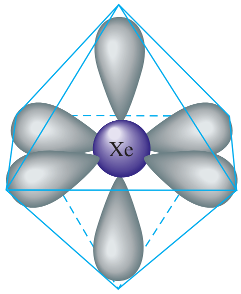
Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4). Predict its structure and whether it has a dipole moment.

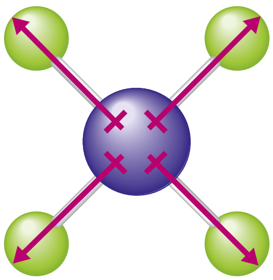
Solution

The Lewis structure for XeF_4 is



The xenon atom in this molecule is surrounded by six pairs of electrons, which means an octahedral arrangement.

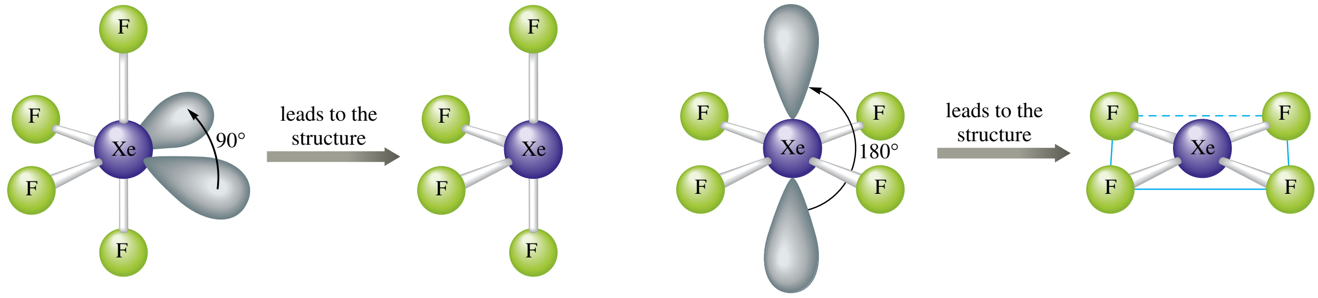




The structure predicted for this molecule will depend on how the lone pairs and bonding pairs are arranged. Consider the two possibilities shown in Fig. 8.20. The bonding pairs are indicated by the presence of the fluorine atoms. Since the structure predicted differs in the two cases, we must decide which of these arrangements is preferable. The key is to look at the lone pairs. In the structure in part (a), the lone pair–lone pair angle is 90 degrees; in the structure in part (b), the lone pairs are separated by 180 degrees. Since lone pairs require more room than bonding pairs, a structure with two lone pairs at 90 degrees is unfavorable. Thus the arrangement in Fig. 8.20(b) is preferred, and the molecular structure is predicted to be square planar. Note that this molecule is *not* described as being octahedral. There is an *octahedral arrangement of electron pairs,* but the *atoms* form a **square planar structure.**

Although each Xe—F bond is polar (fluorine has a greater electronegativity than xenon), the square planar arrangement of these bonds causes the polarities to cancel. Thus XeF_4 has no dipole moment, as shown in the margin.

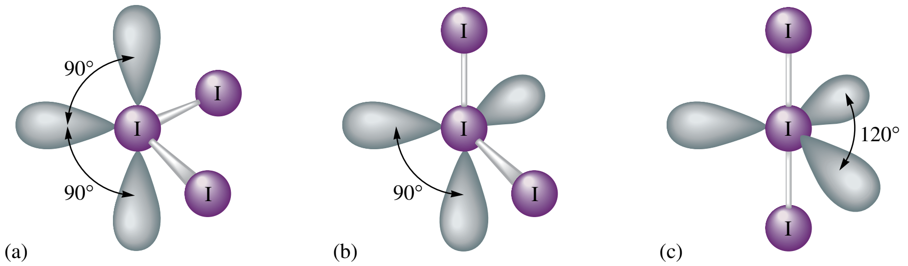
See Exercises 8.95 through 8.98.



(a)

(b)

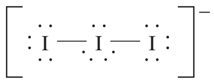
FIGURE 8.20
Possible electron-pair arrangements for XeF_4. Since arrangement (a) has lone pairs at 90 degrees from each other, it is less favorable than arrangement (b), where the lone pairs are at 180 degrees.

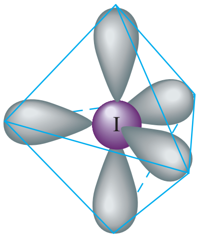


(a) (b) (c)

FIGURE 8.21
Three possible arrangements of the electron pairs in the I_3^- ion. Arrangement (c) is preferred because there are no 90-degree lone pair–lone pair interactions.

We can further illustrate the use of the VSEPR model for molecules or ions with lone pairs by considering the triiodide ion (I_3^-).



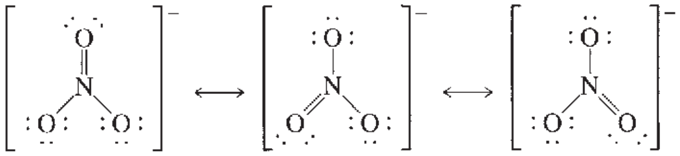


The central iodine atom has five pairs around it, which requires a trigonal bipyramidal arrangement. Several possible arrangements of lone pairs are shown in Fig. 8.21. Note that structures (a) and (b) have lone pairs at 90 degrees, whereas in (c) all lone pairs are at 120 degrees. Thus structure (c) is preferred. The resulting molecular structure for I_3^- is linear:

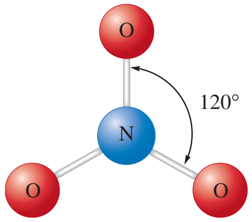
$$[\mathrm{I{-}I{-}I}]^-$$

The VSEPR Model and Multiple Bonds

So far in our treatment of the VSEPR model we have not considered any molecules with multiple bonds. To see how these molecules are handled by this model, let's consider the NO_3^- ion, which requires three resonance structures to describe its electronic structure:



The NO_3^- ion is known to be planar with 120-degree bond angles:



This planar structure is the one expected for three pairs of electrons around a central atom, which means that *a double bond should be counted as one effective pair* in using the VSEPR model. This makes sense because the two pairs of electrons involved in the double bond are *not* independent pairs. Both the electron pairs must be in the space between the nuclei of the two atoms to form the double bond. In other words, the double bond acts as one center of electron density to repel the other pairs of electrons. The same holds true for triple bonds. This leads us to another general rule: *For the VSEPR model, multiple bonds count as one effective electron pair.*

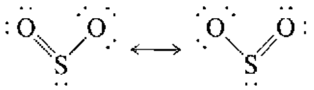
The molecular structure of nitrate also shows us one more important point: *When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.* These rules are illustrated in Sample Exercise 8.14.

Sample Exercise 8.14 Structures of Molecules with Multiple Bonds

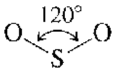
Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?

Solution

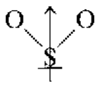
First, we must determine the Lewis structure for the SO_2 molecule, which has 18 valence electrons. The expected resonance structures are



To determine the molecular structure, we must count the electron pairs around the sulfur atom. In each resonance structure the sulfur has one lone pair, one pair in a single bond, and one double bond. Counting the double bond as one pair yields three effective pairs around the sulfur. According to Table 8.6, a trigonal planar arrangement is required, which yields a V-shaped molecule:



Thus the structure of the SO_2 molecule is expected to be V-shaped, with a 120-degree bond angle. The molecule has a dipole moment directed as shown:



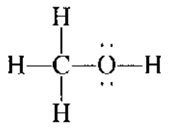
Since the molecule is V-shaped, the polar bonds do not cancel.

See Exercises 8.99 and 8.100.

It should be noted at this point that lone pairs that are oriented at least 120 degrees from other pairs do not produce significant distortions of bond angles. For example, the angle in the SO_2 molecule is actually quite close to 120 degrees. We will follow the general principle that *a 120-degree angle provides lone pairs with enough space so that distortions do not occur. Angles less than 120 degrees are distorted when lone pairs are present.*

Molecules Containing No Single Central Atom

So far we have considered molecules consisting of one central atom surrounded by other atoms. The VSEPR model can be readily extended to more complicated molecules, such as methanol (CH_3OH). This molecule is represented by the following Lewis structure:



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}\overset{..}{\underset{..}{O}}{-}H}$$

The molecular structure can be predicted from the arrangement of pairs around the carbon and oxygen atoms. Note that there are four pairs of electrons around the carbon, which requires a tetrahedral arrangement, as shown in Fig. 8.22(a). The oxygen also has four pairs, which requires a tetrahedral arrangement. However, in this case the tetrahedron will be slightly distorted by the space requirements of the lone pairs [Fig. 8.22(b)]. The overall geometric arrangement for the molecule is shown in Fig. 8.22(c).

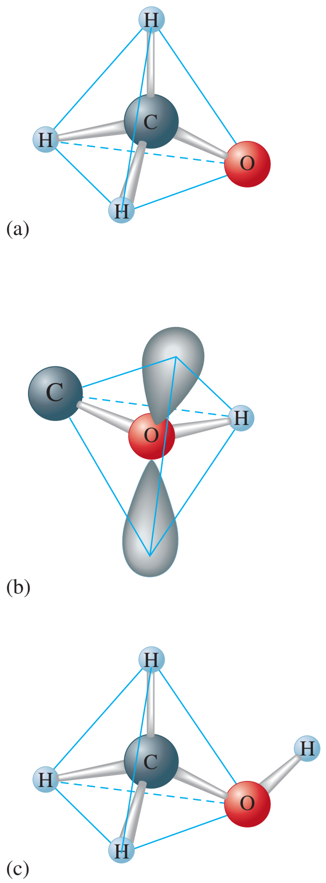


FIGURE 8.22
The molecular structure of methanol. (a) The arrangement of electron pairs and atoms around the carbon atom. (b) The arrangement of bonding and lone pairs around the oxygen atom. (c) The molecular structure.

Summary of the VSEPR Model

The rules for using the VSEPR model to predict molecular structure follow:

- Determine the Lewis structure(s) for the molecule.
- For molecules with resonance structures, use any of the structures to predict the molecular structure.
- Sum the electron pairs around the central atom.
- In counting pairs, count each multiple bond as a single effective pair.
- The arrangement of the pairs is determined by minimizing electron-pair repulsions. These arrangements are shown in Table 8.6.
- Lone pairs require more space than bonding pairs do. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120 degrees.

The VSEPR Model—How Well Does It Work?

The VSEPR model is very simple. There are only a few rules to remember, yet the model correctly predicts the molecular structures of most molecules formed from nonmetallic elements. Molecules of any size can be treated by applying the VSEPR model to each appropriate atom (those bonded to at least two other atoms) in the molecule. Thus we can use this model to predict the structures of molecules with hundreds of atoms. It does,

CHEMICAL IMPACT

Chemical Structure and Communication: Semiochemicals

The queen bee secretes a chemical that prevents the worker bees from raising a competitive sovereign.

In this chapter we have stressed the importance of being able to predict the three-dimensional structure of a molecule. Molecular structure is important because of its effect on chemical reactivity. This is especially true in biological systems, where reactions must be efficient and highly specific. Among the hundreds of types of molecules in the fluids of a typical biological system, the appropriate reactants must find and react only with each other—they must be very discriminating. This specificity depends largely on structure. The molecules are constructed so that only the appropriate partners can approach each other in a way that allows reaction.

Another area where molecular structure is central is in the use of molecules as a means of communication. Examples of a chemical communication occur in humans in the conduction of nerve impulses across synapses, the control of the manufacture and storage of key chemicals in cells, and the senses of smell and taste. Plants and animals also use chemical communication. For example, ants lay down a chemical trail so that other ants can find a particular food supply. Ants also warn their fellow workers of approaching danger by emitting certain chemicals.

Molecules convey messages by fitting into appropriate receptor sites in a very specific way, which is determined by their structure. When a molecule occupies a receptor site, chemical processes are stimulated that produce the appropriate response. Sometimes receptors can be fooled, as in the use of artificial sweeteners—molecules fit the sites on the taste buds that stimulate a "sweet" response in the brain, but they are not metabolized in the same way as natural sugars. Similar deception is useful in insect control. If an area is sprayed

however, fail in a few instances. For example, phosphine (PH_3), which has a Lewis structure analogous to that of ammonia,

would be predicted to have a molecular structure similar to that for NH_3, with bond angles of approximately 107 degrees. However, the bond angles of phosphine are actually 94 degrees. There are ways of explaining this structure, but more rules have to be added to the model.

This again illustrates the point that simple models are bound to have exceptions. In introductory chemistry we want to use simple models that fit the majority of cases; we are willing to accept a few failures rather than complicate the model. The amazing thing about the VSEPR model is that such a simple model predicts correctly the structures of so many molecules.

with synthetic female sex attractant molecules, the males of that species become so confused that mating does not occur.

A *semiochemical* is a molecule that delivers a message between members of the same or different species of plant or animal. There are three groups of these chemical messengers: allomones, kairomones, and pheromones. Each is of great ecological importance.

An *allomone* is defined as a chemical that somehow gives adaptive advantage to the producer. For example, leaves of the black walnut tree contain a herbicide, juglone, that appears after the leaves fall to the ground. Juglone is not toxic to grass or certain grains, but it is effective against plants such as apple trees that would compete for the available water and food supplies.

Antibiotics are also allomones, since the microorganisms produce them to inhibit other species from growing near them.

Many plants produce bad-tasting chemicals to protect themselves from plant-eating insects and animals. The familiar compound nicotine deters animals from eating the tobacco plant. The millipede sends an unmistakable “back off” message by squirting a predator with benzaldehyde and hydrogen cyanide.

Defense is not the only use of allomones, however. Flowers use scent as a way to attract pollinating insects. Honeybees, for instance, are guided to alfalfa and flowers by a series of sweet-scented compounds.

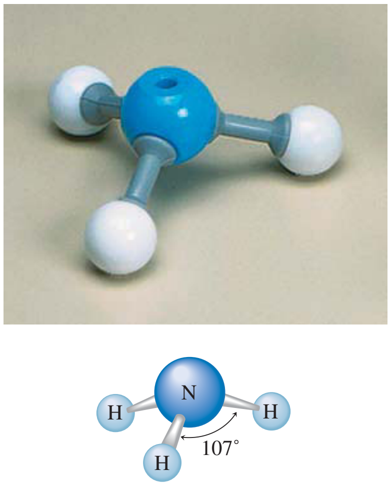
Kairomones are chemical messengers that bring advantageous news to the receiver, and the floral scents are kairomones from the honeybees’ viewpoint. Many predators are guided by kairomones emitted by their food. For example, apple skins exude a chemical that attracts the codling moth larva. In some cases kairomones help the underdog. Certain marine mollusks can pick up the “scent” of their predators, the sea stars, and make their escape.

Pheromones are chemicals that affect receptors of the same species as the donor. That is, they are specific within a species. *Releaser pheromones* cause an immediate reaction in the receptor, and *primer pheromones* cause long-term effects. Examples of releaser pheromones are sex attractants of insects, generated in some species by the males and in others by the females. Sex pheromones also have been found in plants and mammals.

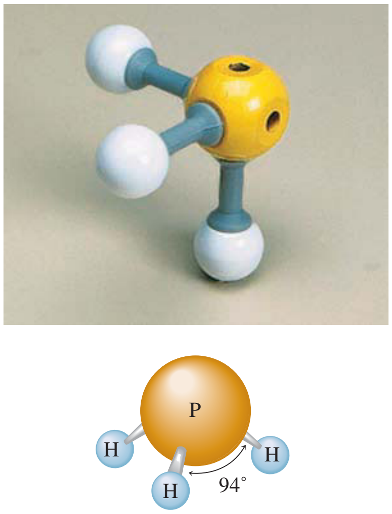
Alarm pheromones are highly volatile compounds (ones easily changed to a gas) released to warn of danger. Honeybees produce isoamyl acetate ($C_7H_{14}O_2$) in their sting glands. Because of its high volatility, this compound does not linger after the state of alert is over. Social behavior in insects is characterized by the use of *trail pheromones,* which are used to indicate a food source. Social insects such as bees, ants, wasps, and termites use these substances. Since trail pheromones are less volatile compounds, the indicators persist for some time.

Primer pheromones, which cause long-term behavioral changes, are harder to isolate and identify. One example, however, is the “queen substance” produced by queen honeybees. All the eggs in a colony are laid by one queen bee. If she is removed from the hive or dies, the worker bees are activated by the absence of the queen substance and begin to feed royal jelly to bee larvae so as to raise a new queen. The queen substance also prevents the development of the workers’ ovaries so that only the queen herself can produce eggs.

Many studies of insect pheromones are now under way in the hope that they will provide a method of controlling insects that is more efficient and safer than the current chemical pesticides.



NH_3



PH_3

Key Terms

Section 8.1

bond energy
ionic bonding
ionic compound
Coulomb's law
bond length
covalent bonding
polar covalent bond

Section 8.2

electronegativity

Section 8.3

dipolar
dipole moment

Section 8.4

isoelectronic ions

Section 8.5

lattice energy

Section 8.8

single bond
double bond
triple bond

Section 8.9

localized electron (LE) model
lone pair
bonding pair

Section 8.10

Lewis structure
duet rule
octet rule

Section 8.12

resonance
resonance structure
formal charge

Section 8.13

molecular structure
valence shell electron-pair repulsion (VSEPR) model
linear structure
trigonal planar structure
tetrahedral structure
trigonal pyramid
trigonal bipyramid
octahedral structure
square planar structure

For Review

Chemical bonds

- Hold groups of atoms together
- Occur when a group of atoms can lower its total energy by aggregating
- Types of chemical bonds
  - Ionic: electrons are transferred to form ions
  - Covalent: equal sharing of electrons
  - Polar covalent: unequal electron sharing
- Percent ionic character of a bond X—Y

$$\frac{\text{Measured dipole moment of X—Y}}{\text{Calculated dipole moment for } X^+Y^-} \times 100\%$$

- Electronegativity: the relative ability of an atom to attract shared electrons
  - The polarity of a bond depends on the electronegativity difference of the bonded atoms
- The spacial arrangement of polar bonds in a molecule determines whether the molecule has a dipole moment

Ionic bonding

- An ion has a different size than its parent atom
  - An anion is larger than its parent ion
  - A cation is smaller than its parent atom
- Lattice energy: the change in energy when ions are packed together to form an ionic solid

Bond energy

- The energy necessary to break a covalent bond
- Increases as the number of shared pairs increases
- Can be used to estimate the enthalpy change for a chemical reaction

Lewis structures

- Show how the valence electron pairs are arranged among the atoms in a molecule or polyatomic ion
- Stable molecules usually contain atoms that have their valence orbitals filled
  - Leads to a duet rule for hydrogen
  - Leads to an octet rule for second-row elements
  - The atoms of elements in the third row and beyond can exceed the octet rule
- Several equivalent Lewis structures can be drawn for some molecules, a concept called resonance
- When several nonequivalent Lewis structures can be drawn for a molecule, formal charge is often used to choose the most appropriate structure(s)

VSEPR model

- Based on the idea that electron pairs will be arranged around a central atom in a way that minimizes the electron repulsions
- Can be used to predict the geometric structure of most molecules

REVIEW QUESTIONS

1. Distinguish between the terms *electronegativity* versus *electron affinity, covalent bond* versus *ionic bond,* and *pure covalent bond* versus *polar covalent bond.*

Characterize the types of bonds in terms of electronegativity difference. Energetically, why do ionic and covalent bonds form?

2. When an element forms an anion, what happens to the radius? When an element forms a cation, what happens to the radius? Why? Define the term *isoelectronic*. When comparing sizes of ions, which ion has the largest radius and which ion has the smallest radius in an isoelectronic series? Why?
3. Define the term *lattice energy*. Why, energetically, do ionic compounds form? Figure 8.11 illustrates the energy changes involved in the formation of $MgO(s)$ and $NaF(s)$. Why is the lattice energy of $MgO(s)$ so different from that of $NaF(s)$? The magnesium oxide is composed of Mg^{2+} and O^{2-} ions. Energetically, why does $Mg^{2+}O^{2-}$ form and not $Mg^{+}O^{-}$? Why doesn't $Mg^{3+}O^{3-}$ form?
4. Explain how bond energies can be used to estimate ΔH for a reaction. Why is this an estimate of ΔH? How do the product bond strengths compare to the reactant bond strengths for an exothermic reaction? For an endothermic reaction? What is the relationship between the number of bonds between two atoms and bond strength? Bond length?
5. Give a rationale for the octet rule and the duet rule for H in terms of orbitals. Give the steps for drawing a Lewis structure for a molecule or ion. In general, molecules and ions always follow the octet rule unless it is impossible. The three types of exceptions are molecules/ions with too few electrons, molecules/ions with an odd number of electrons, and molecules/ions with too many electrons. Which atoms sometimes have fewer than 8 electrons around them? Give an example. Which atoms sometimes have more than 8 electrons around them? Give some examples. Why are odd-electron species generally very reactive and uncommon? Give an example of an odd-electron molecule.
6. Explain the terms *resonance* and *delocalized electrons*. When a substance exhibits resonance, we say that none of the individual Lewis structures accurately portrays the bonding in the substance. Why do we draw resonance structures?
7. Define formal charge and explain how to calculate it. What is the purpose of the formal charge? Organic compounds are composed mostly of carbon and hydrogen, but also may have oxygen, nitrogen, and/or halogens in the formula. Formal charge arguments work very well for organic compounds when drawing the best Lewis structure. How do C, H, N, O, and Cl satisfy the octet rule in organic compounds so as to have a formula charge of zero?
8. Explain the main postulate of the VSEPR model. List the five base geometries (along with bond angles) that most molecules or ions adopt to minimize electron-pair repulsions. Why are bond angles sometimes slightly less than predicted in actual molecules as compared to what is predicted by the VSEPR model?
9. Give two requirements that should be satisfied for a molecule to be polar. Explain why CF_4 and XeF_4 are nonpolar compounds (have no dipole moments) while SF_4 is polar (has a dipole moment). Is CO_2 polar? What about COS? Explain.
10. Consider the following compounds: CO_2, SO_2, KrF_2, SO_3, NF_3, IF_3, CF_4, SF_4, XeF_4, PF_5, IF_5, and SCl_6. These 12 compounds are all examples of different molecular structures. Draw the Lewis structures for each and predict the molecular structure. Predict the bond angles and the polarity of each. (A polar molecule has a dipole moment, while a nonpolar molecule does not.) See Exercises 89 and 90 for the molecular structures based on the trigonal bipyramid and the octahedral geometries.

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Explain the electronegativity trends across a row and down a column of the periodic table. Compare these trends with those of ionization energies and atomic radii. How are they related?
2. The ionic compound AB is formed. The charges on the ions may be $+1, -1$; $+2, -2$; $+3, -3$; or even larger. What are the factors that determine the charge for an ion in an ionic compound?
3. Using only the periodic table, predict the most stable ion for Na, Mg, Al, S, Cl, K, Ca, and Ga. Arrange these from largest to smallest radius, and explain why the radius varies as it does. Compare your predictions with Fig. 8.8.
4. The bond energy for a C—H bond is about 413 kJ/mol in CH_4 but 380 kJ/mol in $CHBr_3$. Although these values are relatively close in magnitude, they are different. Explain why they are different. Does the fact that the bond energy is lower in $CHBr_3$ make any sense? Why?
5. Consider the following statement: "Because oxygen wants to have a negative two charge, the second electron affinity is more negative than the first." Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect statements and explain.
6. Which has the greater bond lengths: NO_2^- or NO_3^-? Explain.
7. The following ions are best described with resonance structures. Draw the resonance structures, and using formal charge arguments, predict the best Lewis structure for each ion.
   a. NCO^-
   b. CNO^-
8. Would you expect the electronegativity of titanium to be the same in the species Ti, Ti^{2+}, Ti^{3+}, and Ti^{4+}? Explain.
9. The second electron affinity values for both oxygen and sulfur are unfavorable (endothermic). Explain.
10. What is meant by a chemical bond? Why do atoms form bonds with each other? Why do some elements exist as molecules in nature instead of as free atoms?
11. Why are some bonds ionic and some covalent?
12. Does a Lewis structure tell which electrons come from which atoms? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

13. Some plant fertilizer compounds are $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$, K_2O, P_2O_5, and KCl. Which of these compounds contain both ionic and covalent bonds?
14. Some of the important properties of ionic compounds are as follows:
    i. low electrical conductivity as solids and high conductivity in solution or when molten
    ii. relatively high melting and boiling points
    iii. brittleness
    iv. solubility in polar solvents
    How does the concept of ionic bonding discussed in this chapter account for these properties?
15. What is the electronegativity trend? Where does hydrogen fit into the electronegativity trend for the other elements in the periodic table?
16. Give one example of a compound having a linear molecular structure that has an overall dipole moment (is polar) and one example that does not have an overall dipole moment (is nonpolar). Do the same for molecules that have trigonal planar and tetrahedral molecular structures.
17. When comparing the size of different ions, the general radii trend discussed in Chapter 7 is generally not very useful. What do you concentrate on when comparing sizes of ions to each other or when comparing the size of an ion to its neutral atom?
18. In general, the higher the charge on the ions in an ionic compound, the more favorable the lattice energy. Why do some stable ionic compounds have $+1$ charged ions even though $+4$, $+5$, $+6$, charged ions would have a more favorable lattice energy?
19. Combustion reactions of fossil fuels provide most of the energy needs of the world. Why are combustion reactions of fossil fuels so exothermic?
20. Which of the following statements is(are) true? Correct the false statements.
    a. It is impossible to satisfy the octet rule for all atoms in XeF_2.
    b. Because SF_4 exists, then OF_4 should also exist because oxygen is in the same family as sulfur.
    c. The bond in NO^+ should be stronger than the bond in NO^-.
    d. As predicted from the two Lewis structures for ozone, one oxygen-oxygen bond is stronger than the other oxygen-oxygen bond.
21. Three resonance structures can be drawn for CO_2. Which resonance structure is best from a formal charge standpoint?
22. Which of the following statements is(are) true? Correct the false statements.
    a. The molecules SeS_3, SeS_2, PCl_5, $TeCl_4$, ICl_3, and $XeCl_2$ all exhibit at least one bond angle which is approximately 120°.
    b. The bond angle in SO_2 should be similar to the bond angle in CS_2 or SCl_2.
    c. Of the compounds CF_4, KrF_4, and SeF_4, only SeF_4 exhibits an overall dipole moment (is polar).
    d. Central atoms in a molecule adopt a geometry of the bonded atoms and lone pairs about the central atom in order to maximize electron repulsions.

Exercises

In this section similar exercises are paired.

Chemical Bonds and Electronegativity

23. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements.
    a. C, N, O
    b. S, Se, Cl
    c. Si, Ge, Sn
    d. Tl, S, Ge

24. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements.
a. Na, K, Rb
b. B, O, Ga
c. F, Cl, Br
d. S, O, F

25. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.
a. C—F, Si—F, Ge—F
b. P—Cl or S—Cl
c. S—F, S—Cl, S—Br
d. Ti—Cl, Si—Cl, Ge—Cl

26. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.
a. C—H, Si—H, Sn—H
b. Al—Br, Ga—Br, In—Br, Tl—Br
c. C—O or Si—O
d. O—F or O—Cl

27. Repeat Exercises 23 and 25, this time using the values for the electronegativities of the elements given in Fig. 8.3. Are there differences in your answers?

28. Repeat Exercises 24 and 26, this time using the values for the electronegativities of the elements given in Fig. 8.3. Are there differences in your answers?

29. Which of the following incorrectly shows the bond polarity? Show the correct bond polarity for those that are incorrect.
a. $^{\delta+}\text{H—F}^{\delta-}$
b. $^{\delta+}\text{Cl—I}^{\delta-}$
c. $^{\delta+}\text{Si—S}^{\delta-}$
d. $^{\delta+}\text{Br—Br}^{\delta-}$
e. $^{\delta+}\text{O—P}^{\delta-}$

30. Indicate the bond polarity (show the partial positive and partial negative ends) in the following bonds.
a. C—O
b. P—H
c. H—Cl
d. Br—Te
e. Se—S

31. Hydrogen has an electronegativity value between boron and carbon and identical to phosphorus. With this in mind, rank the following bonds in order of decreasing polarity: P—H, O—H, N—H, F—H, C—H.

32. Rank the following bonds in order of increasing ionic character: N—O, Ca—O, C—F, Br—Br, K—F.

Ions and Ionic Compounds

33. Write electron configurations for the most stable ion formed by each of the elements Fr, Be, P, Cl, and Se (when in stable ionic compounds).

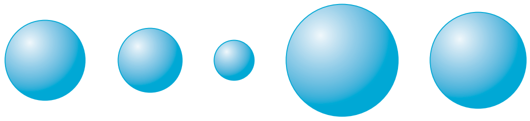
34. Write electron configurations for
a. the cations Mg^{2+}, K^{+}, and Al^{3+}.
b. the anions N^{3-}, O^{2-}, F^{-}, and Te^{2-}.

35. Which of the following ions have noble gas electron configurations?
a. Fe^{2+}, Fe^{3+}, Sc^{3+}, Co^{3+}
b. Tl^{+}, Te^{2-}, Cr^{3+}
c. Pu^{4+}, Ce^{4+}, Ti^{4+}
d. Ba^{2+}, Pt^{2+}, Mn^{2+}

36. What noble gas has the same election configuration as each of the ions in the following compounds?
a. cesium sulfide
b. strontium fluoride
c. calcium nitride
d. aluminum bromide

37. Give three ions that are isoelectronic with xenon. Place these ions in order of increasing size.

38. Consider the ions Sc^{3+}, Cl^{-}, K^{+}, Ca^{2+}, and S^{2-}. Match these ions to the following pictures that represent the relative sizes of the ions.



39. For each of the following groups, place the atoms and/or ions in order of decreasing size.
a. Cu, Cu^{+}, Cu^{2+}
b. Ni^{2+}, Pd^{2+}, Pt^{2+}
c. O, O^{-}, O^{2-}
d. La^{3+}, Eu^{3+}, Gd^{3+}, Yb^{3+}
e. Te^{2-}, I^{-}, Cs^{+}, Ba^{2+}, La^{3+}

40. For each of the following groups, place the atoms and/or ions in order of decreasing size.
a. V, V^{2+}, V^{3+}, V^{5+}
b. Na^{+}, K^{+}, Rb^{+}, Cs^{+}
c. Te^{2-}, I^{-}, Cs^{+}, Ba^{2+}
d. P, P^{-}, P^{2-}, P^{3-}
e. O^{2-}, S^{2-}, Se^{2-}, Te^{2-}

41. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
a. Al and S
b. K and N
c. Mg and Cl
d. Cs and Br

42. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
a. Ga and I
b. Na and O
c. Sr and F
d. Ca and P

43. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.
a. NaCl, KCl
b. LiF, LiCl
c. $Mg(OH)_2$, MgO
d. $Fe(OH)_2$, $Fe(OH)_3$
e. NaCl, Na_2O
f. MgO, BaS

44. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.
a. LiF, CsF
b. NaBr, NaI
c. $BaCl_2$, BaO
d. Na_2SO_4, $CaSO_4$
e. KF, K_2O
f. Li_2O, Na_2S

45. Use the following data to estimate ΔH_f° for potassium chloride.

$$K(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow KCl(s)$$

Lattice energy	−690. kJ/mol
Ionization energy for K	419 kJ/mol
Electron affinity of Cl	−349 kJ/mol
Bond energy of Cl_2	239 kJ/mol
Enthalpy of sublimation for K	64 kJ/mol

46. Use the following data to estimate ΔH_f° for magnesium fluoride.

$$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$$

Lattice energy	−3916 kJ/mol
First ionization energy of Mg	735 kJ/mol
Second ionization energy of Mg	1445 kJ/mol
Electron affinity of F	−328 kJ/mol
Bond energy of F_2	154 kJ/mol
Enthalpy of sublimation of Mg	150. kJ/mol

47. Consider the following energy changes:

	ΔH (kJ/mol)
$Mg(g) \rightarrow Mg^+(g) + e^-$	735
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	1445
$O(g) + e^- \rightarrow O^-(g)$	−141
$O^-(g) + e^- \rightarrow O^{2-}(g)$	878

Magnesium oxide exists as $Mg^{2+}O^{2-}$ and not as Mg^+O^-. Explain.

48. Compare the electron affinity of fluorine to the ionization energy of sodium. Is the process of an electron being "pulled" from the sodium atom to the fluorine atom exothermic or endothermic? Why is NaF a stable compound? Is the overall formation of NaF endothermic or exothermic? How can this be?

49. $LiI(s)$ has a heat of formation of −272 kJ/mol and a lattice energy of −753 kJ/mol. The ionization energy of $Li(g)$ is 520. kJ/mol, the bond energy of $I_2(g)$ is 151 kJ/mol, and the electron affinity of $I(g)$ is −295 kJ/mol. Use these data to determine the heat of sublimation of $Li(s)$.

50. Use the following data to estimate ΔH for the reaction $S^-(g) + e^- \rightarrow S^{2-}(g)$. Include an estimate of uncertainty.

	ΔH_f°	**Lattice Energy**	**I.E. of M**	**ΔH_{sub} of M**
Na_2S	−365	−2203	495	109
K_2S	−381	−2052	419	90
Rb_2S	−361	−1949	409	82
Cs_2S	−360	−1850	382	78

$$S(s) \longrightarrow S(g) \qquad \Delta H = 277 \text{ kJ/mol}$$
$$S(g) + e^- \longrightarrow S^-(g) \qquad \Delta H = -200 \text{ kJ/mol}$$

Assume that all values are known to ±1 kJ/mol.

51. Rationalize the following lattice energy values:

Compound	**Lattice Energy (kJ/mol)**
CaSe	−2862
Na_2Se	−2130
CaTe	−2721
Na_2Te	−2095

52. The lattice energies of $FeCl_3$, $FeCl_2$, and Fe_2O_3 are (in no particular order) −2631, −5359, and −14,774 kJ/mol. Match the appropriate formula to each lattice energy. Explain.

Bond Energies

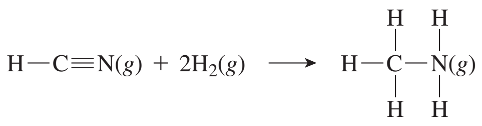
53. Use bond energy values (Table 8.4) to estimate ΔH for each of the following reactions in the gas phase.

a. $H_2 + Cl_2 \rightarrow 2HCl$

b. $N{\equiv}N + 3H_2 \rightarrow 2NH_3$

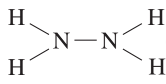
54. Use bond energy values (Table 8.4) to estimate ΔH for each of the following reactions.

a.



$$H{-}C{\equiv}N(g) + 2H_2(g) \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{N}}(g)$$

b.

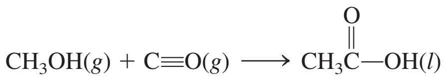


$(l) + 2F_2(g) \longrightarrow N{\equiv}N(g) + 4HF(g)$

55. Use bond energies (Table 8.4) to predict ΔH for the isomerization of methyl isocyanide to acetonitrile:

$$CH_3N{\equiv}C(g) \longrightarrow CH_3C{\equiv}N(g)$$

56. Acetic acid is responsible for the sour taste of vinegar. It can be manufactured using the following reaction:



$$CH_3OH(g) + C{\equiv}O(g) \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OH(l)$$

Use tabulated values of bond energies (Table 8.4) to estimate ΔH for this reaction.

57. Use bond energies to predict ΔH for the combustion of ethanol:

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

58. Use bond energies to estimate ΔH for the combustion for one mole of acetylene:

$$C_2H_2(g) + \tfrac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$$

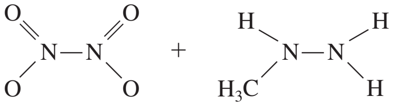
59. Use bond energies to estimate ΔH for the following reaction:

$$H_2O_2(aq) + CH_3OH(aq) \longrightarrow H_2CO(aq) + 2H_2O(l)$$

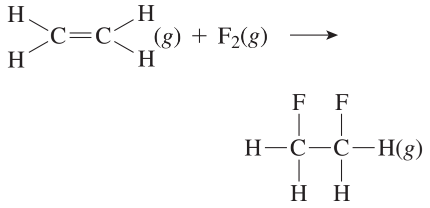
60. The space shuttle orbiter utilizes the oxidation of methyl hydrazine by dinitrogen tetroxide for propulsion:

$$5N_2O_4(l) + 4N_2H_3CH_3(l) \longrightarrow 12H_2O(g) + 9N_2(g) + 4CO_2(g)$$

Use bond energies to estimate ΔH for this reaction. The structures for the reactants are:



61. Consider the following reaction:



$\Delta H = -549$ kJ

Estimate the carbon–fluorine bond energy given that the C—C bond energy is 347 kJ/mol, the C═C bond energy is 614 kJ/mol, and the F—F bond energy is 154 kJ/mol.

62. Consider the following reaction:

$$A_2 + B_2 \longrightarrow 2AB \qquad \Delta H = -285 \text{ kJ}$$

The bond energy for A_2 is one-half the amount of the AB bond energy. The bond energy of B_2 = 432 kJ/mol. What is the bond energy of A_2?

63. Compare your answers from parts a and b of Exercise 53 with ΔH values calculated for each reaction using standard enthalpies of formation in Appendix 4. Do enthalpy changes calculated from bond energies give a reasonable estimate of the actual values?

64. Compare your answer from Exercise 56 to the ΔH value calculated from standard enthalpies of formation in Appendix 4. Explain any discrepancies.

65. The standard enthalpies of formation for S(*g*), F(*g*), $SF_4(g)$, and $SF_6(g)$ are +278.8, +79.0, −775, and −1209 kJ/mol, respectively.

a. Use these data to estimate the energy of an S—F bond.

b. Compare your calculated values to the value given in Table 8.4. What conclusions can you draw?

c. Why are the ΔH_f° values for S(*g*) and F(*g*) not equal to zero, since sulfur and fluorine are elements?

66. Use the following standard enthalpies of formation to estimate the N—H bond energy in ammonia: N(*g*), 472.7 kJ/mol; H(*g*), 216.0 kJ/mol; $NH_3(g)$, −46.1 kJ/mol. Compare your value to the one in Table 8.4.

Lewis Structures and Resonance

67. Write Lewis structures that obey the octet rule for each of the following.

a. HCN	**d.** NH_4^+	**g.** CO_2
b. PH_3	**e.** H_2CO	**h.** O_2
c. $CHCl_3$	**f.** SeF_2	**i.** HBr

Except for HCN and H_2CO, the first atom listed is the central atom. For HCN and H_2CO, carbon is the central atom.

68. Write Lewis structures that obey the octet rule for each of the following molecules and ions. (In each case the first atom listed is the central atom.)

a. $POCl_3$, SO_4^{2-}, XeO_4, PO_4^{3-}, ClO_4^-

b. NF_3, SO_3^{2-}, PO_3^{3-}, ClO_3^-

c. ClO_2^-, SCl_2, PCl_2^-

d. Considering your answers to parts a, b, and c, what conclusions can you draw concerning the structures of species containing the same number of atoms and the same number of valence electrons?

69. One type of exception to the octet rule are compounds with central atoms having fewer than eight electrons around them. BeH_2 and BH_3 are examples of this type of exception. Draw the Lewis structures for BeH_2 and BH_3.

70. Lewis structures can be used to understand why some molecules react in certain ways. Write the Lewis structures for the reactants and products in the reactions described below.

a. Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.

b. Boron trihydride accepts a pair of electrons from ammonia, forming BH_3NH_3.

Give a possible explanation for why these two reactions occur.

71. The most common type of exception to the octet rule are compounds or ions with central atoms having more than eight electrons around them. PF_5, SF_4, ClF_3 and Br_3^- are examples of this type of exception. Draw the Lewis structure for these compounds or ions. Which elements, when they have to, can have more than eight electrons around them? How is this rationalized?

72. SF_6, ClF_5, and XeF_4 are three compounds whose central atoms do not follow the octet rule. Draw Lewis structures for these compounds.

73. Write Lewis structures for the following. Show all resonance structures where applicable.

a. NO_2^-, NO_3^-, N_2O_4 (N_2O_4 exists as $O_2N—NO_2$.)

b. OCN^-, SCN^-, N_3^- (Carbon is the central atom in OCN^- and SCN^-.)

74. Some of the important pollutants in the atmosphere are ozone (O_3), sulfur dioxide, and sulfur trioxide. Write Lewis structures for these three molecules. Show all resonance structures where applicable.

75. Benzene (C_6H_6) consists of a six-membered ring of carbon atoms with one hydrogen bonded to each carbon. Write Lewis structures for benzene, including resonance structures.

76. Borazine ($B_3N_3H_6$) has often been called "inorganic" benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms with one hydrogen bonded to each boron and nitrogen.

77. An important observation supporting the concept of resonance in the localized electron model was that there are only three different structures of dichlorobenzene ($C_6H_4Cl_2$). How does this fact support the concept of resonance (see Exercise 75)?

78. Consider the following bond lengths:

C—O 143 pm	C═O 123 pm	C≡O 109 pm

In the CO_3^{2-} ion, all three C—O bonds have identical bond lengths of 136 pm. Why?

79. Place the species below in order of shortest to longest nitrogen–nitrogen bond.

$$N_2 \qquad N_2F_4 \qquad N_2F_2$$

(N_2F_4 exists as $F_2N—NF_2$, and N_2F_2 exists as FN—NF.)

80. Order the following species with respect to carbon–oxygen bond length (longest to shortest).

CO, CO_2, CO_3^{2-}, CH_3OH

What is the order from the weakest to the strongest carbon–oxygen bond? (CH_3OH exists as $H_3C—OH$.)

Formal Charge

81. Write Lewis structures that obey the octet rule for the following species. Assign the formal charge for each central atom.

a. $POCl_3$ **e.** SO_2Cl_2
b. SO_4^{2-} **f.** XeO_4
c. ClO_4^- **g.** ClO_3^-
d. PO_4^{3-} **h.** NO_4^{3-}

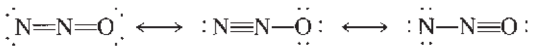
82 Write Lewis structures for the species in Exercise 81 that involve minimum formal charges.

83. Write the Lewis structure for O_2F_2 (O_2F_2 exists as F—O—O—F). Assign oxidation states and formal charges to the atoms in O_2F_2. This compound is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or formal charges more useful in accounting for these properties of O_2F_2?

84. Oxidation of the cyanide ion produces the stable cyanate ion, OCN^-. The fulminate ion, CNO^-, on the other hand, is very unstable. Fulminate salts explode when struck; $Hg(CNO)_2$ is used in blasting caps. Write the Lewis structures and assign formal charges for the cyanate and fulminate ions. Why is the fulminate ion so unstable? (C is the central atom in OCN^- and N is the central atom in CNO^-.)

85. When molten sulfur reacts with chlorine gas, a vile-smelling orange liquid forms that has an empirical formula of SCl. The structure of this compound has a formal charge of zero on all elements in the compound. Draw the Lewis structure for the vile-smelling orange liquid.

86. Nitrous oxide (N_2O) has three possible Lewis structures:



$$\mathrm{N{=}N{=}O} \longleftrightarrow \mathrm{:N{\equiv}N{-}O:} \longleftrightarrow \mathrm{:N{-}N{\equiv}O:}$$

Given the following bond lengths,

N—N	167 pm	N═O	115 pm
N═N	120 pm	N—O	147 pm
N≡N	110 pm		

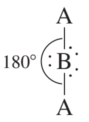
rationalize the observations that the N—N bond length in N_2O is 112 pm and that the N—O bond length is 119 pm. Assign formal charges to the resonance structures for N_2O. Can you eliminate any of the resonance structures on the basis of formal charges? Is this consistent with observation?

Molecular Structure and Polarity

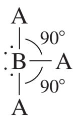
87. Predict the molecular structure and bond angles for each molecule or ion in Exercises 67 and 73.

88. Predict the molecular structure and bond angles for each molecule or ion in Exercises 68 and 74.

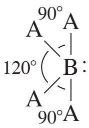
89. There are several molecular structures based on the trigonal bipyramid geometry (see Table 8.6). Three such structures are



Linear



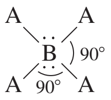
T-shaped



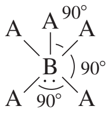
See-saw

Which of the compounds in Exercises 71 and 72 have these molecular structures?

90. Two variations of the octahedral geometry (see Table 8.6) are illustrated below.



Square planar



Square pyramid

Which of the compounds in Exercises 71 and 72 have these molecular structures?

91. Predict the molecular structure (including bond angles) for each of the following.

a. SeO_3
b. SeO_2

92. Predict the molecular structure (including bond angles) for each of the following.

a. PCl_3
b. SCl_2
c. SiF_4

93. Predict the molecular structure (including bond angles) for each of the following. (See Exercises 89 and 90.)

a. $XeCl_2$
b. ICl_3
c. TeF_4
d. PCl_5

94. Predict the molecular structure (including bond angles) for each of the following. (See Exercises 89 and 90.)

a. ICl_5
b. $XeCl_4$
c. $SeCl_6$

95. Which of the molecules in Exercise 91 have dipole moments (are polar)?

96. Which of the molecules in Exercise 92 have dipole moments (are polar)?

97. Which of the molecules in Exercise 93 have dipole moments (are polar)?

98. Which of the molecules in Exercise 94 have dipole moments (are polar)?

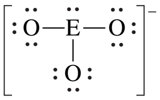
99. Write Lewis structures and predict the molecular structures of the following. (See Exercises 89 and 90.)

a. OCl_2, KrF_2, BeH_2, SO_2
b. SO_3, NF_3, IF_3
c. CF_4, SeF_4, KrF_4
d. IF_5, AsF_5

Which of these compounds are polar?

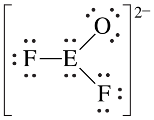
100. Write Lewis structures and predict whether each of the following is polar or nonpolar.
- **a.** HOCN (exists as HO—CN)
- **b.** COS
- **c.** XeF_2
- **d.** CF_2Cl_2
- **e.** SeF_6
- **f.** H_2CO (C is the central atom.)

101. Consider the following Lewis structure where E is an unknown element:



What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion.

102. Consider the following Lewis structure where E is an unknown element:



What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion. (See Exercises 89 and 90.)

103. The molecules BF_3, CF_4, CO_2, PF_5, and SF_6 are all nonpolar, even though they all contain polar bonds. Why?

104. Two different compounds have the formula XeF_2Cl_2. Write Lewis structures for these two compounds, and describe how measurement of dipole moments might be used to distinguish between them.

Additional Exercises

105. Arrange the following in order of increasing radius and increasing ionization energy.
- **a.** N^+, N, N^-
- **b.** Se, Se^-, Cl, Cl^+
- **c.** Br^-, Rb^+, Sr^{2+}

106. For each of the following, write an equation that corresponds to the energy given.
- **a.** lattice energy of NaCl
- **b.** lattice energy of NH_4Br
- **c.** lattice energy of MgS
- **d.** O═O double bond energy beginning with $O_2(g)$ as a reactant

107. Use bond energies (Table 8.4), values of electron affinities (Table 7.7), and the ionization energy of hydrogen (1312 kJ/mol) to estimate ΔH for each of the following reactions.
- **a.** $HF(g) \rightarrow H^+(g) + F^-(g)$
- **b.** $HCl(g) \rightarrow H^+(g) + Cl^-(g)$
- **c.** $HI(g) \rightarrow H^+(g) + I^-(g)$
- **d.** $H_2O(g) \rightarrow H^+(g) + OH^-(g)$

(Electron affinity of $OH(g) = -180.$ kJ/mol.)

108. Write Lewis structures for CO_3^{2-}, HCO_3^-, and H_2CO_3. When acid is added to an aqueous solution containing carbonate or bicarbonate ions, carbon dioxide gas is formed. We generally say that carbonic acid (H_2CO_3) is unstable. Use bond energies to estimate ΔH for the reaction (in the gas phase)

$$H_2CO_3 \longrightarrow CO_2 + H_2O$$

Specify a possible cause for the instability of carbonic acid.

109. Which member of the following pairs would you expect to be more energetically stable? Justify each choice.
- **a.** NaBr or $NaBr_2$
- **b.** ClO_4 or ClO_4^-
- **c.** SO_4 or XeO_4
- **d.** OF_4 or SeF_4

110. What do each of the following sets of compounds/ions have in common with each other?
- **a.** SO_3, NO_3^-, CO_3^{2-}
- **b.** O_3, SO_2, NO_2^-

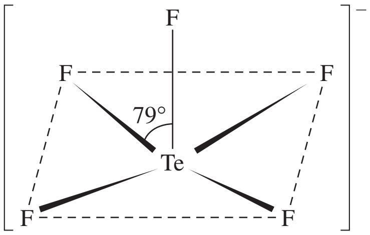
111. What do each of the following sets of compounds/ions have in common with each other? See your Lewis structures for Exercises 91 through 94.
- **a.** $XeCl_4$, $XeCl_2$
- **b.** ICl_5, TeF_4, ICl_3, PCl_3, SCl_2, SeO_2

112. Although both Br_3^- and I_3^- ions are known, the F_3^- ion has not been observed. Explain.

113. Refer back to Exercises 81 and 82. Would you make the same prediction for the molecular structure for each case using the Lewis structure obtained in Exercise 81 as compared with the one obtained in Exercise 82?

114. Which of the following molecules have dipole moments? For the molecules that are polar, indicate the polarity of each bond and the direction of the net dipole moment of the molecule.
- **a.** CH_2Cl_2, $CHCl_3$, CCl_4
- **b.** CO_2, N_2O
- **c.** PH_3, NH_3

115. The structure of TeF_5^- is



Draw a complete Lewis structure for TeF_5^-, and explain the distortion from the ideal square pyramidal structure. (See Exercise 90.)

Challenge Problems

116. An alternative definition of electronegativity is

$$\text{Electronegativity} = \text{constant (I.E.} - \text{E.A.)}$$

where I.E. is the ionization energy and E.A. is the electron affinity using the sign conventions of this book. Use data in

Chapter 7 to calculate the (I.E. − E.A.) term for F, Cl, Br, and I. Do these values show the same trend as the electronegativity values given in this chapter? The first ionization energies of the halogens are 1678, 1255, 1138, and 1007 kJ/mol, respectively. (*Hint:* Choose a constant so that the electronegativity of fluorine equals 4.0. Using this constant, calculate relative electronegativities for the other halogens and compare to values given in the text.)

117. Calculate the standard heat of formation of the compound ICl(*g*) at 25°C, and show your work. (*Hint:* Use Table 8.4 and Appendix 4.)

118. Given the following information:

Heat of sublimation of Li(*s*) = 166 kJ/mol
Bond energy of HCl = 427 kJ/mol
Ionization energy of Li(*g*) = 520. kJ/mol
Electron affinity of Cl(*g*) = −349 kJ/mol
Lattice energy of LiCl(*s*) = −829 kJ/mol
Bond energy of H_2 = 432 kJ/mol

Calculate the net change in energy for the following reaction:

$$2\mathrm{Li}(s) + 2\mathrm{HCl}(g) \longrightarrow 2\mathrm{LiCl}(s) + \mathrm{H_2}(g)$$

119. Use data in this chapter (and Chapter 7) to discuss why MgO is an ionic compound but CO is not an ionic compound.

120. Think of forming an ionic compound as three steps (this is a simplification, as with all models): (1) removing an electron from the metal; (2) adding an electron to the nonmetal; and (3) allowing the metal cation and nonmetal anion to come together.

a. What is the sign of the energy change for each of these three processes?

b. In general, what is the sign of the sum of the first two processes? Use examples to support your answer.

c. What must be the sign of the sum of the three processes?

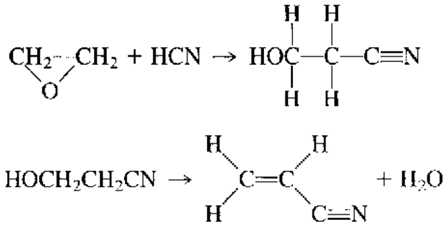
d. Given your answer to part c, why do ionic bonds occur?

e. Given your above explanations, why is NaCl stable but not Na_2Cl? $NaCl_2$? What about MgO compared to MgO_2? Mg_2O?

121. The compound NF_3 is quite stable, but NCl_3 is very unstable (NCl_3 was first synthesized in 1811 by P. L. Dulong, who lost three fingers and an eye studying its properties). The compounds NBr_3 and NI_3 are unknown, although the explosive compound $NI_3 \cdot NH_3$ is known. Account for the instability of these halides of nitrogen.

122. Three processes that have been used for the industrial manufacture of acrylonitrile (CH_2CHCN), an important chemical used in the manufacture of plastics, synthetic rubber, and fibers, are shown below. Use bond energy values (Table 8.4) to estimate Δ*H* for each of the reactions.

a.



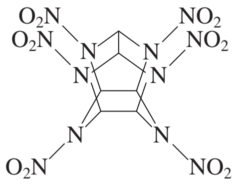
b. $4\mathrm{CH_2{=}CHCH_3} + 6\mathrm{NO} \xrightarrow[\text{Ag}]{700°\text{C}} 4\mathrm{CH_2{=}CHCN} + 6\mathrm{H_2O} + \mathrm{N_2}$

The nitrogen–oxygen bond energy in nitric oxide (NO) is 630. kJ/mol.

c. $2\mathrm{CH_2{=}CHCH_3} + 2\mathrm{NH_3} + 3\mathrm{O_2} \xrightarrow[425-510°\text{C}]{\text{Catalyst}} 2\mathrm{CH_2{=}CHCN} + 6\mathrm{H_2O}$

d. Is the elevated temperature noted in parts b and c needed to provide energy to endothermic reactions?

123. The compound hexaazaisowurtzitane is the highest-energy explosive known (*C & E News,* Jan. 17, 1994, p. 26). The compound, also known as CL-20, was first synthesized in 1987. The method of synthesis and detailed performance data are still classified because of CL-20's potential military application in rocket boosters and in warheads of "smart" weapons. The structure of CL-20 is



CL-20

In such shorthand structures, each point where lines meet represents a carbon atom. In addition, the hydrogens attached to the carbon atoms are omitted; each of the six carbon atoms has one hydrogen atom attached. Finally, assume that the two O atoms in the NO_2 groups are attached to N with one single bond and one double bond.

Three possible reactions for the explosive decomposition of CL-20 are

i. $\mathrm{C_6H_6N_{12}O_{12}}(s) \rightarrow 6\mathrm{CO}(g) + 6\mathrm{N_2}(g) + 3\mathrm{H_2O}(g) + \frac{3}{2}\mathrm{O_2}(g)$

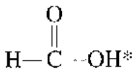
ii. $\mathrm{C_6H_6N_{12}O_{12}}(s) \rightarrow 3\mathrm{CO}(g) + 3\mathrm{CO_2}(g) + 6\mathrm{N_2}(g) + 3\mathrm{H_2O}(g)$

iii. $\mathrm{C_6H_6N_{12}O_{12}}(s) \rightarrow 6\mathrm{CO_2}(g) + 6\mathrm{N_2}(g) + 3\mathrm{H_2}(g)$

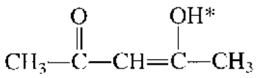
a. Use bond energies to estimate Δ*H* for these three reactions.

b. Which of the above reactions releases the largest amount of energy per kilogram of CL-20?

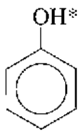
124. Many times extra stability is characteristic of a molecule or ion in which resonance is possible. How could this be used to explain the acidities of the following compounds? (The acidic hydrogen is marked by an asterisk.) Part c shows resonance in the C_6H_5 ring.

a.


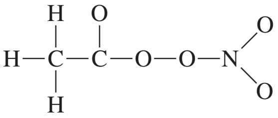
$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}OH^*}$

b.


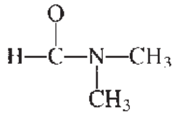
$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH{=}\overset{\overset{OH^*}{|}}{C}{-}CH_3}$

c.


125. Peroxacetyl nitrate, or PAN, is present in photochemical smog. Draw Lewis structures (including resonance forms) for PAN. The skeletal arrangement is



126. Draw a Lewis structure for the *N,N*-dimethylformamide molecule. The skeletal structure is



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{|}}{C}{-}\underset{\underset{\displaystyle CH_3}{|}}{N}{-}CH_3}$$

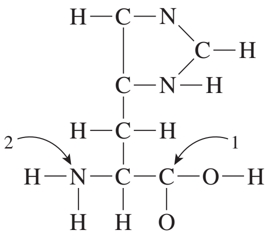
Various types of evidence lead to the conclusion that there is some double bond character to the C—N bond. Draw one or more resonance structures that support this observation.

127. Predict the molecular structure for each of the following. (See Exercises 89 and 90.)

a. $BrFI_2$
b. XeO_2F_2
c. $TeF_2Cl_3^-$

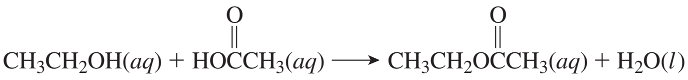
For each formula there are at least two different structures that can be drawn using the same central atom. Draw all possible structures for each formula.

128. The study of carbon-containing compounds and their properties is called *organic chemistry*. Besides carbon atoms, organic compounds also can contain hydrogen, oxygen, and nitrogen atoms (as well as other types of atoms). A common trait of simple organic compounds is to have Lewis structures where all atoms have a formal charge of zero. Consider the following incomplete Lewis structure for an organic compound called *histidine* (an amino acid, which is the building block of all proteins found in our bodies):



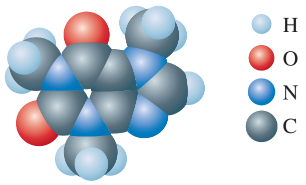
Draw a complete Lewis structure for histidine in which all atoms have a formal charge of zero. What should be the approximate bond angles about the carbon atom labeled 1 and the nitrogen atom labeled 2?

129. Using bond energies, estimate ΔH for the following reaction:



$$\mathrm{CH_3CH_2OH}(aq) + \mathrm{HO\overset{\overset{\displaystyle O}{\|}}{C}CH_3}(aq) \longrightarrow \mathrm{CH_3CH_2O\overset{\overset{\displaystyle O}{\|}}{C}CH_3}(aq) + \mathrm{H_2O}(l)$$

130. Consider the following computer-generated model of caffeine.



Draw a Lewis structure for caffeine in which all atoms have a formal charge of zero.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

131. A compound, XF_5, is 42.81% fluorine by mass. Identify the element X. What is the molecular structure of XF_5?

132. A polyatomic ion is composed of C, N, and an unknown element X. The skeletal Lewis structure of this polyatomic ion is $[X{-}C{-}N]^-$. The ion X^{2-} has an electron configuration of $[Ar]4s^23d^{10}4p^6$. What is element X? Knowing the identity of X, complete the Lewis structure of the polyatomic ion, including all important resonance structures.

133. Identify the following elements based on their electron configurations and rank them in order of increasing electronegativity: $[Ar]4s^13d^5$; $[Ne]3s^23p^3$; $[Ar]4s^23d^{10}4p^3$; $[Ne]3s^23p^5$.

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

134. Identify the five compounds of H, N, and O described below. For each compound, write a Lewis structure that is consistent with the information given.

a. All the compounds are electrolytes, although not all of them are strong electrolytes. Compounds C and D are ionic and compound B is covalent.

b. Nitrogen occurs in its highest possible oxidation state in compounds A and C; nitrogen occurs in its lowest possible oxidation state in compounds C, D, and E. The formal charge on both nitrogens in compound C is +1; the formal charge on the only nitrogen in compound B is 0.

c. Compounds A and E exist in solution. Both solutions give off gases. Commercially available concentrated solutions of compound A are normally 16 *M*. The commercial, concentrated solution of compound E is 15 *M*.

d. Commercial solutions of compound E are labeled with a misnomer that implies that a binary, gaseous compound of nitrogen and hydrogen has reacted with water to produce ammonium ions and hydroxide ions. Actually, this reaction occurs to only a slight extent.

e. Compound D is 43.7% N and 50.0% O by mass. If compound D were a gas at STP, it would have a density of 2.86 g/L.

f. A formula unit of compound C has one more oxygen than a formula unit of compound D. Compounds C and A have one ion in common when compound A is acting as a strong electrolyte.

g. Solutions of compound C are weakly acidic; solutions of compound A are strongly acidic; solutions of compounds B and E are basic. The titration of 0.726 g of compound B requires 21.98 mL of 1.000 *M* HCl for complete neutralization.

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl 7e.**