

9

Ionic and Covalent Bonding



The shape of snowflakes results from bonding (and intermolecular) forces in H_2O .

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Molten salts and aqueous solutions of salts are electrically conducting. This conductivity results from the motion of ions in the liquids. This suggests the possibility that ions exist in certain solids, held together by the attraction of ions of opposite charge.

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Not all bonds can be ionic. Hydrogen, H_2 , is a clear example, in which there is a strong bond between two like atoms. The bonding in the hydrogen molecule is covalent. A covalent bond forms between atoms by the sharing of a pair of electrons.

The properties of a substance, such as sodium chloride (Figure 9.1), are determined in part by the chemical bonds that hold the atoms together. A *chemical bond* is a strong attractive force that exists between certain atoms in a substance. In Chapter 2 we described how sodium (a silvery metal) reacts with chlorine (a pale greenish yellow gas) to produce sodium chloride (table salt, a white solid). The substances in this reaction are quite different, as are their chemical bonds. Sodium chloride, NaCl, consists of Na^+ and Cl^- ions held in a regular arrangement, or crystal, by *ionic bonds*. Ionic bonding results from the attractive force of oppositely charged ions.

A second kind of chemical bond is a *covalent bond*. In a covalent bond, two atoms share valence electrons (outer-shell electrons), which are attracted to the positively charged cores of both atoms, thus linking them. For example, chlorine gas consists of Cl_2 molecules. You would not expect the two Cl atoms in each Cl_2 molecule to acquire the opposite charges required for ionic bonding. Rather, a covalent bond holds the two atoms together. This is consistent with the equal sharing of electrons that you would expect between identical atoms. In most molecules, the atoms are linked by covalent bonds.

Metallic bonding, seen in sodium and other metals, represents another important type of bonding. A crystal of sodium metal consists of a regular arrangement of sodium atoms. The valence electrons of these atoms move throughout the crystal, attracted to the positive cores of all Na^+ ions. This attraction holds the crystal together.

What determines the type of bonding in each substance? How do you describe the bonding in various substances? In this chapter we will look at some

See pages 364–365 for the Media Summary.

simple, useful concepts of bonding that can help us answer these questions. We will be concerned with ionic and covalent bonds in particular.



FIGURE 9.1 ▲

Sodium chloride crystals

Natural crystals of sodium chloride mineral (halite).

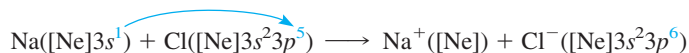
Ionic Bonds

The first explanation of chemical bonding was suggested by the properties of *salts*, substances now known to be ionic. Salts are generally crystalline solids that melt at high temperatures. Sodium chloride, for example, melts at 801°C . A molten salt (the liquid after melting) conducts an electric current. A salt dissolved in water gives a solution that also conducts an electric current. The electrical conductivity of the molten salt and the salt solution results from the motion of ions in the liquids. This suggests the possibility that ions exist in certain solids, held together by the attraction of opposite charges.

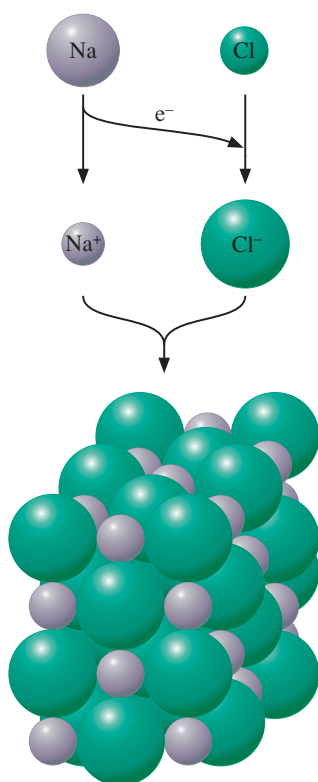
9.1 Describing Ionic Bonds

An **ionic bond** is a chemical bond formed by the electrostatic attraction between positive and negative ions. The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other. The atom that loses electrons becomes a *cation* (positive ion), and the atom that gains electrons becomes an *anion* (negative ion). Any given ion tends to attract as many neighboring ions of opposite charge as possible. When large numbers of ions gather together, they form an ionic solid. The solid normally has a regular, crystalline structure that allows for the maximum attraction of ions, given their particular sizes.

To understand why ionic bonding occurs, consider the transfer of a valence electron from a sodium atom (electron configuration $[\text{Ne}]3s^1$) to the valence shell of a chlorine atom ($[\text{Ne}]3s^23p^5$). You can represent the electron transfer by the following equation:



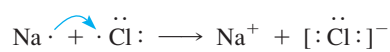
As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration. The sodium atom has lost its $3s$ electron and has taken on the neon configuration, $[\text{Ne}]$. The chlorine atom has accepted the electron into its $3p$ subshell and has taken on the argon configuration, $[\text{Ne}]3s^23p^6$. Such noble-gas configurations and the corresponding ions are particularly stable. This stability of the ions accounts in part for the formation of the ionic solid NaCl . Once a cation or anion forms, it attracts ions of opposite charge. Within the sodium chloride crystal, NaCl , every Na^+ ion is surrounded by six Cl^- ions, and every Cl^- ion by six Na^+ ions. (Figure 2.19 shows the arrangement of ions in the NaCl crystal.)



Lewis Electron-Dot Symbols

You can simplify the preceding equation for the electron transfer between Na and Cl by writing Lewis electron-dot symbols for the atoms and monatomic ions. A **Lewis electron-dot symbol** is a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element. Table 9.1 lists Lewis symbols and corresponding valence-shell electron configurations for the atoms of the second and third periods. Note that dots are placed one to each side of a letter symbol until all four sides are occupied. Then the dots are written two to a side until all valence electrons are accounted for. The exact placement of the single dots is immaterial. For example, the single dot in the Lewis symbol for chlorine can be written on any one of the four sides. [This pairing of dots does not always correspond to the pairing of electrons in the ground state. Thus, you write $\cdot\text{B}\cdot$ for boron, rather than $:\text{B}\cdot$, which more closely corresponds to the ground-state configuration $[\text{He}]2s^22p^1$. The first symbol better reflects boron's chemistry, in which each single electron (single dot) tends to be involved in bond formation.]

The equation representing the transfer of an electron from the sodium atom to the chlorine atom is



The noble-gas configurations of the ions are apparent from the symbols. No dots are shown for the cation. (All valence electrons have been removed, leaving the noble-gas core.) Eight dots are shown in brackets for the anion (noble-gas configuration ns^2np^6).

TABLE 9.1

Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

Period	IA ns^1	IIA ns^2	IIIA ns^2np^1	IVA ns^2np^2	VA ns^2np^3	VIA ns^2np^4	VIIA ns^2np^5	VIIIA ns^2np^6
Second	$\text{Li} \cdot$	$\cdot \text{Be} \cdot$	$\cdot \text{B} \cdot$	$\cdot \text{C} \cdot$	$:\text{N} \cdot$	$:\ddot{\text{O}} \cdot$	$:\ddot{\text{F}} \cdot$	$:\ddot{\text{Ne}}:$
Third	$\text{Na} \cdot$	$\cdot \text{Mg} \cdot$	$\cdot \text{Al} \cdot$	$\cdot \text{Si} \cdot$	$:\text{P} \cdot$	$:\ddot{\text{S}} \cdot$	$:\ddot{\text{Cl}} \cdot$	$:\ddot{\text{Ar}}:$

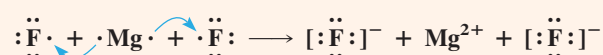
Example 9.1**Using Lewis Symbols to Represent Ionic Bond Formation**

Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations.

Problem Strategy Write down the Lewis symbols for the two atoms. Note how many electrons the metal atom should lose to assume a noble-gas configuration (all of the dots, representing valence electrons) and how many electrons the nonmetal atom should gain to assume such a configuration (enough to give eight dots about the atomic symbol). Represent the transfer of electrons between ions diagrammatically in the form of an equation.

Solution The Lewis symbols for the atoms are $\cdot\ddot{\text{F}}\cdot$ and $\cdot\text{Mg}\cdot$ (see Table 9.1). The magnesium atom loses

two electrons to assume a noble-gas configuration. But because a fluorine atom can accept only one electron to fill its valence shell, two fluorine atoms must take part in the electron transfer. We can represent this electron transfer as follows:



Answer Check Check that you have the correct symbols for the atoms and that the symbols for the ions do have noble-gas configurations.

Exercise 9.1

Represent the transfer of electrons from magnesium to oxygen atoms to assume noble-gas configurations. Use Lewis electron-dot symbols.

■ See Problems 9.37 and 9.38.

Energy Involved in Ionic Bonding

You have seen in a qualitative way why a sodium atom and a chlorine atom might be expected to form an ionic bond. It is instructive, however, to look at the energy changes involved in ionic bond formation. From this analysis, you can gain further understanding of why certain atoms bond ionically and others do not.

If atoms come together and bond, there should be a net decrease in energy, because the bonded state should be more stable and therefore at a lower energy level. Consider again the formation of an ionic bond between a sodium atom and a chlorine atom. You can think of this as occurring in two steps: (1) An electron is transferred between the two separate atoms to give ions. (2) The ions then attract one another to form an ionic bond. In reality, the transfer of the electron and the formation of an ionic bond occur simultaneously, rather than in discrete steps, as the atoms approach one another. But the *net* quantity of energy involved is the same whether the steps occur one after the other or at the same time.

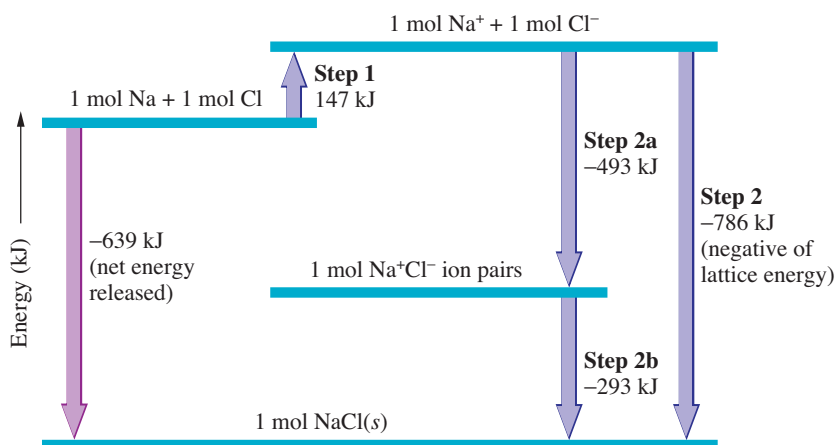
The first step requires removal of the 3s electron from the sodium atom and the addition of this electron to the valence shell of the chlorine atom. Removing the electron from the sodium atom requires energy (the first ionization energy of the sodium atom, which equals 496 kJ/mol). Adding the electron to the chlorine atom releases energy (the electron affinity of the chlorine atom, which equals −349 kJ/mol). < It requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom. That is, the formation of ions from the atoms is not in itself energetically favorable. It requires additional energy equal to at least (496 − 349) kJ/mol, or 147 kJ/mol, to form ions (Figure 9.2, Step 1).

When positive and negative ions bond, however, more than enough energy is released to supply this additional requirement. What principally determines the energy released when ions bond is the attraction of oppositely charged ions. You can estimate this energy from *Coulomb's law* if you make the simplifying assumption that the ions are spheres, just touching, with a distance between nuclei equal to that in the NaCl crystal. From experiment, this distance is 282 pm, or 2.82×10^{-10} m.

Ionization energies and electron affinities of atoms were discussed in Section 8.6.

FIGURE 9.2**Energetics of ionic bonding**

The transfer of an electron from an Na atom to a Cl atom is not in itself energetically favorable; it requires 147 kJ/mol of energy (Step 1). However, 493 kJ of energy is released when these oppositely charged ions come together to form ion pairs (Step 2a). Moreover, additional energy (293 kJ) is released when these ion pairs form the solid NaCl crystal (Step 2b). The lattice energy released when one mole each of Na^+ and Cl^- ions react to produce $\text{NaCl}(s)$ is 786 kJ/mol, and the overall process of NaCl formation is energetically favorable, releasing 639 kJ/mol if one starts with gaseous Na and Cl atoms.



According to Coulomb's law, the energy E obtained in bringing two ions with electric charges Q_1 and Q_2 from infinite separation to a distance r apart is

$$E = \frac{kQ_1Q_2}{r}$$

Here k is a physical constant, equal to $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$ (C is the symbol for coulomb); the charge on Na^+ is $+e$ and that on Cl^- is $-e$, where e equals $1.602 \times 10^{-19} \text{ C}$. Therefore,

$$E = \frac{-(8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2) \times (1.602 \times 10^{-19} \text{ C})^2}{2.82 \times 10^{-10} \text{ m}} = -8.18 \times 10^{-19} \text{ J}$$

The minus sign means energy is released. This energy is for the formation of one ion pair. To express this for one mole of NaCl, we multiply by Avogadro's number, 6.02×10^{23} . We obtain -493 kJ/mol for the energy obtained when one mole of Na^+ and one mole of Cl^- come together to form NaCl ion pairs (Figure 9.2, Step 2a). <

The attraction of oppositely charged ions does not stop with the bonding of pairs of ions. The maximum attraction of ions of opposite charge with the minimum repulsion of ions of the same charge is obtained with the formation of the crystalline solid. Then additional energy is released (Figure 9.2, Step 2b).

The energy released when a crystalline solid forms from ions is related to the lattice energy of the solid. The **lattice energy** is the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase. For sodium chloride, the process is



The distances between ions in the crystal are continuously enlarged until the ions are very far apart. The energy required for this process is the lattice energy of NaCl. You can calculate this energy from Coulomb's law or obtain an experimental value from thermodynamic data. The value, $+786 \text{ kJ/mol}$, is for just the opposite process of the one we were considering earlier, in which ions come together to bond, forming the solid. When ions come together to bond, this energy is -786 kJ/mol (Figure 9.2, Step 2). Consequently, the net energy obtained when gaseous Na and Cl atoms form solid NaCl is $(-786 + 147) \text{ kJ/mol} = -639 \text{ kJ/mol}$. The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

The energy value -493 kJ/mol is approximate, because of the simplifying assumption we made.

From this energy analysis, you can see that two elements bond ionically if the ionization energy of one is sufficiently small and the electron affinity of the other is sufficiently large and negative. This situation exists between a reactive metal (which has low ionization energy) and a reactive nonmetal (which has large negative electron affinity). In general, bonding between a metal and a nonmetal is ionic. This energy analysis also explains why ionic bonding normally results in a solid rather than in ion-pair molecules.

Lattice Energies from the Born–Haber Cycle

The preceding energy analysis requires us to know the lattice energy of solid sodium chloride. Direct experimental determination of the lattice energy of an ionic solid is difficult. However, this quantity can be indirectly determined from experiment by means of a thermochemical “cycle” originated by Max Born and Fritz Haber in 1919 and now called the *Born–Haber cycle*. The reasoning is based on Hess’s law.

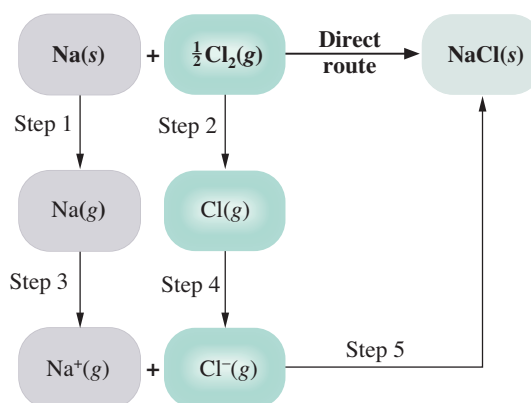
To obtain the lattice energy of NaCl, you think of solid sodium chloride being formed from the elements by two different routes, as shown in Figure 9.3. In one route, NaCl(s) is formed directly from the elements, Na(s) and $\frac{1}{2}\text{Cl}_2(\text{g})$. The enthalpy change for this is ΔH_f° , which is given in Table 6.2 as -411 kJ per mole of NaCl. The second route consists of five steps:

1. *Sublimation of sodium.* Metallic sodium is vaporized to a gas of sodium atoms. (*Sublimation* is the transformation of a solid to a gas.) The enthalpy change for this process, measured experimentally, is 108 kJ per mole of sodium.
2. *Dissociation of chlorine.* Chlorine molecules are dissociated to atoms. The enthalpy change for this equals the Cl—Cl bond dissociation energy, which is 240 kJ per mole of bonds, or 120 kJ per mole of Cl atoms.
3. *Ionization of sodium.* Sodium atoms are ionized to Na^+ ions. The enthalpy change is essentially the ionization energy of atomic sodium, which equals 496 kJ per mole of Na.
4. *Formation of chloride ion.* The electrons from the ionization of sodium atoms are transferred to chlorine atoms. The enthalpy change for this is the electron affinity of atomic chlorine, which equals -349 kJ per mole of Cl atoms.
5. *Formation of NaCl(s) from ions.* The ions Na^+ and Cl^- formed in Steps 3 and 4 combine to give solid sodium chloride. Because this process is just the reverse of the one corresponding to the lattice energy (breaking the solid into ions), the enthalpy change is the negative of the lattice energy. If we let U be the lattice energy, the enthalpy change for Step 5 is $-U$.

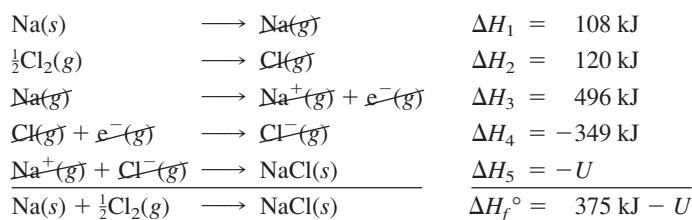
FIGURE 9.3 ▶

Born–Haber cycle for NaCl

The formation of NaCl(s) from the elements is accomplished by two different routes. The direct route is the formation reaction (shown in boldface), and the enthalpy change is ΔH_f° . The indirect route occurs in five steps.



Let us write these five steps and add them. We also add the corresponding enthalpy changes, following Hess's law.



In summing the equations, we have canceled terms that appear on both the left and right sides of the arrows. The final equation is simply the formation reaction for $\text{NaCl}(s)$. Adding the enthalpy changes, we find that the enthalpy change for this formation reaction is $375 \text{ kJ} - U$. But the enthalpy of formation has been determined calorimetrically and equals -411 kJ . Equating these two values, we get

$$375 \text{ kJ} - U = -411 \text{ kJ}$$

Solving for U yields the lattice energy of NaCl :

$$U = (375 + 411) \text{ kJ} = 786 \text{ kJ}$$

Properties of Ionic Substances

Typically, ionic substances are high-melting solids. Sodium chloride, NaCl , ordinary salt, melts at 801°C , and magnesium oxide, MgO , a ceramic, melts at 2800°C . The explanation for the high melting points of these substances is simple.

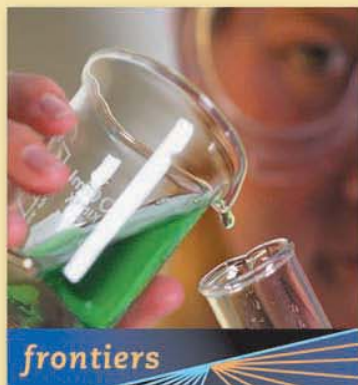
Small, spherical cations and anions interact by strong bonds that essentially depend on the electrical force of attraction described by Coulomb's law. Large groups of such cations and anions attract one another with strong ionic bonds linking all of the ions together, forming a crystalline solid. When you heat any solid, the atoms or ions of that solid begin to vibrate; and, as you raise the temperature, these atoms or ions vibrate through larger and larger distances. At a high enough temperature, the atoms or ions of the solid may move sufficiently far apart that the solid melts to a liquid (or the solid may simply decompose to different substances). The temperature at which melting occurs depends on the strength of the interaction between the atoms or ions. Typical ionic solids require high temperatures for this process to occur because of the strong interactions between the ions.

Coulomb's law also explains why magnesium oxide, which is composed of ions having double charges (Mg^{2+} and O^{2-}), has such a high melting point compared with sodium chloride (Na^+ and Cl^-). Coulomb interactions depend on the product of the ion charges. For NaCl , this is 1×1 , whereas for MgO , this is 2×2 , or 4 times greater. (Coulomb's law also depends on the distance between charges, or ions, which is about the same in NaCl and MgO .) The much larger Coulomb interaction in MgO requires a much greater temperature to initiate melting.

The liquid melt from an ionic solid consists of ions, and so the liquid conducts an electric current. If the ionic solid dissolves in a molecular liquid, such as water, the resulting solution consists of ions dispersed among molecules; the solution also conducts an electric current.

Recently, as the accompanying essay on ionic liquids describes, chemists have prepared ionic substances that behave atypically. Their unusual properties are the result of large, nonspherical cations that lead to especially weak ionic bonding. The melting points of these ionic substances are unusually low; often they are liquids at room temperature (that is, their melting points are below room temperature).

A Chemist Looks at . . .



Ionic Liquids and Green Chemistry

New substances with peculiar or strange behavior have always intrigued chemists. The German chemist Hennig Brand in 1669 discovered a white, waxy solid that he called “cold fire,” because it glowed in the dark—a

strange property then and still captivating today. He tried to keep the recipe (lengthy boiling of putrid urine) secret, but people’s fascination with the waxy solid, which was white phosphorus, proved irresistible.

Modern chemists continue to expand the boundaries of known materials. They have discovered plastics that conduct electricity like metals and materials that look solid but are so porous they are almost as light as air. Now chemists have produced room-temperature ionic liquids (Figure 9.4). Most of these are clear, well-behaved substances that look and pour much like water, and like water their strength is as solvents (liquids that dissolve other substances). In fact, they promise to be “super solvents.”



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FIGURE 9.4 ▲

Room-temperature ionic liquid

Hélène Olivier of the French Petroleum Institute displays a tube containing an ionic liquid (including a blue nickel compound) with a hydrocarbon liquid above it. Typical liquids, such as a hydrocarbon, are molecular substances, whereas ionic liquids are composed of ions.

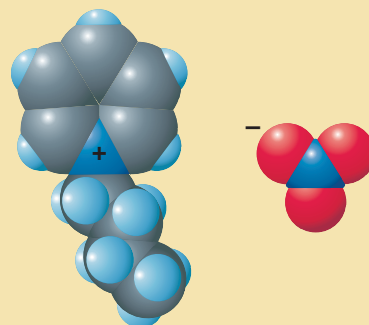


FIGURE 9.5 ▲

The ions composing an ionic liquid

Shown here are space-filling models of the ions composing *N*-butylpyridinium nitrate. Note the bulky cation and small nitrate anion.

Given a material—an organic substance, a plastic, or even a rock—researchers believe you will be able to find an ionic liquid that is capable of dissolving it!

Compare room-temperature ionic liquids with their more prosaic cousins. Sodium chloride, a typical example, is solid at room temperature and doesn’t melt until exposed to temperatures over 800°C. The molten liquid, though clear, is very corrosive (chemically reactive). The high melting point of sodium chloride is easily explained. It consists of small, spherical ions that pack closely together. Thus, the ions interact strongly, giving a solid with a high melting point. Room-temperature ionic liquids, by contrast, consist of large, nonspherical cations with various anions (Figure 9.5). It is the large, bulky cations that keep the ions from packing closely; the large distances between ions result in weak interactions, yielding a substance whose melting point is often well below room temperature.

The demand for *green chemistry*, the commercial production of chemicals using environmentally sound methods, has spurred much of the research into ionic liquids. Many chemical processes use volatile organic solvents. These solvents are liquids that evaporate easily into the surrounding air, where they can contribute to air pollution. Organic solvents are often flammable, too. Ionic liquids are neither volatile nor flammable. In addition to these environmental rewards, however, ionic liquids appear to offer another bonus: The proper choice of ionic liquid may improve the yield and lower the costs of a chemical process.

■ See Problems 9.111 and 9.112.

9.2 Electron Configurations of Ions

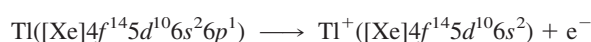
In the previous section, we described the formation of ions from atoms. Often you can understand what monatomic ions form by looking at the electron configurations of the atoms and deciding what configurations you would expect for the ions.

Ions of the Main-Group Elements

In Chapter 2, we listed the common monatomic ions of the main-group elements (Table 2.3). Most of the cations are obtained by removing all the valence electrons from the atoms of metallic elements. Once these atoms have lost their valence electrons, they have stable noble-gas or pseudo-noble-gas configurations. The stability of these configurations can be seen by looking at the successive ionization energies of some atoms. Table 9.2 lists the first through the fourth ionization energies of Na, Mg, and Al. The energy needed to remove the first electron from the Na atom is only 496 kJ/mol (first ionization energy). But the energy required to remove another electron (the second ionization energy) is nearly ten times greater (4,562 kJ/mol). The electron in this case must be taken from Na^+ , which has a neon configuration. Magnesium and aluminum atoms are similar. Their valence electrons are easily removed, but the energy needed to take an electron from either of the ions that result (Mg^{2+} and Al^{3+}) is extremely high. That is why no compounds are found with ions having charges greater than the group number.

The loss of successive electrons from an atom requires increasingly more energy. Consequently, Group IIIA elements show less tendency to form ionic compounds than do Group IA and IIA elements, which primarily form ionic compounds. Boron, in fact, forms no compounds with B^{3+} ions. The bonding is normally covalent, a topic discussed later in this chapter. However, the tendency to form ions becomes greater going down any column of the periodic table because of decreasing ionization energy. The remaining elements of Group IIIA do form compounds containing $3+$ ions.

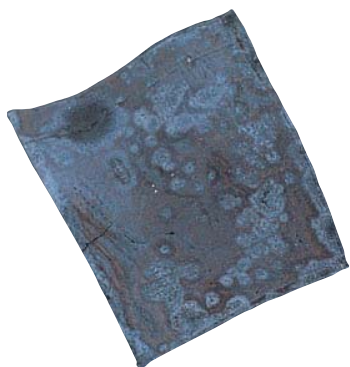
There is also a tendency for Group IIIA to VA elements of higher periods, particularly Period 6, to form compounds with ions having a positive charge of two less than the group number. Thallium in IIIA, Period 6, has compounds with $1+$ ions and compounds with $3+$ ions. Ions with charge equal to the group number minus two are obtained when the np electrons of an atom are lost but the ns^2 electrons are retained. For example,



Few compounds of $4+$ ions are known because the energy required to form ions is so great. The first three elements of Group IVA—C, Si, and Ge—are nonmetals (or metalloids) and usually form covalent rather than ionic bonds. Tin and lead, however, the fourth and fifth elements of Group IVA, commonly form compounds with $2+$ ions

TABLE 9.2		Ionization Energies of Na, Mg, and Al (in kJ/mol)*			
Element	Successive Ionization Energies				
	First	Second	Third	Fourth	
Na	496	4,562	6,912	9,543	
Mg	738	1,451	7,733	10,540	
Al	578	1,817	2,745	11,577	

*Energies for the ionization of valence electrons lie to the left of the colored line.



Interestingly, lithium metal reacts with nitrogen at room temperature to form a layer of lithium nitride, Li_3N , on the metal surface (see photo above).

(ionic charge equal to the group number minus two). For example, tin forms tin(II) chloride, SnCl_2 , which is an ionic compound. It also forms tin(IV) chloride, SnCl_4 , but this is a covalent, not an ionic, compound. Bismuth, in Group VA, is a metallic element that forms compounds of Bi^{3+} (ionic charge equal to the group number minus two), where only the $6p$ electrons have been lost.

Group VIA and Group VIIA elements, whose atoms have the largest negative electron affinities, would be expected to form monatomic ions by gaining electrons to give noble-gas or pseudo-noble-gas configurations. An atom of a Group VIIA element (valence-shell configuration ns^2np^5) picks up one electron to give a $1-$ anion (ns^2np^6); examples are F^- and Cl^- . (Hydrogen also forms compounds of the $1-$ ion, H^- . The hydride ion, H^- , has a $1s^2$ configuration, like the noble-gas atom helium.) An atom of a Group VIA element (valence-shell configuration ns^2np^4) picks up two electrons to give a $2-$ anion (ns^2np^6); examples are O^{2-} and S^{2-} . Although the electron affinity of nitrogen ($2s^22p^3$) is zero, the N^{3-} ion ($2s^22p^6$) is stable in the presence of certain positive ions, including Li^+ and those of the alkaline earth elements. <

To summarize, the common monatomic ions found in compounds of the main-group elements fall into three categories (see Table 2.3):

1. Cations of Groups IA to IIIA having noble-gas or pseudo-noble-gas configurations. The ion charges equal the group numbers.
2. Cations of Groups IIIA to VA having ns^2 electron configurations. The ion charges equal the group numbers minus two. Examples are Tl^+ , Sn^{2+} , Pb^{2+} , and Bi^{3+} .
3. Anions of Groups VA to VIIA having noble-gas or pseudo-noble-gas configurations. The ion charges equal the group numbers minus eight.

Example 9.2

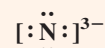
Writing the Electron Configuration and Lewis Symbol for a Main-Group Ion

Write the electron configuration and the Lewis symbol for N^{3-} .

Problem Strategy Recall the three categories of main-group monatomic ions: (1) cations of Groups IA to IIIA usually have ion charges equal to group numbers; (2) cations of Groups IIIA to VA may have ion charges equal to group numbers minus two—an example is Tl^+ ; and (3) anions of Groups VA to VIIA have charges equal to the group numbers minus eight. Write the electron configuration of the atom, and then subtract or add electrons to give the ion. Similarly, write the Lewis symbol of the atom, and subtracting or adding dots to give the ion.

Solution The electron configuration of the N atom is $[\text{He}]2s^22p^3$. By gaining three electrons, the atom

assumes a $3-$ charge and the neon configuration $[\text{He}]2s^22p^6$. The Lewis symbol is



Answer Check Check that the ion has a noble-gas or pseudo-noble-gas configuration and that the Lewis symbol has eight dots, or none, around the atomic symbol.

Exercise 9.2

Write the electron configuration and the Lewis symbol for Ca^{2+} and for S^{2-} .

■ See Problems 9.39 and 9.40.

Exercise 9.3

Write the electron configurations of Pb and Pb^{2+} .

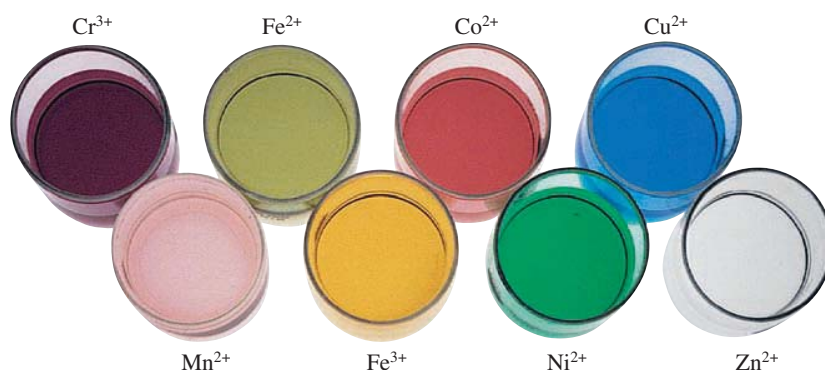
■ See Problems 9.41 and 9.42.

Polyatomic Ions

Many ions, particularly anions, are polyatomic. Some common polyatomic ions are listed in Table 2.5. The atoms in these ions are held together by covalent bonds, which we will discuss in Section 9.4.

FIGURE 9.6**Common transition-metal cations in aqueous solution**

Left to right: Cr^{3+} (red-violet), Mn^{2+} (pale pink), Fe^{2+} (pale green), Fe^{3+} (pale yellow), Co^{2+} (pink), Ni^{2+} (green), Cu^{2+} (blue), Zn^{2+} (colorless).

**Transition-Metal Ions**

Most transition elements form several cations of different charges. For example, iron has the cations Fe^{2+} and Fe^{3+} . Neither has a noble-gas configuration; that would require the energetically impossible loss of eight electrons from the neutral atom.

In forming ions in compounds, the atoms of transition elements generally lose the ns electrons first; then they may lose one or more $(n - 1)d$ electrons. The $2+$ ions are common for the transition elements and are obtained by the loss of the highest-energy s electrons from the atom. Many transition elements also form $3+$ ions by losing one $(n - 1)d$ electron in addition to the two ns electrons. Table 2.4 lists some common transition-metal ions. Many compounds of transition-metal ions are colored because of transitions involving d electrons, whereas the compounds of the main-group elements are usually colorless (Figure 9.6).

Example 9.3**Writing Electron Configurations of Transition-Metal Ions**

Write the electron configurations of Fe^{2+} and Fe^{3+} .

Problem Strategy After obtaining the electron configuration of the atom (using the building-up principle as in Example 8.2 or Example 8.3), remove ns electrons, then $(n - 1)d$ electrons, until you have the correct positive charge on the ion.

Solution The electron configuration of the Fe atom ($Z = 26$) is $[\text{Ar}]3d^64s^2$. To obtain the configuration of Fe^{2+} , remove the $4s^2$ electrons. To obtain the configuration of Fe^{3+} , also remove a $3d$ electron. **The configuration of Fe^{2+} is $[\text{Ar}]3d^6$, and that of Fe^{3+} is $[\text{Ar}]3d^5$.**

Answer Check Check that the number of outer electrons in an ion is correct. The number of outer electrons equals the group number (but count the columns of Group VIIIB as 8, 9, and 10) minus the ion charge. For example, the configuration of Fe^{2+} is given as $[\text{Ar}]3d^6$. Iron is in the first column of Group VIIIB (count 8); the ion has two fewer electrons ($8 - 2 = 6$). This checks with the configuration as written.

Exercise 9.4

of Mn^{2+} .

Write the electron configuration

■ See Problems 9.43 and 9.44.

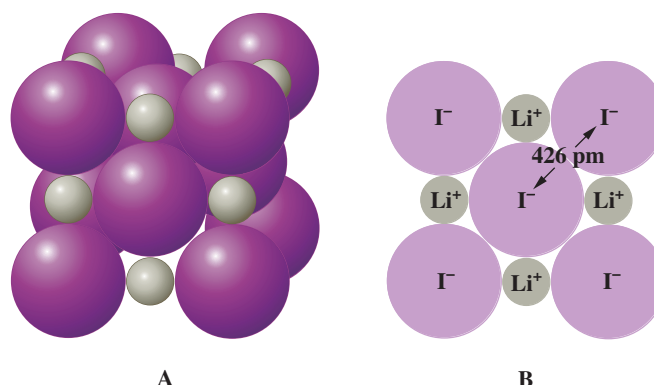
Concept Check 9.1

The following are electron configurations for some ions. Which ones would you expect to see in chemical compounds? State the concept or rule you used to decide for or against any ion.

- a. $\text{Fe}^{2+} [\text{Ar}]3d^44s^2$ b. $\text{N}^{2-} [\text{He}]2s^22p^5$ c. $\text{Zn}^{2+} [\text{Ar}]3d^{10}$
 d. $\text{Na}^{2+} [\text{He}]2s^22p^5$ e. $\text{Ca}^{2+} [\text{Ne}]3s^23p^6$

FIGURE 9.7 ▶**Determining the iodide ion radius in the lithium iodide (LiI) crystal**

(A) A three-dimensional view of the crystal. (B) Cross section through a layer of ions. Iodide ions are assumed to be spheres in contact with one another. The distance between iodine nuclei (426 pm) is determined experimentally. One-half of this distance (213 pm) equals the iodide ion radius.

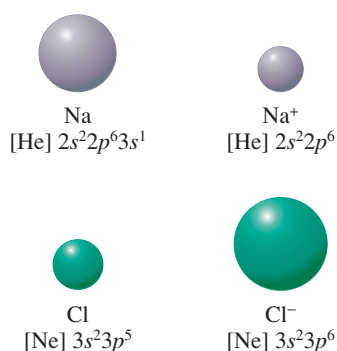


9.3 Ionic Radii

A monatomic ion, like an atom, is a nucleus surrounded by a distribution of electrons. The **ionic radius** is a measure of the size of the spherical region around the nucleus of an ion within which the electrons are most likely to be found. As for an atomic radius, defining an ionic radius is somewhat arbitrary, because an electron distribution never abruptly ends. However, if we imagine ions to be spheres of definite size, we can obtain their radii from known distances between nuclei in crystals. (These distances can be determined accurately by observing how crystals diffract x rays.) <

To understand how you compute ionic radii, consider the determination of the radius of an I^- ion in a lithium iodide (LiI) crystal. Figure 9.7 depicts a layer of ions in LiI. The distance between adjacent iodine nuclei equals twice the I^- radius. From x-ray diffraction experiments, the iodine–iodine distance is found to be 426 pm ($1 \text{ pm} = 1 \times 10^{-12} \text{ m}$). Therefore, the I^- radius in LiI is $\frac{1}{2} \times 426 \text{ pm} = 213 \text{ pm}$. Other crystals give approximately the same radius for the I^- ion. Table 9.3, which lists average values of ionic radii obtained from many compounds of the main-group elements, gives 216 pm for the I^- radius.

That you can find values of ionic radii that agree with the known structures of many crystals is strong evidence for the existence of ions in the solid state. Moreover, these values of ionic radii compare with atomic radii in ways that you might expect. For example, you expect a cation to be smaller and an anion to be larger than the corresponding atom (see Figure 9.8).

**FIGURE 9.8** ▲**Comparison of atomic and ionic radii**

Note that the sodium atom loses its outer shell in forming the Na^+ ion. Thus, the cation is smaller than the atom. The Cl^- ion is larger than the Cl atom, because the same nuclear charge holds a greater number of electrons less strongly.

TABLE 9.3		Ionic Radii (in pm) of Some Main-Group Elements				
Period	IA	IIA	IIIA	VIA	VIIA	
2	Li ⁺	Be ²⁺		O ^{2−}	F [−]	
	60	31		140	136	
3	Na ⁺	Mg ²⁺	Al ³⁺	S ^{2−}	Cl [−]	
	95	65	50	184	181	
4	K ⁺	Ca ²⁺	Ga ³⁺	Se ^{2−}	Br [−]	
	133	99	62	198	195	
5	Rb ⁺	Sr ²⁺	In ³⁺	Te ^{2−}	I [−]	
	148	113	81	221	216	
6	Cs ⁺	Ba ²⁺	Tl ³⁺			
	169	135	95			

A cation formed when an atom loses all its valence electrons is smaller than the atom because it has one less shell of electrons. But even when only some of the valence electrons are lost from an atom, the ion is smaller. With fewer electrons in the valence orbitals, the electron–electron repulsion is initially less, so these orbitals can shrink to increase the attraction of the electrons for the nucleus. Similarly, because an anion has more electrons than the atom, the electron–electron repulsion is greater, so the valence orbitals expand. Thus, the anion radius is larger than the atomic radius.

Exercise 9.5

Which has the larger radius, S or S^{2-} ? Explain.

■ See Problems 9.45 and 9.46.

The ionic radii of the main-group elements shown in Table 9.3 follow a regular pattern, just as atomic radii do. *Ionic radii increase down any column because of the addition of electron shells.*

Exercise 9.6

Without looking at Table 9.3, arrange the following ions in order of increasing ionic radius: Sr^{2+} , Mg^{2+} , Ca^{2+} . (You may use a periodic table.)

■ See Problems 9.47 and 9.48.

The pattern across a period becomes clear if you look first at the cations and then at the anions. For example, in the third period we have

Cation	Na^+	Mg^{2+}	Al^{3+}
Radius (pm)	95	65	50

All of these ions have the neon configuration $1s^2 2s^2 2p^6$ but different nuclear charges; that is, they are isoelectronic. **Isoelectronic** refers to different species having the same number and configuration of electrons. To understand the decrease in radius from Na^+ to Al^{3+} , imagine the nuclear charge (atomic number) of Na^+ to increase. With each increase of charge, the orbitals contract due to the greater attractive force of the nucleus. Thus, in any isoelectronic sequence of atomic ions, the ionic radius decreases with increasing atomic number (just as it does for the atoms).

If you look at the anions in the third-period elements, you notice that they are much larger than the cations in the same period. This abrupt increase in ionic radius is due to the fact that the anions S^{2-} and Cl^- have configurations with one more shell of electrons than the cations. And because these anions also constitute an isoelectronic sequence (with argon configuration), the ionic radius decreases with atomic number (as with the atoms):

Anion	S^{2-}	Cl^-
Radius (pm)	184	181

Thus, in general, across a period the cations decrease in radius. When you reach the anions, there is an abrupt increase in radius, and then the radius again decreases.

Example 9.4

Using Periodic Trends to Obtain Relative Ionic Radii

Without looking at Table 9.3, arrange the following ions in order of decreasing ionic radius: F^- , Mg^{2+} , O^{2-} . (You may use a periodic table.)

Problem Strategy Note that in a series of isoelectronic ions, the ion radius decreases with an increase in nuclear charge (or atomic number).

Solution Note that F^- , Mg^{2+} , and O^{2-} are isoelectronic. If you arrange them by increasing nuclear charge,

they will be in order of decreasing ionic radius. **The order is O^{2-} , F^- , Mg^{2+} .**

Answer Check Check that the ions are isoelectronic by writing their electron configurations.

Exercise 9.7 Without looking at Table 9.3, arrange the following ions in order of increasing ionic radius: Cl^- , Ca^{2+} , P^{3-} . (You may use a periodic table.)

■ See Problems 9.49 and 9.50.

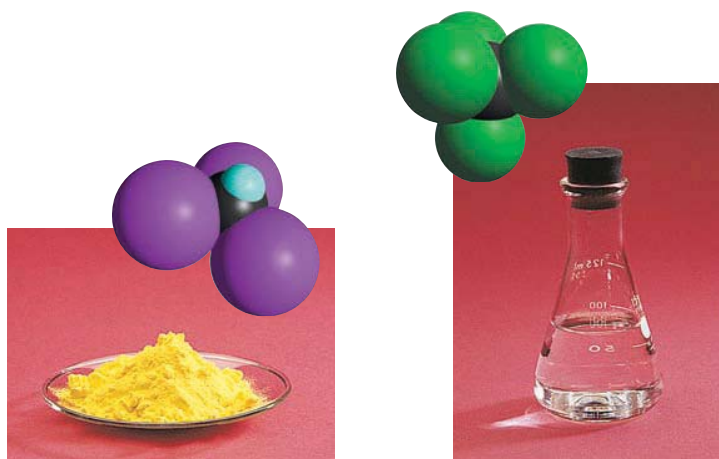
Covalent Bonds

G. N. Lewis (1875–1946) was professor of chemistry at the University of California at Berkeley. Well known for work on chemical bonding, he was also noted for his research in molecular spectroscopy and thermodynamics (the study of heat involved in chemical and physical processes).

In the preceding sections we looked at ionic substances, which are typically high-melting solids. Many substances, however, are molecular—gases, liquids, or low-melting solids consisting of molecules (Figure 9.9). A molecule is a group of atoms, frequently nonmetal atoms, strongly linked by chemical bonds. Often the forces that hold atoms together in a molecular substance cannot be understood on the basis of the attraction of oppositely charged ions (the ionic model). An obvious example is the molecule H_2 , in which the two H atoms are held together tightly and no ions are present. In 1916 Gilbert Newton Lewis proposed that the strong attractive force between two atoms in a molecule results from a **covalent bond**, a chemical bond formed by the sharing of a pair of electrons between atoms. < In 1926 Walter Heitler and Fritz London showed that the covalent bond in H_2 could be quantitatively explained by the newly discovered theory of quantum mechanics. We will discuss the descriptive aspects of covalent bonding in the following sections.

FIGURE 9.9**Two molecular substances**

Left: Iodoform, CHI_3 , is a low-melting, yellow solid (m.p. 120°C). Right: Carbon tetrachloride, CCl_4 , is a colorless liquid.



9.4 Describing Covalent Bonds

Consider the formation of a covalent bond between two H atoms to give the H_2 molecule. As the atoms approach one another, their $1s$ orbitals begin to overlap. Each electron can then occupy the space around both atoms. In other words, the two electrons can be shared by the atoms (Figure 9.10). The electrons are attracted simultaneously by the positive charges of the two hydrogen nuclei. This attraction that bonds the electrons to both nuclei is the force holding the atoms together. Although ions do not exist in H_2 , the force that holds the atoms together can still be regarded as arising from the attraction of oppositely charged particles: nuclei and electrons.

It is interesting to see how the potential energy of the atoms changes as they approach and then bond. Figure 9.11 shows the potential energy of the atoms for various distances between nuclei. The potential energy of the atoms when they are some distance apart is indicated by a position on the potential-energy curve at the far right. As the atoms approach (moving from right to left on the potential-energy curve), the potential energy gets lower and lower. The decrease in energy is a reflection of the bonding of the atoms. Eventually, as the atoms get close enough, the repulsion of the positive charges on the nuclei becomes larger than the attraction of electrons for nuclei. In other words, the potential energy reaches a minimum value and then increases. The distance between nuclei at this minimum energy is called the *bond length* of H_2 . It is the normal distance between nuclei in the molecule.

Now imagine the reverse process. You start with the H_2 molecule, the atoms at their normal bond length apart (at the minimum of the potential-energy curve). To separate the atoms in the molecule, energy must be added (you move along the curve to the flat portion at the right). The energy that must be added is called the *bond dissociation energy*. The larger the bond dissociation energy, the stronger the bond.

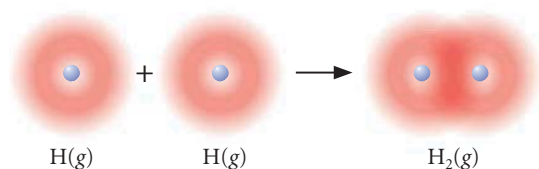
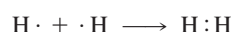


FIGURE 9.10 ▲
The electron probability distribution for the H_2 molecule

The electron density (shown in red) occupies the space around both atoms.

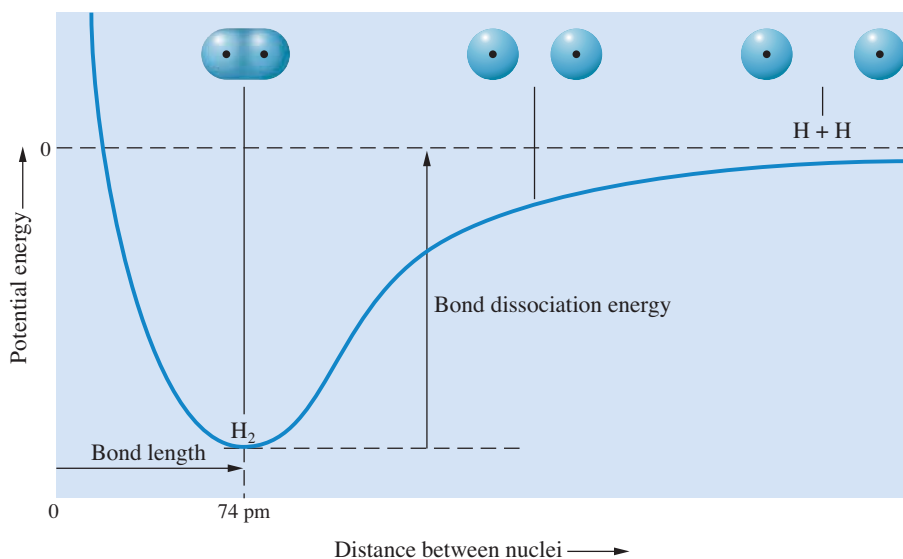
Lewis Formulas

You can represent the formation of the covalent bond in H_2 from atoms as follows:



This uses the Lewis electron-dot symbol for the hydrogen atoms and represents the covalent bond by a pair of dots. Recall that the two electrons from the covalent bond

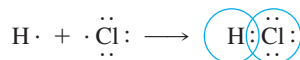
FIGURE 9.11 ►
Potential-energy curve for H_2
The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve.



spend part of the time in the region of each atom. In this sense, each atom in H_2 has a helium configuration. We can draw a circle about each atom to emphasize this.

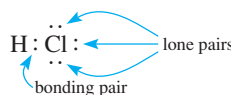


The formation of a bond between H and Cl to give an HCl molecule can be represented in a similar way.



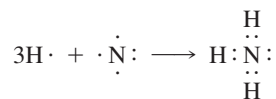
As the two atoms approach each other, unpaired electrons on each atom pair up to form a covalent bond. The pair of electrons is shared by the two atoms. Each atom then acquires a noble-gas configuration of electrons, the H atom having two electrons about it (as in He), and the Cl atom having eight valence electrons about it (as in Ar).

A formula using dots to represent valence electrons is called a **Lewis electron-dot formula**. An electron pair represented by a pair of dots in such a formula is either a **bonding pair** (an electron pair shared between two atoms) or a **lone**, or **nonbonding, pair** (an electron pair that remains on one atom and is not shared). For example,



Bonding pairs are often represented by dashes rather than by pairs of dots.

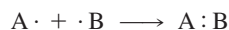
Frequently, the number of covalent bonds formed by an atom equals the number of unpaired electrons shown in its Lewis symbol. Consider the formation of NH_3 .



Each bond is formed between an unpaired electron on one atom and an unpaired electron on another atom. In many instances, the number of bonds formed by an atom in Groups IVA to VIIA equals the number of unpaired electrons, which is eight minus the group number. For example, a nitrogen atom (Group VA) forms $8 - 5 = 3$ covalent bonds. <

Coordinate Covalent Bonds

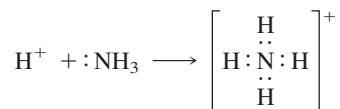
When bonds form between atoms that both donate an electron, you have



However, it is possible for both electrons to come from the same atom. A **coordinate covalent bond** is a bond formed when both electrons of the bond are donated by one atom:



A coordinate covalent bond is not essentially different from other covalent bonds; it involves the sharing of a pair of electrons between two atoms. An example is the formation of the ammonium ion, in which an electron pair on the N atom of NH_3 forms a bond with H^+ .



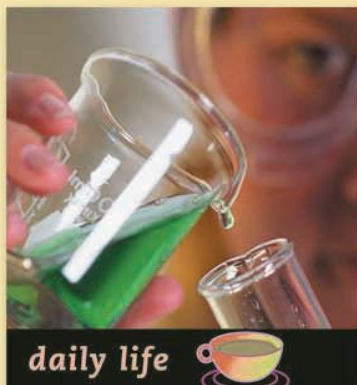
The new N—H bond is clearly identical to the other N—H bonds.

Octet Rule

In each of the molecules we have described so far, the atoms have obtained noble-gas configurations through the sharing of electrons. Atoms other than hydrogen have

The numbers of unpaired electrons in the Lewis symbols for the atoms of elements in Groups IA and IIIA equal the group numbers. But except for the first elements of these groups, the atoms usually form ionic bonds.

A Chemist Looks at . . .



Chemical Bonds in Nitroglycerin

Nitroglycerin gained a nasty reputation soon after its discovery in 1846. Unless kept cold, the pale yellow, oily liquid detonates from even the mildest vibration. In the French film *The Wages of Fear*, four men agree to drive two

trucks loaded with nitroglycerin over mountainous roads from a remote village in South America. They are to drive the nitroglycerin to an out-of-control oil-well fire, where the explosive will be used to close off the well. On the way, they find the road obstructed by a huge boulder that has rolled across it, and they decide to blast the boulder out of their way using some of their explosive cargo. You see one of the men gingerly pouring nitroglycerin from a thermos bottle down a stick and into a hole in the rock. Beads of sweat form on his contorted face, while he tries desperately to suspend his breathing and any extra movement that might set off the nitroglycerin.

Here is the structure of nitroglycerin (also see the molecular model in Figure 9.12):

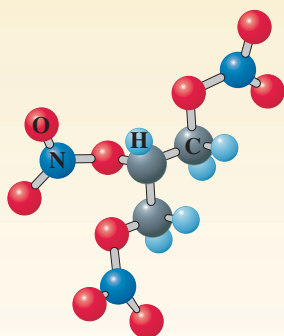
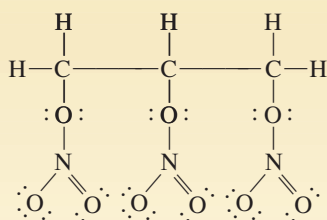
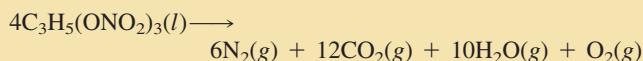


FIGURE 9.12 ▲

Molecular model of nitroglycerin

In this ball-and-stick model, carbon atoms are gray, hydrogen atoms are light blue, oxygen atoms are red, and nitrogen atoms are dark blue.

With just a little jostling, nitroglycerin, $\text{C}_3\text{H}_5(\text{ONO}_2)_3$, can rearrange its atoms to give stable products:



The stability of the products results from their strong bonds, which are much stronger than those in nitroglycerin. Nitrogen, for example, has a strong nitrogen–nitrogen triple bond, and carbon dioxide has two strong carbon–oxygen double bonds. The explosive force of the reaction results from both the rapid reaction and from the large volume increase on forming gaseous products.

In 1867, the Swedish chemist Alfred Nobel discovered that nitroglycerin behaved better when absorbed on diatomaceous earth, a crumbly rock, giving an explosive mixture that Nobel called *dynamite*. Part of the wealth he made from his explosive factories was left in trust to establish the Nobel Prizes. Although explosives are often associated in people's minds with war, they do have many peacetime uses, including road building, mining, and demolition (Figure 9.13).



FIGURE 9.13 ▲

Demolition of a building

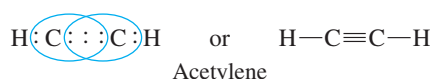
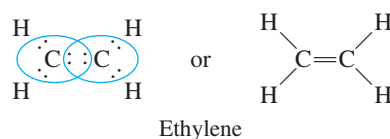
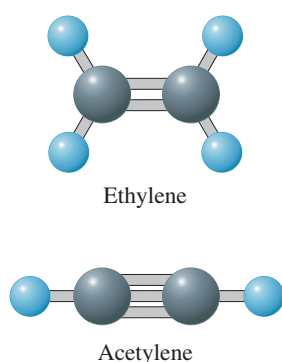
Explosives are placed at predetermined positions so that when they are detonated, the building collapses on itself.

■ See Problems 9.113 and 9.114.

obtained eight electrons in their valence shells; hydrogen atoms have obtained two. *The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms) is known as the **octet rule**.* Many of the molecules we will discuss follow the octet rule. Some do not.

Multiple Bonds

In the molecules we have described so far, each of the bonds has been a **single bond**—that is, a covalent bond in which a single pair of electrons is shared by two atoms. But it is possible for atoms to share two or more electron pairs. A **double bond** is a covalent bond in which two pairs of electrons are shared by two atoms. A **triple bond** is a covalent bond in which three pairs of electrons are shared by two atoms. As examples, consider ethylene, C_2H_4 , and acetylene, C_2H_2 . Their Lewis formulas are



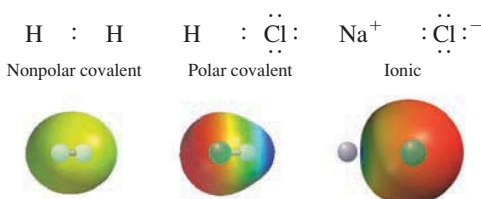
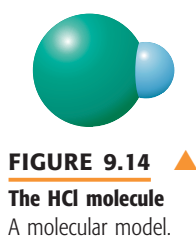
Note the octet of electrons on each C atom. Double bonds form primarily with C, N, O, and S atoms. Triple bonds form mostly to C and N atoms.

9.5

Polar Covalent Bonds; Electronegativity

A covalent bond involves the sharing of at least one pair of electrons between two atoms. When the atoms are alike, as in the case of the H—H bond of H_2 , the bonding electrons are shared equally. That is, the electrons spend the same amount of time in the vicinity of each atom. But when the two atoms are of different elements, the bonding electrons need not be shared equally. A **polar covalent bond** (or simply *polar bond*) is a covalent bond in which the bonding electrons spend more time near one atom than the other. For example, in the case of the HCl molecule (Figure 9.14), the bonding electrons spend more time near the chlorine atom than the hydrogen atom.

You can consider the polar covalent bond as intermediate between a *nonpolar* covalent bond, as in H_2 , and an ionic bond, as in NaCl. From this point of view, an ionic bond is simply an extreme example of a polar covalent bond. To illustrate, we can represent the bonding in H_2 , HCl, and NaCl with electron-dot formulas as follows:

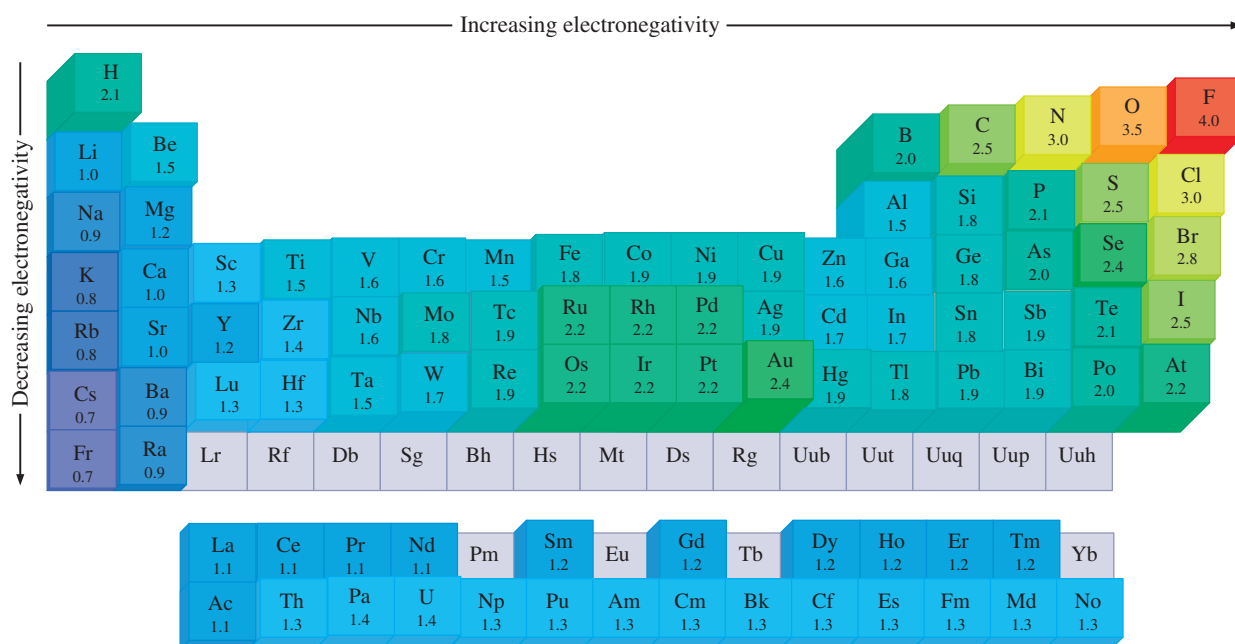


The bonding pairs of electrons are equally shared in H_2 , unequally shared in HCl, and essentially not shared in NaCl. Thus, it is possible to arrange different bonds to form a gradual transition from nonpolar covalent to ionic.

Electronegativity is a measure of the ability of an atom in a molecule to draw bonding electrons to itself. Several electronegativity scales have been proposed. In 1934 Robert S. Mulliken suggested on theoretical grounds that the electronegativity (X) of an atom be given as half its ionization energy ($I.E.$) minus electron affinity ($E.A.$). <

$$X = \frac{I.E. - E.A.}{2}$$

Robert S. Mulliken received the Nobel Prize in chemistry in 1966 for his work on molecular orbital theory (discussed in Chapter 10).

**FIGURE 9.15** ▲**Electronegativities of the elements**

The values given are those of Pauling (those in gray are not known).

Linus Pauling received the Nobel Prize in chemistry in 1954 for his work on the nature of the chemical bond. In 1962 he received the Nobel Peace Prize.

The electronegativity difference in metal-metal bonding would also be small. This bonding frequently involves delocalized metallic bonding, briefly described in Section 9.7.

An atom such as fluorine that tends to pick up electrons easily (large negative *E.A.*) and hold on to them strongly (large *I.E.*) has a large electronegativity. On the other hand, an atom such as lithium or cesium that loses electrons readily (small *I.E.*) and has little tendency to gain electrons (small negative or positive *E.A.*) has a small electronegativity. Until recently, only a few electron affinities had been measured. For this reason, Mulliken's scale has had limited utility. A more widely used scale was derived earlier by Linus Pauling from bond energies, which are discussed later in this chapter. Pauling's electronegativity values are given in Figure 9.15. Because electronegativities depend somewhat on the bonds formed, these values are actually average ones. <

Fluorine, the most electronegative element, was assigned a value of 4.0 on Pauling's scale. Lithium, at the left end of the same period, has a value of 1.0. Cesium, in the same column but below lithium, has a value of 0.7. *In general, electronegativity increases from left to right and decreases from top to bottom in the periodic table.* Metals are the least electronegative elements (they are *electropositive*) and nonmetals the most electronegative.

The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the polarity to be expected in a bond. When this difference is small, the bond is nonpolar. When it is large, the bond is polar (or, if the difference is very large, perhaps ionic). The electronegativity differences for the bonds H—H, H—Cl, and Na—Cl are 0.0, 0.9, and 2.1, respectively, following the expected order. Differences in electronegativity explain why ionic bonds usually form between a metal atom and a nonmetal atom; the electronegativity difference would be largest between these elements. On the other hand, covalent bonds form primarily between two nonmetals because the electronegativity differences are small. <

Example 9.5**Using Electronegativities to Obtain Relative Bond Polarities**

Use electronegativity values (Figure 9.15) to arrange the following bonds in order of increasing polarity: P—H, H—O, C—Cl.

Problem Strategy Order the bonds by the increasing positive value of the difference of electronegativities of the atoms forming the bond. The

(continued)

(continued)

bonds should then be roughly in order of increasing polarity.

Solution The absolute values of the electronegativity differences are P—H, 0.0; H—O, 1.4; C—Cl, 0.5. Hence, the order is **P—H, C—Cl, H—O**.

Answer Check Make sure you have the correct electronegativities and differences.

Exercise 9.8 Using electronegativities, decide which of the following bonds is most polar: C—O, C—S, H—Br.

■ See Problems 9.57 and 9.58.

Lewis formulas do not directly convey information about molecular shape. For example, the Lewis formula of methane, CH₄, is written as the flat (two-dimensional) formula



The actual methane molecule, however, is not flat; it has a three-dimensional structure, as explained in Chapter 10.

You can use an electronegativity scale to predict the direction in which the electrons shift during bond formation; the electrons are pulled toward the more electronegative atom. For example, consider the H—Cl bond. Because the Cl atom ($X = 3.0$) is more electronegative than the H atom ($X = 2.1$), the bonding electrons in H—Cl are pulled toward Cl. Because the bonding electrons spend most of their time around the Cl atom, that end of the bond acquires a partial negative charge (indicated δ^-). The H-atom end of the bond has a partial positive charge (δ^+). You can show this as follows:



The HCl molecule is said to be a *polar molecule*. We will say more about polar molecules when we look at molecular structures in Chapter 10.

9.6

Writing Lewis Electron-Dot Formulas

The Lewis electron-dot formula of a molecule is similar to the structural formula in that it shows how atoms are bonded. Bonding electron pairs are indicated either by two dots or by a dash. In addition to the bonding electrons, however, an electron-dot formula shows the positions of lone pairs of electrons, whereas the structural formula does not. Thus, the electron-dot formula is a simple two-dimensional representation of the positions of electrons in a molecule. In the next chapter we will see how to predict the three-dimensional shape of a molecule from the two-dimensional electron-dot formula. In this section we will discuss the steps for writing the electron-dot formula for a molecule made from atoms of the main-group elements. <

Before you can write the Lewis formula of a molecule (or a polyatomic ion), you must know the *skeleton structure* of the molecule. The skeleton structure tells you which atoms are bonded to one another (without regard to whether the bonds are single or not).

Normally the skeleton structure must be found by experiment. For simple molecules, you can often predict the skeleton structure. For instance, many small molecules or polyatomic ions consist of a central atom around which are bonded atoms of greater electronegativity, such as F, Cl, and O. Note the structural formula (and molecular model) of phosphorus oxychloride, POCl₃ (Figure 9.16). The phosphorus atom is surrounded by more electronegative atoms. (In some cases, H atoms surround a more electronegative atom as in H₂O and NH₃, but H cannot be a central atom because it normally forms only one bond.) Similarly, *oxoacids* are substances in which O atoms (and possibly other electronegative atoms) are bonded to a central atom, with one or more H atoms usually bonded to O atoms. An example is chlorosulfonic acid, HSO₃Cl (Figure 9.17).

Another useful idea for predicting skeleton structures is that molecules or polyatomic ions with symmetrical formulas often have symmetrical structures. For

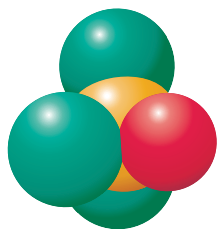
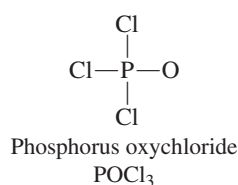


FIGURE 9.16 ▲
Lewis formula and molecular model of phosphorus oxychloride molecule

The central atom, P, is surrounded by O and Cl atoms.

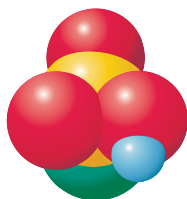
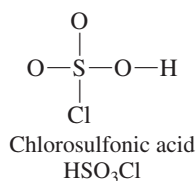


FIGURE 9.17 ▲

Lewis formula and molecular model of chlorosulfonic acid molecule

This oxoacid has the central atom, S, surrounded by O atoms and a Cl atom.

example, disulfur dichloride, S₂Cl₂, is symmetrical, with the more electronegative Cl atoms around the S atoms: Cl—S—S—Cl.

Once you know the skeleton structure of a molecule, you can find the Lewis formula by applying the following four steps. These steps allow you to write electron-dot formulas even when the central atom does not follow the octet rule.

- Step 1:** Calculate the total number of valence electrons for the molecule by summing the number of valence electrons (= group number) for each atom. If you are writing the Lewis formula of a polyatomic anion, you *add* the number of negative charges to this total. (For CO₃²⁻ you add 2 because the -2 charge indicates that there are two more electrons than are provided by the neutral atoms.) For a polyatomic cation, you *subtract* the number of positive charges from the total. (For NH₄⁺ you subtract 1.)
- Step 2:** Write the skeleton structure of the molecule or ion, connecting every bonded pair of atoms by a pair of dots (or a dash).
- Step 3:** Distribute electrons to the atoms surrounding the central atom (or atoms) to satisfy the octet rule for these surrounding atoms.
- Step 4:** Distribute the remaining electrons as pairs to the central atom (or atoms), after subtracting the number of electrons already distributed from the total found in Step 1. If there are fewer than eight electrons on the central atom, this suggests that a multiple bond is present. (Two electrons fewer than an octet suggests a double bond; four fewer suggests a triple bond or two double bonds.) To obtain a multiple bond, move one or two electron pairs (depending on whether the bond is to be double or triple) from a surrounding atom to the bond connecting the central atom. Atoms that often form multiple bonds are C, N, O, and S.

The next several examples illustrate how to write the Lewis electron-dot formula for a small molecule, given the molecular formula.

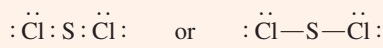
Example 9.6

Writing Lewis Formulas (Single Bonds Only)

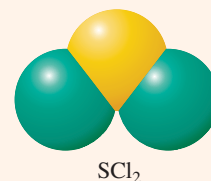
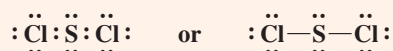
Sulfur dichloride, SCl₂, is a red, fuming liquid used in the manufacture of insecticides. Write the Lewis formula for the molecule.

Problem Strategy You follow the four steps: (1) Calculate the total number of valence electrons. (2) Write the skeleton structure with two electrons to each bond between atoms. (3) Distribute electrons to the outer atoms to satisfy the octet rule. (4) Distribute the remaining electrons to the central atom.

Solution The number of valence electrons from an atom equals the group number: 6 for S, 7 for each Cl, for a total of 20 electrons. You expect the skeleton structure to have S as the central atom, with the more electronegative Cl atoms bonded to it. After connecting atoms by electron pairs and distributing electrons to the outer atoms, you have



This accounts for 8 electron pairs, or 16 electrons. Subtracting this from the total number of electrons (20) gives 4 electrons, or 2 electron pairs. You place these on the central atom (S). The final Lewis formula is



(continued)

(continued)

Answer Check In general, atoms surrounding the central atom have four electron pairs (an octet) about them. Note that our answer follows this “octet” rule. Even the central atom often follows this octet rule, as it does here. (We will see some exceptions to this octet rule for the central atom, however.)

Exercise 9.9 Dichlorodifluoromethane, CCl_2F_2 , is a gas used as a refrigerant and aerosol propellant. Write the Lewis formula for CCl_2F_2 .

■ See Problems 9.61 and 9.62.

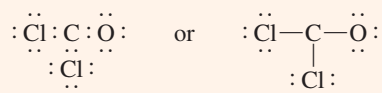
Example 9.7

Writing Lewis Formulas (Including Multiple Bonds)

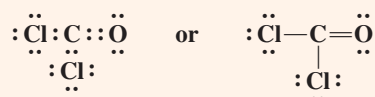
Carbonyl chloride, or phosgene, COCl_2 , is a highly toxic gas used as a starting material for the preparation of polyurethane plastics. What is the electron-dot formula of COCl_2 ?

Problem Strategy You follow the four steps as in the previous example, but after distributing the remaining electrons to the central atom, you find that it does not have an octet. To rectify this, you transfer an electron pair from an outer atom to form a double bond (part of Step 4). Do you move the electron pair from the Cl or the O atom? It helps to remember that C, N, O, and S atoms often form double bonds. In this case, you move the electron pair from the O atom.

Solution The total number of valence electrons is $4 + 6 + (2 \times 7) = 24$. You expect the more electropositive atom, C, to be central, with the O and Cl atoms bonded to it. After distributing electron pairs to these surrounding atoms, you have

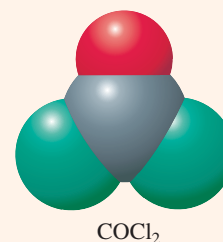


This accounts for all 24 valence electrons, leaving only 6 electrons on C. This is two fewer than an octet, so you move a pair of electrons on the O atom to give a carbon–oxygen double bond. The electron-dot formula of COCl_2 is



Answer Check Note that the atoms surrounding the central atom have four electron pairs about them; that is, they follow the octet rule. The central atom also follows the octet rule, although exceptions occur.

Exercise 9.10 Write the electron-dot formula of carbon dioxide, CO_2 .



■ See Problems 9.63 and 9.64.

Example 9.8

Writing Lewis Formulas (Ionic Species)

Obtain the electron-dot formula (Lewis formula) of the BF_4^- ion.

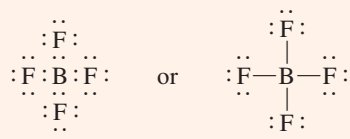
Problem Strategy After calculating the total number of valence electrons for the neutral atoms, you add or subtract electrons to account for the ion charge. If the ion is negative,

(continued)

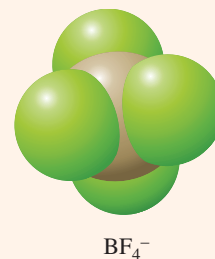
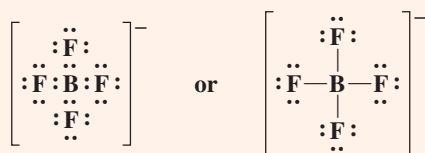
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add electrons to give the negative charge. If the ion is positive, subtract electrons to give the positive charge. Once you have the total number of valence electrons in the ion, proceed with the rest of the steps to write the electron-dot formula.

Solution The total valence electrons provided by the boron and four fluorine atoms is $3 + (4 \times 7) = 31$. Because the anion has a charge of -1 , it has one more electron than is provided by the neutral atoms. Thus, the total number of valence electrons is 32 (or 16 electron pairs). You assume that the skeleton structure has boron as the central atom, with the more electronegative F atoms bonded to it. After connecting the B and F atoms by bonds and placing electron pairs around the F atoms to satisfy the octet rule, you obtain



This uses up all 32 electrons. The charge on the entire ion is indicated by the minus sign written as a superscript to square brackets enclosing the electron-dot formula.



Answer Check Note that the atoms surrounding the central atom have four electron pairs about them; that is, they follow the octet rule. The central atom also follows the octet rule, although exceptions occur.

Exercise 9.11 Write the electron-dot formula of a. the hydronium ion, H_3O^{+} ; b. the chlorite ion, ClO_2^{-} .

■ See Problems 9.65 and 9.66.

Concept Check 9.2

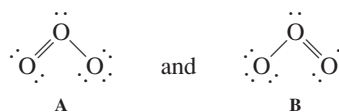
Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2 . Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?

- a. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$ b. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$ c. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$
 d. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$ e. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}$ f. $\text{:}\ddot{\text{F}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{N}}\text{:}\ddot{\text{F}}\text{:}$

9.7 Delocalized Bonding: Resonance

We have assumed up to now that the bonding electrons are localized in the region between two atoms. In some cases, however, this assumption does not fit the

experimental data. Suppose, for example, that you try to write an electron-dot formula for ozone, O_3 . You find that you can write two formulas:



In formula A, the oxygen–oxygen bond on the left is a double bond and the oxygen–oxygen bond on the right is a single bond. In formula B, the situation is just the opposite. Experiment shows, however, that both bonds in O_3 are identical. Therefore, neither formula can be correct. <

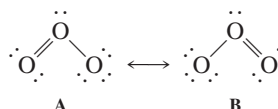
According to theory, one of the bonding pairs in ozone is spread over the region of all three atoms rather than associated with a particular oxygen–oxygen bond. This is called **delocalized bonding**, a type of bonding in which a bonding pair of electrons is spread over a number of atoms rather than localized between two. We might symbolically describe the delocalized bonding in ozone as follows:



(For clarity, only the bonding pairs are given.) The broken line indicates a bonding pair of electrons that spans three nuclei rather than only two. In effect, the oxygen–oxygen bond is neither a single bond nor a double bond but an intermediate type.

A single electron-dot formula cannot properly describe delocalized bonding. Instead, a resonance description is often used. According to the **resonance description**, you describe the electron structure of a molecule having delocalized bonding by writing all possible electron-dot formulas. These are called the *resonance formulas* of the molecule. The actual electron distribution of the molecule is a composite of these resonance formulas.

The electron structure of ozone can be described in terms of the two resonance formulas presented at the start of this section. By convention, we usually write all of the resonance formulas and connect them by double-headed arrows. For ozone we would write



Unfortunately, this notation can be misinterpreted. It does not mean that the ozone molecule flips back and forth between two forms. There is only one ozone molecule. The double-headed arrow means that you should form a mental picture of the molecule by fusing the various resonance formulas. The left oxygen–oxygen bond is double in formula A and the right one is double in formula B, so you must picture an electron pair that actually encompasses both bonds.

Attempting to write electron-dot formulas leads you to recognize that delocalized bonding exists in many molecules. Whenever you can write several plausible electron-dot formulas—which often differ merely in the allocation of single and double bonds to the same kinds of atoms (as in ozone)—you can expect delocalized bonding

Example 9.9

Writing Resonance Formulas

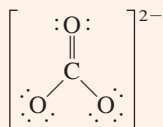
Describe the electron structure of the carbonate ion, CO_3^{2-} , in terms of electron-dot formulas.

Problem Strategy Write at least one electron-dot formula for a molecule or ion. If the formula has both single and multiple bonds, note whether it is possible to write other electron-dot formulas differing only in the placement of single and double bonds.

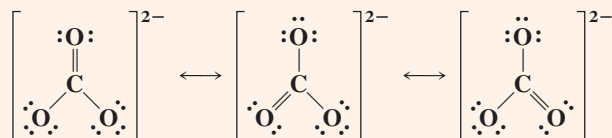
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The lengths of the two oxygen–oxygen bonds (that is, the distances between the atomic nuclei) are both 128 pm.

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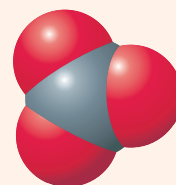
Solution One possible electron-dot formula for the carbonate ion is

Because you expect all carbon–oxygen bonds to be equivalent, you must describe the electron structure in resonance terms.

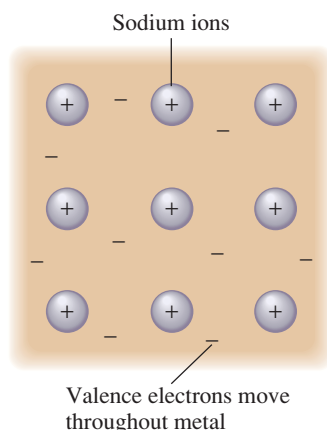


You expect one electron pair to be delocalized over the region of all three carbon–oxygen bonds.

Answer Check Note that the skeleton structure is the same for all resonance formulas. This must be so, because they represent the same molecule. Also, note that the atoms about the central atom follow the octet rule. (The central atom in this case also follows the octet rule.)

CO₃²⁻**Exercise 9.12**Describe the bonding in NO₃⁻ using resonance formulas.

■ See Problems 9.67, 9.68, 9.69, and 9.70.

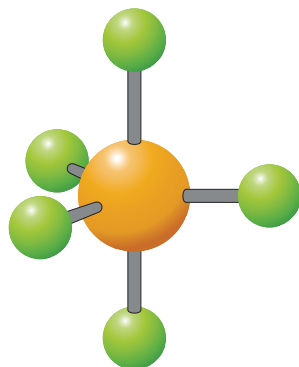
**FIGURE 9.18** ▲**Delocalized bonding in sodium metal**

The metal consists of positive sodium ions in a “sea” of valence electrons. Valence (bonding) electrons are free to move throughout the metal crystal (beige area).

Metals are extreme examples of delocalized bonding. A sodium metal crystal, for example, can be regarded as an array of Na⁺ ions surrounded by a “sea” of electrons (Figure 9.18). The valence, or bonding, electrons are delocalized over the entire metal crystal. The freedom of these electrons to move throughout the crystal is responsible for the electrical conductivity of a metal.

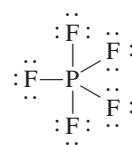
9.8 | Exceptions to the Octet Rule

Many molecules composed of atoms of the main-group elements have electronic structures that satisfy the octet rule, but a number of them do not. A few molecules, such as NO, have an odd number of electrons and so cannot satisfy the octet rule. Other exceptions to the octet rule fall into two groups—one a group of molecules with an atom having fewer than eight valence electrons around it and the other a group of molecules with an atom having more than eight valence electrons around it.

**FIGURE 9.19** ▲

Phosphorus pentafluoride, PF₅
A ball-and-stick molecular model.

The exceptions in which the central atom has more than eight valence electrons around it are fairly numerous. Phosphorus pentafluoride is a simple example. This is a colorless gas of PF₅ molecules. Each molecule consists of a phosphorus atom surrounded by the more electronegative fluorine atoms (Figure 9.19). Following the steps outlined in Section 9.6, you arrive at the following electron-dot formula, in which the phosphorus atom has ten valence electrons around it:



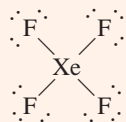
The octet rule stems from the fact that the main-group elements in most cases employ only an ns and three np valence-shell orbitals in bonding, and these orbitals hold eight electrons. Elements of the second period are restricted to these orbitals, but from the third period on, the elements also have unfilled nd orbitals, which may be used in bonding. For example, the valence-shell configuration of phosphorus is $3s^23p^3$. Using just these $3s$ and $3p$ orbitals, the phosphorus atom can accept only three additional electrons, forming three covalent bonds (as in PF_3). However, more bonds can be formed if the empty $3d$ orbitals of the atom are used. If each of the five electrons of the phosphorus atom is paired with unpaired electrons of fluorine atoms, PF_5 can be formed. In this way, phosphorus forms both the trifluoride and the pentafluoride. By contrast, nitrogen (which has no available d orbitals in its valence shell) forms only the trifluoride, NF_3 .

Example 9.10**Writing Lewis Formulas (Exceptions to the Octet Rule)**

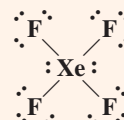
Xenon, a noble gas, forms a number of compounds. One of these is xenon tetrafluoride, XeF_4 , a white, crystalline solid first prepared in 1962. What is the electron-dot formula of the XeF_4 molecule?

Problem Strategy You follow the four steps outlined in Section 9.6. In Step 4, when you distribute the remaining electrons to the central atom, you find that it has more than an octet.

Solution There are 8 valence electrons from the Xe atom and 7 from each F atom, for a total of 36 valence electrons. For the skeleton structure, you draw the Xe atom surrounded by the electronegative F atoms. After placing electron pairs on the F atoms to satisfy the octet rule for them, you have



This accounts for 16 pairs, or 32 electrons. A total of 36 electrons is available, so you put an additional $36 - 32 = 4$ electrons (2 pairs) on the Xe atom. The Lewis formula is



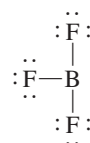
Answer Check Note that the atoms surrounding the central atom follow the octet rule, although the central atom itself does not. The central atom is from a period greater than 2, so it has a valence shell that can accommodate more than eight electrons.

Exercise 9.13

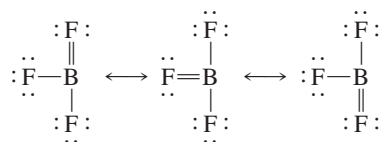
Sulfur tetrafluoride, SF_4 , is a colorless gas. Write the electron-dot formula of the SF_4 molecule.

■ See Problems 9.71 and 9.72.

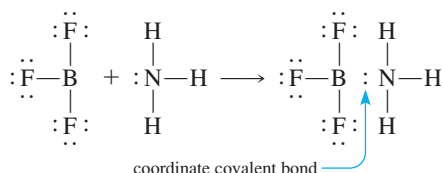
The other group of exceptions to the octet rule consists mostly of molecules containing Group IIA or IIIA atoms. Consider boron trifluoride, BF_3 . The molecule consists of boron surrounded by the much more electronegative fluorine atoms. The total number of valence electrons is $3 + (3 \times 7) = 24$. If you connect boron and fluorine atoms by electron pairs and fill out the fluorine atoms with octets of electrons, you obtain



If you now follow with Step 4 of the procedure outlined in Section 9.6, you note that the boron atom has only six electrons on it. You write the following resonance formulas, each having a double bond:



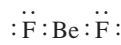
In fact, there is evidence to suggest that the first formula written—the one with all single bonds and in which boron has only six electrons around it—describes the chemistry of boron trifluoride very well. For example, boron trifluoride reacts with molecules having a lone pair, such as with ammonia, NH_3 , to give the compound BF_3NH_3 . The reaction is easy to describe in terms of the formula in which boron has only six electrons around it.



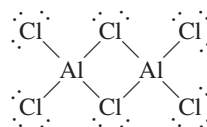
In this reaction, a coordinate covalent bond forms between the boron and nitrogen atoms, and the boron achieves an octet of electrons.

The chemistry of BF_3 thus appears to support an electron structure with boron having only six electrons around it. No doubt, resonance involving all four of the Lewis formulas that we have drawn best describes the actual electron structure of boron trifluoride, but the relative importance of the different resonance formulas is not settled. <

Other examples of molecules with Group IIIA atoms (such as Al) or Group IIA atoms (such as Be) display electron structures similar to that of boron trifluoride. For example, the BeF_2 molecule (found in the vapor over the heated solid BeF_2) has the Lewis formula



Aluminum chloride, AlCl_3 , offers an interesting study in bonding. At room temperature, the substance is a white, crystalline solid and an ionic compound, as might be expected for a binary compound of a metal and a nonmetal. However, the substance has a relatively low melting point (192°C) for an ionic compound. Apparently this is due to the fact that instead of melting to a liquid of ions, as happens with most ionic solids, the compound forms Al_2Cl_6 molecules (Figure 9.20), with Lewis formula



Each atom has an octet of electrons around it. Note that two of the Cl atoms are in *bridge* positions, with each Cl atom having two covalent bonds. When this liquid is heated, it vaporizes as Al_2Cl_6 molecules. As the vapor is further heated, these molecules break up into AlCl_3 molecules. These molecules have an electron structure similar to that of BF_3 .

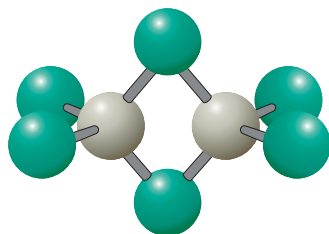


FIGURE 9.20 ▲

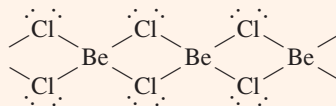
The Al_2Cl_6 molecule

A ball-and-stick molecular model.

The B–F bond length (130 pm) is shorter than expected for a single bond (152 pm), which indicates partial double-bond character. See the discussion in Section 9.10 on bond length and bond order.

Exercise 9.14

Beryllium chloride, BeCl_2 , is a solid substance consisting of long (essentially infinite) chains of atoms with Cl atoms in bridge positions.

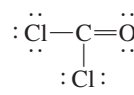


However, if the solid is heated, it forms a vapor of BeCl_2 molecules. Write the electron-dot formula of the BeCl_2 molecule.

■ See Problems 9.73 and 9.74.

9.9 Formal Charge and Lewis Formulas

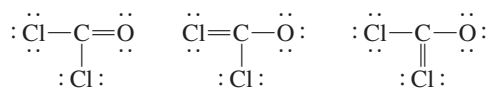
Earlier we looked at writing the Lewis formula for carbonyl chloride, COCl_2 (Example 9.7). In the solution to that example, we wrote the answer as follows:



You may recall that we had to decide whether to draw the double bond between C and O or between C and Cl. We decided in favor of a carbon-oxygen double bond by applying the simple idea that multiple bonds most likely involve C, N, O, and S atoms. In this section, we will describe how you can use the concept of formal charge to determine the best Lewis formula. Formal charge is also a help in writing the skeleton structure of a molecule.

The **formal charge** of an atom in a Lewis formula is *the hypothetical charge you obtain by assuming that bonding electrons are equally shared between bonded atoms and that the electrons of each lone pair belong completely to one atom*. < When you use the Lewis formula that most clearly describes the bonding, the formal charges give you an approximate distribution of electrons in the molecule. Let us see how you would obtain the formal charges, given several possible Lewis formulas of a molecule, and how you would use these formal charges to determine the best Lewis formula.

You begin by writing the possible Lewis formulas. For COCl_2 , you can write



For each formula, you apply the following *rules for formal charge* to assign the valence electrons to individual atoms:

1. Half of the electrons of a bond are assigned to each atom in the bond (counting each dash as two electrons).
2. Both electrons of a lone pair are assigned to the atom to which the lone pair belongs.

You calculate the formal charge on an atom by taking the number of valence electrons on the free atom (equal to the group number) and subtracting the number of electrons you assigned the atom by the rules of formal charge; that is,

$$\text{Formal charge} = \text{valence electrons on free atom} - \frac{1}{2}(\text{number of electrons in a bond}) - (\text{number of lone-pair electrons})$$

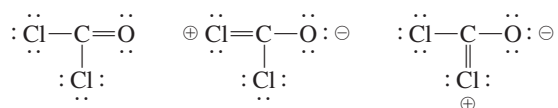
As a check on your work, you should note that the sum of the formal charges equals the charge on the molecular species (zero for a neutral molecule).

The rules for computing oxidation number are similar, except that both bonding electrons are assigned to the more electronegative atom.

Consider a Cl atom in the first Lewis formula we wrote for COCl_2 . You begin by counting the electrons assigned to the Cl atom by the rules of formal charge. You have 1 electron from the single bond and 6 from the lone-pair electrons, for a total of 7. The formal charge of Cl equals the number of valence electrons (7) less the number of assigned electrons (7). This gives a formal charge of 0 for the Cl atom. Similar calculations of formal charge give 0 for each of the other atoms in the Lewis formula.

Now look at the second Lewis formula we wrote for COCl_2 and assign the electrons by the rules for formal charge. For the Cl atom having the double bond, you count 2 electrons from the double bond and 4 from the lone pairs, for a total of 6. The formal charge of the Cl atom is $7 - 6 = +1$. For the O atom, you count 1 electron from the single bond and 6 from the lone-pair electrons, for a total of 7. The number of valence electrons on the free O atom is 6, so the formal charge of the O atom is $6 - 7 = -1$. The formal charge of each of the other atoms is 0.

We indicate the formal charges in a Lewis formula by inserting circled numbers near the atoms (writing + for +1 and - for -1). For the formulas given earlier for COCl_2 , the formal charges are shown as follows:



Now we can discuss three rules that are useful in writing Lewis formulas.

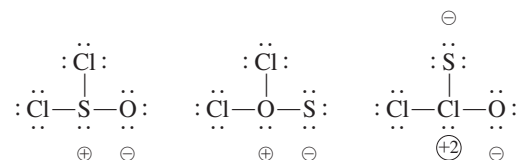
RULE A Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.

RULE B When two proposed Lewis formulas for a molecule have the same magnitudes of formal charges, choose the one having the negative formal charge on the more electronegative atom.

RULE C When possible, choose Lewis formulas that do not have like charges on adjacent atoms.

The second and third formulas for COCl_2 have formal charges on the Cl and O atoms. The first formula, however, has zero formal charges for all atoms. So by Rule A, this formula most closely approximates the actual electron distribution. You would write it as the best description by a single Lewis formula. (To be more precise, you could consider a resonance description involving all three Lewis formulas. However, the Lewis formulas would not participate equally in the resonance description; the first one would predominate.)

You can also use formal charges to help you choose the most likely skeleton structure from several possibilities. Consider thionyl chloride, SOCl_2 . Which of the following Lewis formulas is most plausible? Note that these Lewis formulas have quite different atomic arrangements, so they should not be considered as simply different resonance formulas of the same molecule.

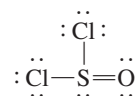


You can verify these formal charges using the method we have outlined here. The last formula has a +2 formal charge on the Cl atom, which is larger in magnitude than the formal charges on any atoms in the other two formulas. Therefore, using Rule A, you would not consider the last formula a plausible structure. To choose between the first and second structures, you apply Rule B. According to this rule, you would choose the first structure over the second, because the first one associates a negative formal charge with the more electronegative atom (O), whereas the second structure

SOCl₂

associates a positive charge with the more electronegative atom. Note that this application of formal charge gives the same result that you would obtain by assuming that the least electronegative atom is the central atom.

Now that you have one Lewis formula with the appropriate skeleton structure for SOCl₂, you should explore the possibility of other Lewis formulas with this skeleton structure. You can write a Lewis formula that has a sulfur–oxygen double bond.



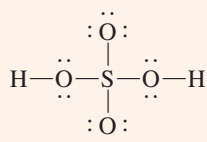
This formula has formal charges of zero for each atom; so according to Rule A, it should be closer to the actual electron distribution than the previous formula. (You could write a resonance description involving both formulas.) Note that the sulfur atom has 10 electrons around it. As long as the atom has available *d* orbitals for bonding (as any element in the third and higher periods will have), the atom need not obey the octet rule. The next example further illustrates the application of formal charges in choosing the appropriate Lewis formula.

Example 9.11**Using Formal Charges to Determine the Best Lewis Formula**

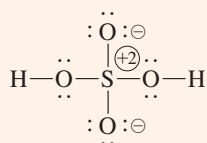
Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H₂SO₄, according to the rules of formal charge.

Problem Strategy Draw the skeleton structure of the molecule or ion, and then follow the steps for writing electron-dot formulas. Note that you can move electron pairs into bonding regions to obtain additional formulas (having multiple bonds). The formal charge of an atom in a formula equals the group number of the atom minus the number of electrons assigned to the atom by the rules of formal charge (half of the electrons of connecting bonds plus all of the lone-pair electrons on the atom). Apply Rules A, B, and C given before this example to decide which Lewis formula is best.

Solution Assume a skeleton structure in which the S atom is surrounded by the more electronegative O atoms; the H atoms are then attached to two of the O atoms. The following is a possible Lewis formula having single bonds:

H₂SO₄

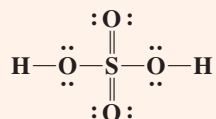
You calculate the formal charge of each O atom bonded to an H atom as follows: You assign the O atom 2 electrons from the two single bonds and 4 electrons from the two lone pairs, for a total of 6 electrons. Because the number of valence electrons on the O atom is 6, the formal charge is $6 - 6 = 0$. For each of the other two O atoms, you assign 1 electron from the one single bond and 6 electrons from the three lone pairs, for a total of 7. The formal charge is $6 - 7 = -1$. For the S atom, you assign 4 electrons from the four single bonds, for a total of 4. Because the number of valence electrons is 6, the formal charge is $6 - 4 = +2$. The formal charge of each of the H atoms is $1 - 1 = 0$. The Lewis formula with formal charges is



(continued)

(continued)

You can also write a Lewis formula that has zero formal charges for atoms, if you form sulfur–oxygen double bonds:



To the top O atom, you assign 2 electrons from the double bond and 4 electrons from the two lone pairs, for a total of 6 electrons. The formal charge is $6 - 6 = 0$. To the S atom, you assign a total of 6 electrons from bonds. The formal charge is $6 - 6 = 0$. The formal charges of the other atoms are also 0. Thus, this Lewis formula should be a better representation of the electron distribution in the H_2SO_4 molecule.

Answer Check The sum of the formal charges on any formula should equal the charge on the species, which is zero for a neutral molecule.

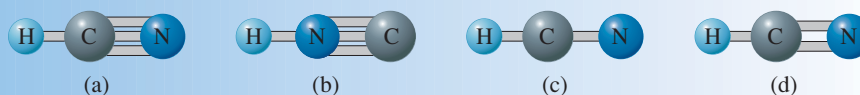
Exercise 9.15

Write the Lewis formula that best describes the phosphoric acid molecule, H_3PO_4 .

■ See Problems 9.77 and 9.78.

Concept Check 9.3

Which of the models shown below most accurately represents the hydrogen cyanide molecule, HCN? Write the electron-dot formula that most closely agrees with this model. State any concept or rule you used in arriving at your answer.

**9.10****Bond Length and Bond Order**

Bond length (or **bond distance**) is the distance between the nuclei in a bond. Bond lengths are determined experimentally using x-ray diffraction or the analysis of molecular spectra. Knowing the bond length in a particular molecule can sometimes provide a clue to the type of bonding present.

In many cases, bond lengths for covalent single bonds in compounds can be predicted from covalent radii. **Covalent radii** are values assigned to atoms in such a way that the sum of covalent radii of atoms A and B predicts an approximate A—B bond length. Thus, the radius of the Cl atom might be taken to be half the Cl—Cl bond length (198 pm). The covalent radius of Cl would be $\frac{1}{2} \times 198 \text{ pm} = 99 \text{ pm}$. Table 9.4 lists single-bond covalent radii for nonmetallic elements.

To predict the bond length of C—Cl, you add the covalent radii of the two atoms, C and Cl. You get $(77 + 99) \text{ pm} = 176 \text{ pm}$, which compares favorably with the experimental value of 178 pm found in most compounds.

TABLE 9.4

Single-Bond Covalent Radii for Nonmetallic Elements (in pm)

				H
				37
B	C	N	O	F
88	77	70	66	64
	Si	P	S	Cl
	117	110	104	99
		As	Se	Br
		121	117	114
			Te	I
			137	133

Although a double bond is stronger than a single bond, it is not necessarily less reactive. Ethylene, $\text{CH}_2=\text{CH}_2$, for example, is more reactive than ethane, CH_3-CH_3 , where carbon atoms are linked through a single bond. The reactivity of ethylene results from the simultaneous formation of a number of strong single bonds. See Section 9.11.

Exercise 9.16

in Table 9.4.

Estimate the O—H bond length in H₂O from the covalent radii listed

■ See Problems 9.79, 9.80, 9.81, and 9.82.

See the margin note at the bottom of the preceding page.

The **bond order**, defined in terms of the Lewis formula, is *the number of pairs of electrons in a bond*. For example, in C : C the bond order is 1 (single bond); in C : : C the bond order is 2 (double bond). Bond length depends on bond order. As the bond order increases, the bond strength increases and the nuclei are pulled inward, decreasing the bond length. Look at carbon–carbon bonds. The average C—C bond length is 154 pm, whereas C=C is 134 pm long and C≡C is 120 pm long. <

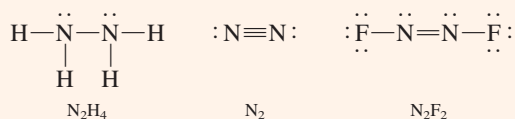
Example 9.12

Relating Bond Order and Bond Length

Consider the molecules N₂H₄, N₂, and N₂F₂. Which molecule has the shortest nitrogen–nitrogen bond? Which has the longest nitrogen–nitrogen bond?

Problem Strategy First, write the electron-dot formulas for the molecules. Then note that the length of a bond between atoms decreases with bond order.

Solution First write the Lewis formulas:



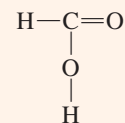
The nitrogen–nitrogen bond should be shortest in N₂, where it is a triple bond, and longest in N₂H₄, where it is a single bond. (Experimental values for the

nitrogen–nitrogen bond lengths are 109 pm for N₂, 122 pm for N₂F₂, and 147 pm for N₂H₄.)

Answer Check Check that you have written the electron-dot formulas correctly.

Exercise 9.17

Formic acid, isolated in 1670, is the irritant in ant bites. The structure of formic acid is



One of the carbon–oxygen bonds has a length of 136 pm; the other is 123 pm long. What is the length of the C=O bond in formic acid?

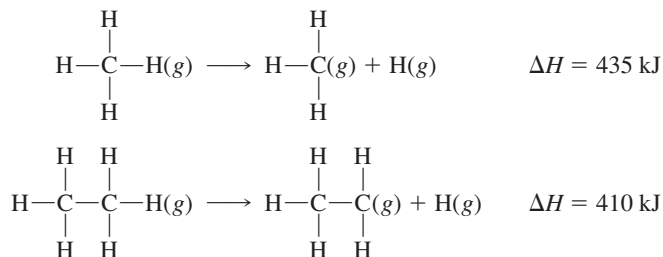
■ See Problems 9.83 and 9.84.

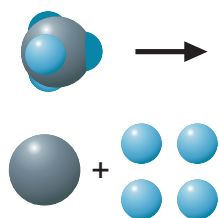
9.11

Bond Energy

In Section 9.4, when we described the formation of a covalent bond, we introduced the concept of bond dissociation energy, the energy required to break a particular bond in a molecule (see Figure 9.11). The bond dissociation energy is a measure of the strength of a particular bond and is essentially the *enthalpy change* for a gas-phase reaction in which a bond breaks. The enthalpy change, ΔH , is the heat absorbed in a reaction carried out at constant pressure (heat of reaction).

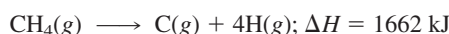
Consider the experimentally determined enthalpy changes for the breaking, or dissociation, of a C—H bond in methane, CH₄, and in ethane, C₂H₆, in the gas phase:





Note that the ΔH values are approximately the same in the two cases. This suggests that the enthalpy change for the dissociation of a C—H bond may be about the same in other molecules. Comparisons of this sort lead to the conclusion that we can obtain approximate values of energies of various bonds.

We define the A—B **bond energy** (denoted BE) as *the average enthalpy change for the breaking of an A—B bond in a molecule in the gas phase*. For example, to calculate a value for the C—H bond energy, or $BE(\text{C—H})$, you might look at the experimentally determined enthalpy change for the breaking of all the C—H bonds in methane:



Because four C—H bonds are broken, you obtain an average value for breaking one C—H bond by dividing the enthalpy change for the reaction by 4:

$$BE(\text{C—H}) = \frac{1}{4} \times 1662 \text{ kJ} = 416 \text{ kJ}$$

Similar calculations with other molecules, such as ethane, would yield approximately the same values for the C—H bond energy.

Table 9.5 lists values of some bond energies. Because it takes energy to break a bond, bond energies are always positive numbers. When a bond is formed, the energy is equal to the negative of the bond energy (energy is released).

Bond energy is a measure of the strength of a bond: the larger the bond energy, the stronger the chemical bond. Note from Table 9.5 that the bonds C—C, C=C, and C≡C have energies of 346, 602, and 835 kJ/mol, respectively. These numbers indicate that the triple bond is stronger than the double bond, which in turn is stronger than the single bond.

You can use this table of bond energies to estimate heats of reaction, or enthalpy changes, ΔH , for gaseous reactions. To illustrate this, find ΔH for the following reaction (Figure 9.21):

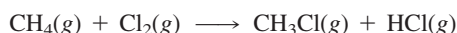


TABLE 9.5

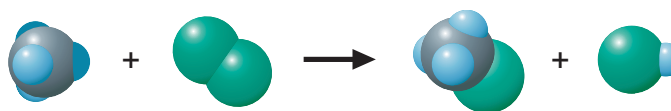
Bond Energies (in kJ/mol)*

	Single Bonds								
	H	C	N	O	S	F	Cl	Br	I
H	432								
C	411	346							
N	386	305	167						
O	459	358	201	142					
S	363	272	—	—	226				
F	565	485	283	190	284	155			
Cl	428	327	313	218	255	249	240		
Br	362	285	—	201	217	249	216	190	
I	295	213	—	201	—	278	208	175	149
Multiple Bonds									
C=C	602		C=N	615	C=O		745 (799 in CO ₂)		
C≡C	835		C≡N	887	C≡O		1072		
N=N	418		N=O	607	S=O (in SO ₂)		532		
N≡N	942		O=O	494	S=O (in SO ₃)		469		

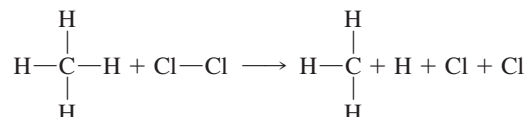
*Data are taken from J. E. Huheey, Keiter, and Keiter, *Inorganic Chemistry*, 4th ed. (New York: HarperCollins, 1993), pp. A21–A34.

FIGURE 9.21 ▶**Reaction of methane with chlorine**

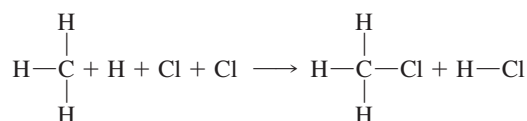
Molecular models illustrate the reaction
 $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$.



You can *imagine* that the reaction takes place in steps involving the breaking and forming of bonds. Starting with the reactants, you suppose that one C—H bond and the Cl—Cl bond break.



The enthalpy change is $BE(\text{C}-\text{H}) - BE(\text{Cl}-\text{Cl})$. Now you reassemble the fragments to give the products.



In this case, C—Cl and H—Cl bonds are formed, and the enthalpy change equals the negative of the bond energies $-BE(\text{C}-\text{Cl}) - BE(\text{H}-\text{Cl})$. Substituting bond-energy values from Table 9.5, you get the enthalpy of reaction.

$$\begin{aligned} \Delta H &\approx BE(\text{C}-\text{H}) + BE(\text{Cl}-\text{Cl}) - BE(\text{C}-\text{Cl}) - BE(\text{H}-\text{Cl}) \\ &= (411 + 240 - 327 - 428) \text{ kJ} \\ &= -104 \text{ kJ} \end{aligned}$$

The negative sign means that heat is released by the reaction. Because the bond-energy concept is only approximate, this value is only approximate (the experimental value is -101 kJ).

In general, the enthalpy of reaction is (approximately) equal to the sum of the bond energies for bonds broken minus the sum of the bond energies for bonds formed.

Rather than calculating a heat of reaction from bond energies, you usually obtain the heat of reaction from thermochemical data, because these are generally known more accurately. If the thermochemical data are not known, however, bond energies can give you a reasonable estimate of the heat of reaction.

Bond energies are perhaps of greatest value when you try to explain heats of reaction or to understand the relative stabilities of compounds. In general, a reaction is exothermic (gives off heat) if weak bonds are replaced by strong bonds (see Figure 9.22). In the reaction we just discussed, two bonds were broken and replaced by two new, stronger bonds. In the following example, a strong bond ($\text{C}=\text{C}$) is replaced by two weaker ones (two $\text{C}-\text{C}$ bonds). Although the single bond is weaker than the double bond, as you would expect, two $\text{C}-\text{C}$ bonds *together* create an energetically more stable situation than one $\text{C}=\text{C}$ bond.

FIGURE 9.22 ▼**Explosion of nitrogen triiodide-ammonia complex**

The red-brown complex of nitrogen triiodide and ammonia is so sensitive to explosion that it can be detonated with a feather. Nitrogen–iodine single bonds are replaced by very stable nitrogen–nitrogen triple bonds (N_2) and iodine–iodine single bonds (I_2).



Instrumental Methods



Infrared Spectroscopy and Vibrations of Chemical Bonds

A chemical bond acts like a stiff spring connecting nuclei. As a result, the nuclei in a molecule vibrate, rather than maintaining fixed positions relative to each other. Nuclear

vibration is depicted in Figure 9.23, which shows a spring model of HCl.

This vibration of molecules is revealed in their absorption of infrared radiation. (An instrument for observing the absorption of infrared radiation is shown in Figure 9.24.) The frequency of radiation absorbed equals the frequencies of nuclear vibrations. For example, the H—Cl bond vibrates at a frequency of 8.652×10^{13} vibrations per second. If radiation of this frequency falls on the molecule, it absorbs the radiation, which is in the infrared region, and begins vibrating more strongly.

The infrared absorption spectrum of a molecule of even moderate size can have a rather complicated

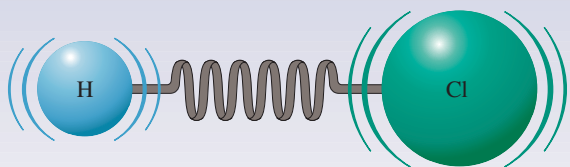


FIGURE 9.23 ▲

Vibration of the HCl molecule

The vibrating molecule is represented here by a spring model. The atoms in the molecule vibrate; that is, they move constantly back and forth.



FIGURE 9.24 ▲

A Fourier transform infrared (FTIR) spectrometer

A Nicolet 560 E.S.P.T-IR spectrometer.

appearance. Figure 9.25 shows the infrared (IR) spectrum of ethyl butyrate, a compound present in pineapple flavor. The complicated appearance of the IR spectrum is actually an advantage. Two different compounds are unlikely to have exactly the same IR spectrum. Therefore, the IR spectrum can act as a compound's "fingerprint."

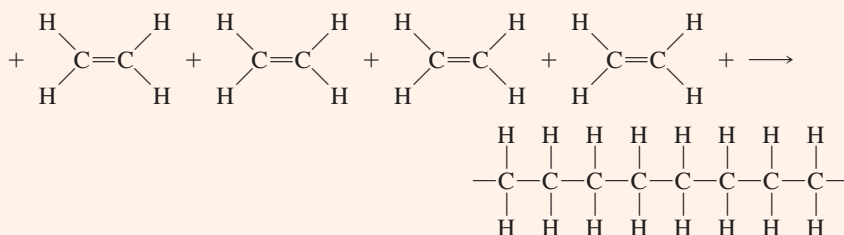
The IR spectrum of a compound can also yield structural information. Suppose you would like to obtain the structural formula of ethyl butyrate. The molecular formula, determined from combustion analysis, is $C_6H_{12}O_2$. Important information about this structure can be obtained from Figure 9.25.

You first need to be able to read such a spectrum. Instead of plotting an IR spectrum in frequency units (since

Example 9.13

Estimating ΔH from Bond Energies

Polyethylene is formed by linking many ethylene molecules into long chains. Estimate the enthalpy change per mole of ethylene for this reaction (shown below), using bond energies.



(continued)

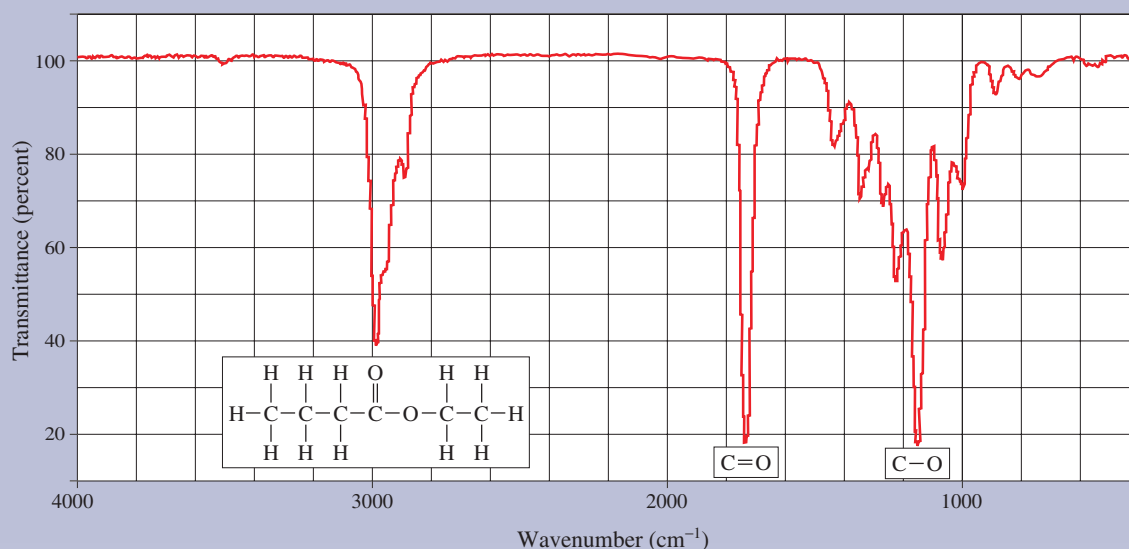


FIGURE 9.25 ▲

Infrared spectrum of ethyl butyrate

Note the peaks corresponding to vibrations of C=O and C—O bonds. The molecular structure is shown at the bottom left. [From NIST Mass Spec Data Center, S.E. Stein, director, "IR and Mass Spectra" in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Eds. W.G. Mallard and P.J. Linstrom, February 2000, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (<http://webbook.nist.gov>). © 1991, 1994, 1996, 1997, 1998, 1999, 2000 copyright by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved.]

the frequencies are very large), you usually would give the frequencies in *wavenumbers*, which are proportional to frequency. To get the wavenumber, you divide the frequency by the speed of light expressed in centimeters per second. For example, HCl absorbs at $(8.652 \times 10^{13} \text{ s}^{-1}) / (2.998 \times 10^{10} \text{ cm/s}) = 2886 \text{ cm}^{-1}$ (wavenumbers). Wavenumber, or sometimes wavelength, is plotted along the horizontal axis.

Percent transmittance—that is, the percent of radiation that passes through a sample—is plotted on the vertical axis. When a molecule absorbs radiation of a given frequency or wavenumber, this is seen in the spectrum as an inverted spike (peak) at that wavenumber. Certain structural

features of molecules appear as absorption peaks in definite regions of the infrared spectrum. For example, the absorption peak at 1730 cm^{-1} is characteristic of the C=O bond. With some knowledge of where various bonds absorb, one can identify other peaks, including that of C—O at 1180 cm^{-1} . (Generally, the IR peak for an A—B bond occurs at lower wavenumber than for an A=B bond.) The IR spectrum does not reveal the complete structure, but it provides important clues. Data from other instruments, such as the mass spectrometer (page 98), give additional clues.

■ See Problems 9.115 and 9.116.

(continued)

Problem Strategy Break bonds in the reactants, and then form new bonds to give the products. The approximate enthalpy change equals the sum of the bond energies for the bonds broken minus the sum of the bond energies for the bonds formed.

Solution Imagine the reaction to involve the breaking of the carbon–carbon double bonds and the formation of carbon–carbon single bonds. For a very long chain, the net result is that for every C=C bond broken, two C—C bonds are formed.

$$\Delta H \approx [602 - (2 \times 346)] \text{ kJ} = -90 \text{ kJ}$$

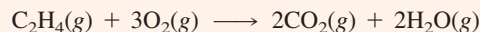
Answer Check Note whether the sign of ΔH agrees with what you would expect. Perhaps weak bonds have been replaced by strong bonds, in which case ΔH should be negative. Here, every double bond is replaced by two single bonds, so ΔH should be negative, as it is.

(continued)

(continued)

Exercise 9.18

Use bond energies to estimate the enthalpy change for the combustion of ethylene, C_2H_4 , according to the equation



■ See Problems 9.85 and 9.86.

A Checklist for Review

Important Terms

ionic bond (9.1)

Lewis electron-dot symbol (9.1)

lattice energy (9.1)

ionic radius (9.3)

isoelectronic (9.3)

covalent bond (9.4)

Lewis electron-dot formula (9.4)

bonding pair (9.4)

lone (nonbonding) pair (9.4)

coordinate covalent bond (9.4)

octet rule (9.4)

single bond (9.4)

double bond (9.4)

triple bond (9.4)

polar covalent bond (9.5)

electronegativity (9.5)

delocalized bonding (9.7)

resonance description (9.7)

formal charge (9.9)

bond length (bond

distance) (9.10)

covalent radii (9.10)

bond order (9.10)

bond energy (9.11)

Summary of Facts and Concepts

An *ionic bond* is a strong attractive force holding ions together. An ionic bond can form between two atoms by the transfer of electrons from the valence shell of one atom to the valence shell of the other. Many similar ions attract one another to form a crystalline solid, in which positive ions are surrounded by negative ions and negative ions are surrounded by positive ions. As a result, ionic solids are typically high-melting solids. Monatomic cations of the main-group elements have charges equal to the group number (or in some cases, the group number minus two). Monatomic anions of the main-group elements have charges equal to the group number minus eight.

A *covalent bond* is a strong attractive force that holds two atoms together by their sharing of electrons. These bonding electrons are attracted simultaneously to both atomic nuclei, and they spend part of the time near one atom and part of the time near the other. If an electron pair is not equally shared, the bond is *polar*. This polarity results from the difference in *electronegativities* of the atoms—that is, from the unequal abilities of the atoms to draw bonding electrons to themselves.

Lewis electron-dot formulas are simple representations of the valence-shell electrons of atoms in molecules and ions. You can apply simple rules to draw these formulas. In molecules with *delocalized bonding*, it is not possible to describe accurately the electron distribution with a single Lewis formula. For these molecules, you must use *resonance*. Although the atoms in Lewis formulas often satisfy the octet rule, *exceptions to the octet rule* are not uncommon. You can obtain the Lewis formulas for these exceptions by following the rules for writing Lewis formulas. The concept of *formal charge* will often help you decide which of several Lewis formulas gives the best description of a molecule or ion.

Bond lengths can be estimated from the *covalent radii* of atoms. Bond length depends on *bond order*; as the bond order increases, the bond length decreases. The *A—B bond energy* is the average enthalpy change when an A—B bond is broken. You can use bond energies to estimate ΔH for gas-phase reactions.

Media Summary

Visit the **student website** at college.hmco.com/pic/ebbing9e to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:



Prepare for Class

- **Video Lessons** Mini lectures from chemistry experts
 - Valence Electrons and Chemical Bonding
 - Ionic Bonds

Lewis Dot Structure for Covalent Bonds
 Predicting Lewis Dot Structures
 An Introduction to Electronegativity
 Resonance Structures
 Formal Charge

Electronegativity, Formal Charge, and Resonance
Bond Properties
Using Bond Dissociation Energies



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Learning Objectives

9.1 Describing Ionic Bonds

- Define *ionic bond*.
- Explain the *Lewis electron-dot symbol* of an atom.
- Use Lewis symbols to represent ionic bond formation.
Example 9.1
- Describe the energetics of ionic bonding.
- Define *lattice energy*.
- Describe the Born–Haber cycle to obtain a lattice energy from thermodynamic data.
- Describe some general properties of ionic substances.

9.2 Electron Configurations of Ions

- State the three categories of monatomic ions of the main-group elements.
- Write the electron configuration and Lewis symbol for a main-group ion. **Example 9.2**
- Note the polyatomic ions given earlier in Table 2.5.
- Note the formation of 2+ and 3+ transition-metal ions.
- Write electron configurations of transition-metal ions.
Example 9.3

9.3 Ionic Radii

- Define *ionic radius*.
- Define *isoelectronic ions*.
- Use periodic trends to obtain relative ionic radii. **Example 9.4**

9.4 Describing Covalent Bonds

- Describe the formation of a covalent bond between two atoms.
- Define *Lewis electron-dot formula*.
- Define *bonding pair* and *lone (nonbonding) pair* of electrons.
- Define *coordinate covalent bond*.
- State the octet rule.
- Define *single bond*, *double bond*, and *triple bond*.

9.5 Polar Covalent Bonds; Electronegativity

- Define *polar covalent bond*.
- Define *electronegativity*.

- State the general periodic trends in the electronegativity.
- Use electronegativity to obtain relative bond polarity.
Example 9.5

9.6 Writing Lewis Electron-Dot Formulas

- Write Lewis formulas with single bonds only. **Example 9.6**
- Write Lewis formulas having multiple bonds. **Example 9.7**
- Write Lewis formulas for ionic species. **Example 9.8**

9.7 Delocalized Bonding; Resonance

- Define *delocalized bonding*.
- Define *resonance description*.
- Write resonance formulas. **Example 9.9**

9.8 Exceptions to the Octet Rule

- Write Lewis formulas (exceptions to the octet rule).
Example 9.10
- Note exceptions to the octet rule in Group IIA and Group IIIA elements.

9.9 Formal Charge and Lewis Formulas

- Define *formal charge*.
- State the rules for obtaining formal charge.
- State two rules useful in writing Lewis formulas.
- Use formal charges to determine the best Lewis formula.
Example 9.11

9.10 Bond Length and Bond Order

- Define *bond length (bond distance)*.
- Define *covalent radii*.
- Define *bond order*.
- Explain how bond order and bond length are related.
Example 9.12

9.11 Bond Energy

- Define *bond energy*.
- Estimate ΔH from bond energies. **Example 9.13**

Self-Assessment and Review Questions

- 9.1** Describe the formation of a sodium chloride crystal from atoms.
- 9.2** Why does sodium chloride normally exist as a crystal rather than as a molecule composed of one cation and one anion?
- 9.3** Explain what energy terms are involved in the formation of an ionic solid from atoms. In what way should these terms change (become larger or smaller) to give the lowest energy possible for the solid?
- 9.4** Define lattice energy for potassium bromide.
- 9.5** Why do most monatomic cations of the main-group elements have a charge equal to the group number? Why do most monatomic anions of these elements have a charge equal to the group number minus eight?
- 9.6** The $2+$ ions of transition elements are common. Explain why this might be expected.
- 9.7** Explain how ionic radii are obtained from known distances between nuclei in crystals.
- 9.8** Describe the trends shown by the radii of the monatomic ions for the main-group elements both across a period and down a column.
- 9.9** Describe the formation of a covalent bond in H_2 from atoms. What does it mean to say that the bonding electrons are shared by the two atoms?
- 9.10** Draw a potential-energy diagram for a molecule such as Cl_2 . Indicate the bond length (194 pm) and the bond dissociation energy (240 kJ/mol).
- 9.11** Give an example of a molecule that has a coordinate covalent bond.
- 9.12** The octet rule correctly predicts the Lewis formula of many molecules involving main-group elements. Explain why this is so.
- 9.13** Describe the general trends in electronegativities of the elements in the periodic table both across a period and down a column.
- 9.14** What is the qualitative relationship between bond polarity and electronegativity difference?
- 9.15** What is a resonance description of a molecule? Why is this concept required if we wish to retain Lewis formulas as a description of the electron structure of molecules?

9.16 Describe the kinds of exceptions to the octet rule that we encounter in compounds of the main-group elements. Give examples.

9.17 What is the relationship between bond order and bond length? Use an example to illustrate it.

9.18 Define bond energy. Explain how one can use bond energies to estimate the heat of reaction.

9.19 Which of the following contains *both* ionic and covalent bonds in the same compound?

- a. BaCO_3 b. MgCl_2
c. BaO d. H_2S
e. SO_4^{2-}

9.20 The radii of the species S , S^+ , and S^- *decrease* in the following order:

- a. $\text{S}^+ > \text{S} > \text{S}^-$
b. $\text{S}^+ > \text{S} > \text{S}$
c. $\text{S} > \text{S}^- > \text{S}^+$
d. $\text{S} > \text{S}^+ > \text{S}^-$
e. $\text{S}^- > \text{S} > \text{S}^+$

9.21 Which of the following is the ground-state electron configuration of a C^{3-} ion?

- a. $1s^2 2s^2 2p^4$
b. $[\text{He}] 2s^2 2p^6$
c. $[\text{He}] 2s^1$
d. $1s^2 2s^2 2p^5$
e. $1s^2 2s^2 2p^6 3s^1$

9.22 The element X below could be

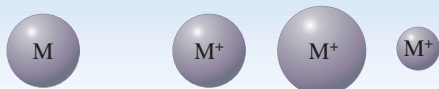


- a. sulfur
b. iodine
c. aluminum
d. phosphorus
e. silicon

Concept Explorations

9.23 Forming Ionic Compounds

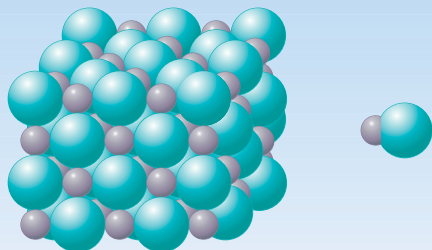
- a. Consider a metal atom, which we will give the symbol M. Metal M can readily form the M^+ cation. If the sphere on the left below represents the metal atom M, which of the other three spheres would probably represent the M^+ cation? Explain your choice.



- b. Consider a nonmetal atom, which we will give the symbol X. The element X is a gas at room temperature and can easily form the X^- anion. If atom X is represented by the sphere on the left below, which of the other three spheres would probably represent the X^- anion. Explain your choice.

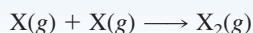


- c. On the basis of the information given previously, write a balanced chemical equation for the reaction that occurs when metal M reacts with nonmetal X. Include state symbols for the reactants and products.
- d. Is the product of the reaction of M and X a molecule or an ionic compound? Provide justification for your answer.
- e. Which of the representations below is the most appropriate to describe the compound of M and X, according to your answer for part d? Explain how you arrived at your choice.

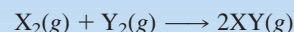


9.24 Bond Energy

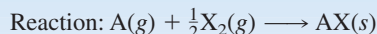
When atoms of the hypothetical element X are placed together, they rapidly undergo reaction to form the X_2 molecule:



- a. Would you predict that this reaction is exothermic or endothermic? Explain.
- b. Is the bond energy of X_2 a positive or a negative quantity? Why?
- c. Suppose ΔH for the reaction is -500 kJ/mol. Estimate the bond energy of the X_2 molecule.
- d. Another hypothetical molecular compound, $Y_2(g)$, has a bond energy of 750 kJ/mol, and the molecular compound $XY(g)$ has a bond energy of 1500 kJ/mol. Using bond-energy information, calculate ΔH for the following reaction.



- e. Given the following information, as well as the information previously presented, predict whether or not the hypothetical ionic compound AX is likely to form. In this compound, A forms the A^+ cation, and X forms the X^- anion. Be sure to justify your answer.



The first ionization energy of A(g) is 400 kJ/mol.

The electron affinity of X(g) is -525 kJ/mol.

The lattice energy of AX(s) is 100 kJ/mol.

- f. If you predicted that no ionic compound would form from the reaction in part e, what minimum amount of AX(s) lattice energy might lead to compound formation?

Conceptual Problems

9.25 You land on a distant planet in another universe and find that the $n = 1$ level can hold a maximum of 4 electrons, the $n = 2$ level can hold a maximum of 5 electrons, and the $n = 3$ level can hold a maximum of 3 electrons. Like our universe, protons have a charge of +1, electrons have a charge of -1 , and opposite charges attract. Also, a filled shell results in greater stability of an atom, so the atom tends to gain or lose electrons to give a filled shell. Predict the formula of a compound that results from the reaction of a neutral metal atom X, which has 7 electrons, and a neutral nonmetal atom Y, which has 3 electrons.

9.26 Which of the following represent configurations of thallium ions in compounds? Explain your decision in each case.

- a. $Tl^{2+} [Xe]4f^{14}5d^{10}6p^1$ b. $Tl^{3+} [Xe]4f^{14}5d^{10}$
 c. $Tl^{4+} [Xe]4f^{14}5d^9$ d. $Tl^+ [Xe]4f^{14}5d^{10}6s^2$

9.27 Below on the left side are models of two atoms, one from a metal, the other from a nonmetal. On the right side are corresponding monatomic ions of those atoms. Decide which of these ions is the cation and which is the anion. Label atoms as "metal" or "nonmetal," as appropriate.



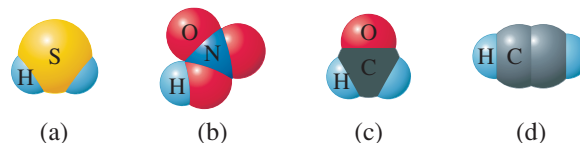
9.28 Predict a possible monatomic ion for Element 117, Uus. Given the spherical models below, which should be labeled "atom" and which should be labeled "ion"?



9.29 Examine each of the following electron-dot formulas and decide whether the formula is correct, or whether you could write a formula that better approximates the electron structure of the molecule. State which concepts or rules you use in each case to arrive at your conclusion.

- a. $\cdot \ddot{N} : \ddot{N} :$ b. $\cdot \ddot{Cl} : C :: N :$
 c. $H : C :: \ddot{F} :$ d. $\begin{array}{c} \cdot \ddot{O} : \\ H : \ddot{O} :: C :: \ddot{O} : H \end{array}$

9.30 For each of the following molecular models, write an appropriate Lewis formula.



9.31 For each of the following molecular formulas, draw the most reasonable skeleton structure.

- a. CH_2Cl_2 b. HNO_2 c. NOF d. N_2O_4

What rule or concept did you use to obtain each structure?

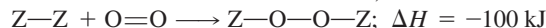
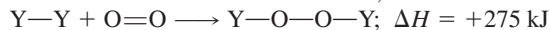
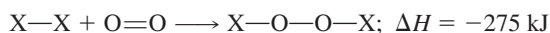
9.32 Below are three resonance formulas for N_2O (nitrous oxide). Rank these in terms of how closely you think each one represents the true electron structure of the molecule. State the rules and concepts you use to do this ranking.

- a. $\text{:}\ddot{\text{N}}\text{—N}\equiv\text{O:}$ b. $\text{:N}\equiv\text{N—}\ddot{\text{O}}\text{:}$ c. $\text{:}\ddot{\text{N}}=\text{N}=\ddot{\text{O}}\text{:}$

9.33 Sodium, Na, reacts with element X to form an ionic compound with the formula Na_3X .

- a. What is the formula of the compound you expect to form when calcium, Ca, reacts with element X?
b. Would you expect this compound to be ionic or molecular?

9.34 The enthalpy change for each of the following reactions was calculated using bond energies. The bond energies of X—O , Y—O , and Z—O are all equal.



- a. Rank the bonds X—X , Y—Y , and Z—Z from strongest to weakest.
b. Compare the energies required to completely dissociate each of the products to atoms.
c. If O_2 molecules were O—O instead of $\text{O}=\text{O}$, how would this change ΔH for each reaction?

Practice Problems

Ionic Bonding

9.35 Write Lewis symbols for the following:

- a. P b. P^{3-} c. Ga d. Ga^{3+}

9.36 Write Lewis symbols for the following:

- a. Br b. Br^- c. Sr d. Sr^{2+}

9.37 Use Lewis symbols to represent the transfer of electrons between the following atoms to form ions with noble-gas configurations:

- a. Ca and Br b. K and I

9.38 Use Lewis symbols to represent the electron transfer between the following atoms to give ions with noble-gas configurations:

- a. Mg and S b. Ba and I

9.39 For each of the following, write the electron configuration and Lewis symbol:

- a. As b. As^{3+} c. Se d. Se^{2-}

9.40 For each of the following, write the electron configuration and Lewis symbol:

- a. In b. In^- c. K^+ d. I^-

9.41 Write the electron configurations of Bi and Bi^{3+} .

9.42 Write the electron configurations of Sn and Sn^{2+} .

9.43 Give the electron configurations of Ni^{2+} and Ni^{3+} .

9.44 Give the electron configurations of Cu^+ and Cu^{2+} .

Ionic Radii

9.45 Arrange the members of each of the following pairs in order of increasing radius and explain the order:

- a. Sr, Sr^{2+} b. Br, Br^-

9.46 Arrange the members of each of the following pairs in order of increasing radius and explain the order:

- a. Te, Te^{2-} b. Al, Al^{3+}

9.47 Without looking at Table 9.3, arrange the following in order of increasing ionic radius: Se^{2-} , Te^{2-} , S^{2-} . Explain how you arrived at this order. (You may use a periodic table.)

9.48 Which has the larger radius, N^{3-} or P^{3-} ? Explain. (You may use a periodic table.)

9.49 Arrange the following in order of increasing ionic radius: F^- , Na^+ , and N^{3-} . Explain this order. (You may use a periodic table.)

9.50 Arrange the following in order of increasing ionic radius: Cl^- , Na^+ , and S^{2-} . Explain this order. (You may use a periodic table.)

Covalent Bonding

9.51 Use Lewis symbols to show the reaction of atoms to form hydrogen selenide, H_2Se . Indicate bonding pairs and lone pairs in the electron-dot formula of this compound.

9.52 Use Lewis symbols to show the reaction of atoms to form arsine, AsH_3 . Indicate which electron pairs in the Lewis formula of AsH_3 are bonding and which are lone pairs.

9.53 Assuming that the atoms form the normal number of covalent bonds, give the molecular formula of the simplest compound of arsenic and bromine atoms.

9.54 Assuming that the atoms form the normal number of covalent bonds, give the molecular formula of the simplest compound of silicon and chlorine atoms.

Polar Covalent Bonds; Electronegativity

9.55 Using a periodic table (not Figure 9.15), arrange the following in order of increasing electronegativity:

- a. P, O, N b. Na, Al, Mg c. C, Al, Si

9.56 With the aid of a periodic table (not Figure 9.15), arrange the following in order of increasing electronegativity:

- a. Sr, Ca, Rb b. Ca, Ge, Ga c. Se, As, Sb

9.57 Arrange the following bonds in order of increasing polarity using electronegativities of atoms: P—O, C—Cl, As—Br.

9.58 Decide which of the following bonds is least polar on the basis of electronegativities of atoms: H—N, Si—Br, N—Cl.

9.59 Indicate the partial charges for the bonds given in Problem 9.57, using the symbols δ^+ and δ^- .

9.60 Indicate the partial charges for the bonds given in Problem 9.58, using the symbols δ^+ and δ^- .

Writing Lewis Formulas

9.61 Write Lewis formulas for the following molecules:

- a. Br₂ b. H₂S c. NF₃

9.62 Write Lewis formulas for the following molecules:

- a. NOCl b. PBr₃ c. IF

9.63 Write Lewis formulas for the following molecules:

- a. P₂ b. COBr₂ c. HNO₂

9.64 Write Lewis formulas for the following molecules:

- a. CO b. BrCN c. N₂F₂

9.65 Write Lewis formulas for the following ions:

- a. ClO⁻ b. SnCl₃⁻ c. S₂²⁻

9.66 Write Lewis formulas for the following ions:

- a. IBr₂⁺ b. ClF₂⁺ c. CN⁻

Resonance

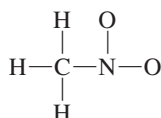
9.67 Write resonance descriptions for the following:

- a. HNO₃ b. SO₃

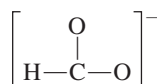
9.68 Write resonance descriptions for the following:

- a. NO₂⁻ b. FNO₂

9.69 Use resonance to describe the electron structure of nitromethane, CH₃NO₂. The skeleton structure is



9.70 Give the resonance description of the formate ion. The skeleton structure is



Exceptions to the Octet Rule

9.71 Write Lewis formulas for the following:

- a. XeF₂ b. SeF₄ c. TeF₆ d. XeF₅⁺

9.72 Write Lewis formulas for the following:

- a. I₃⁻ b. ClF₃ c. IF₄⁻ d. BrF₅

9.73 Write Lewis formulas for the following:

- a. BCl₃ b. TiCl₂⁺ c. BeBr₂

9.74 Write Lewis formulas for the following:

- a. AlI₃ b. BeCl₂ c. BeF₃⁻

Formal Charge and Lewis Formulas

9.75 Write a Lewis formula for each of the following, assuming that the octet rule holds for the atoms. Then obtain the formal charges of the atoms.

- a. O₃ b. CO c. HNO₃

9.76 Write a Lewis formula for each of the following, assuming that the octet rule holds for the atoms. Then obtain the formal charges of the atoms.

- a. ClNO b. POCl₃ c. N₂O (NNO)

9.77 For each of the following, use formal charges to choose the Lewis formula that gives the best description of the electron distribution:

- a. SOF₂
b. H₂SO₃
c. HClO₂

9.78 For each of the following, use formal charges to choose the Lewis formula that gives the best description of the electron distribution:

- a. ClO₂F
b. SO₃⁻
c. BrO₃⁻

Bond Length, Bond Order, and Bond Energy

9.79 Use covalent radii (Table 9.4) to estimate the length of the P—F bond in phosphorus trifluoride, PF₃.

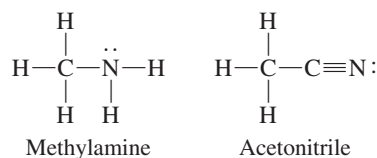
9.80 What do you expect for the B—F bond length in boron trifluoride, BF₃, on the basis of covalent radii (Table 9.4)?

9.81 Calculate the bond length for each of the following single bonds, using covalent radii (Table 9.4):

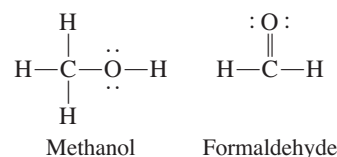
- a. C—H
b. S—Cl
c. Br—Cl
d. Si—O

9.82 Calculate the C—H and C—Cl bond lengths in chloroform, CHCl₃, using values for the covalent radii from Table 9.4. How do these values compare with the experimental values: C—H, 107 pm; C—Cl, 177 pm?

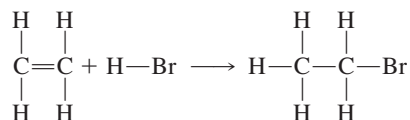
9.83 One of the following compounds has a carbon–nitrogen bond length of 116 pm; the other has a carbon–nitrogen bond length of 147 pm. Match a bond length with each compound.



9.84 Which of the following two compounds has the shorter carbon–oxygen bond?

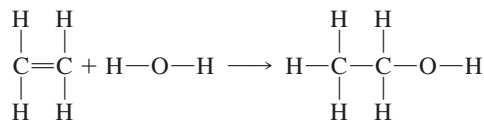


9.85 Use bond energies (Table 9.5) to estimate ΔH for the following gas-phase reaction.



This is called an “addition” reaction, because a compound (HBr) is added across the double bond.

9.86 A commercial process for preparing ethanol (ethyl alcohol), $\text{C}_2\text{H}_5\text{OH}$, consists of passing ethylene gas, C_2H_4 , and steam over an acid catalyst (to speed up the reaction). The gas-phase reaction is



Estimate ΔH for this reaction, using bond energies (Table 9.5).

General Problems

9.87 For each of the following pairs of elements, state whether the binary compound formed is likely to be ionic or covalent. Give the formula and name of the compound.

- a. Sr, O b. C, Br c. Ga, F d. N, Br

9.88 For each of the following pairs of elements, state whether the binary compound formed is likely to be ionic or covalent. Give the formula and name of the compound.

- a. Na, S b. Al, F c. Ca, Cl d. Si, Br

9.89 Give the Lewis formula for the arsenate ion, AsO_4^{3-} . Write the formula of lead(II) arsenate.

9.90 Give the Lewis formula for the selenite ion, SeO_3^{2-} . Write the formula of aluminum selenite.

9.91 Iodic acid, HIO_3 , is a colorless, crystalline compound. What is the electron-dot formula of iodic acid?

9.92 Selenic acid, H_2SeO_4 , is a crystalline substance and a strong acid. Write the electron-dot formula of selenic acid.

9.93 Sodium amide, known commercially as sodamide, is used in preparing indigo, the dye used to color blue jeans. It is an ionic compound with the formula NaNH_2 . What is the electron-dot formula of the amide anion, NH_2^- ?

9.94 Lithium aluminum hydride, LiAlH_4 , is an important reducing agent (an element or compound that generally has a strong tendency to give up electrons in its chemical reactions). Write the electron-dot formula of the AlH_4^- ion.

9.95 Nitronium perchlorate, NO_2ClO_4 , is a reactive salt of the nitronium ion NO_2^+ . Write the electron-dot formula of NO_2^+ .

9.96 Solid phosphorus pentabromide, PBr_5 , has been shown to have the ionic structure $[\text{PBr}_4^+][\text{Br}^-]$. Write the electron-dot formula of the PBr_4^+ cation.

9.97 Write electron-dot formulas for the following:

- a. SeOCl_2 b. CSe_2 c. GaCl_4^- d. C_2^{2-}

9.98 Write electron-dot formulas for the following:

- a. POBr_3 b. Si_2H_6 c. IF_2^+ d. NO^+

9.99 Write Lewis formulas for the following:

- a. SbCl_3 b. ICN c. ICl_3 d. IF_5

9.100 Write Lewis formulas for the following:

- a. AlCl_4^- b. AlF_6^{3-} c. BrF_3 d. IF_6^+

9.101 Give resonance descriptions for the following:

- a. SeO_2 b. N_2O_4

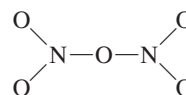
9.102 Give resonance descriptions for the following:

- a. CH_3NO_2 b. $\text{C}_2\text{O}_4^{2-}$

9.103 The compound S_2N_2 has a cyclic structure with alternating sulfur and nitrogen atoms. Draw all resonance formulas in which the atoms obey the octet rule. Of these, select those in which the formal charges of all atoms are closest to zero.

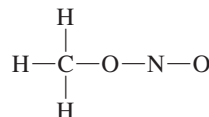
9.104 Acetic acid has the structure $\text{CH}_3\text{CO}(\text{OH})$, in which the OH group is bonded to a C atom. The two carbon–oxygen bonds have different lengths. When an acetic acid molecule loses the H from the OH group to form the acetate ion, the two carbon–oxygen bonds become equal in length. Explain.

9.105 The atoms in N_2O_5 are connected as follows:



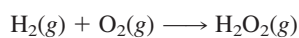
No attempt has been made here to indicate whether a bond is single or double or whether there is resonance. Obtain the Lewis formula (or formulas). The N—O bond lengths are 118 pm and 136 pm. Indicate the lengths of the bonds in the compound.

9.106 Methyl nitrite has the structure

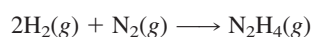


No attempt has been made here to indicate whether a bond is single or double or whether there is resonance. Obtain the Lewis formula (or formulas). The N—O bond lengths are 122 pm and 137 pm. Indicate the lengths of the N—O bonds in the compound.

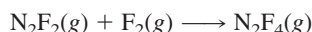
9.107 Use bond energies to estimate ΔH for the reaction



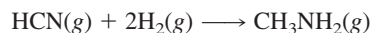
9.108 Use bond energies to estimate ΔH for the reaction



9.109 Use bond energies to estimate ΔH for the reaction



9.110 Use bond energies to estimate ΔH for the reaction



9.111 Compare the properties of an ionic material such as sodium chloride with a room-temperature ionic liquid. Explain this difference.

9.112 What advantages does using an ionic liquid as a solvent have over using an organic solvent?

9.113 Explain the decomposition of nitroglycerin in terms of relative bond energies.

9.114 How did the Swedish chemist Alfred Nobel manage to tame the decomposition of nitroglycerin?

9.115 What property of a chemical bond gives rise to the infrared spectrum of a compound?

9.116 What kind of information can be obtained about a compound from its infrared spectrum?

Strategy Problems

9.117 Which of the following Lewis structures is (or are) *not* correct?



9.118 Which of the following are isoelectronic with the potassium ion, K^{+} ? What are the electron configurations of these species?



9.119 An ion M^{2+} has the configuration $[\text{Ar}]3d^2$, and an atom has the configuration $[\text{Ar}]4s^2$. Identify the ion and the atom.

9.120 Give the symbol of an atomic ion for each of the following electron configurations:

- $1s^2 2s^2 2p^6 3s^2 3p^6$
- $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

9.121 Which of the following molecules possesses a double bond? If none do, so state. Which species has an atom with a nonzero formal charge?



9.122 Which of the following molecules contains *only* double bonds? If none do, so state.



9.123 Draw resonance structures for the azide ion, N_3^{-} , and for the nitronium ion, NO_2^{+} . Decide which resonance structure is the best description of each ion.

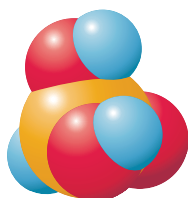
9.124 Two fourth-period atoms, one of a transition metal, M, and the other of a main-group nonmetal, X, form a compound with the formula M_2X_3 . What is the electron configuration of atom X if M is Fe? What is the configuration of X if M is Co?

9.125 Consider hypothetical elements X and Y. Suppose the enthalpy of formation of the compound XY is -336 kJ/mol , the bond energy for X_2 is 414 kJ/mol , and the bond energy for Y_2 is 159 kJ/mol . Estimate the XY bond energy in units of kJ/mol .

9.126 Nitrous oxide, N_2O , has a linear structure NNO. Write resonance formulas for this molecule and from them estimate the NN bond length in the molecule. Use the data in Example 9.12.

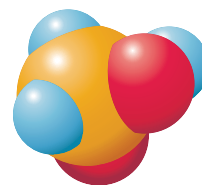
Cumulative-Skills Problems

9.127 Phosphorous acid, H_3PO_3 , has the structure $(\text{HO})_2\text{PHO}$, in which one H atom is bonded to the P atom, and two H atoms are bonded to O atoms. For each bond to an H atom, decide whether it is polar or nonpolar. Assume that only polar-bonded H atoms are acidic. Write the balanced equation for the complete neutralization of phosphorous acid with sodium hydroxide. A 200.0-mL sample of H_3PO_3 requires 22.50 mL of 0.1250 M NaOH for complete neutralization. What is the molarity of the H_3PO_3 solution?



9.128 Hypophosphorous acid, H_3PO_2 , has the structure $(\text{HO})\text{PH}_2\text{O}$, in which two H atoms are bonded to the P atom, and one H atom is bonded to an O atom. For each bond to an H atom,

decide whether it is polar or nonpolar. Assume that only polar-bonded H atoms are acidic. Write the balanced equation for the complete neutralization of hypophosphorous acid with sodium hydroxide. A 200.0-mL sample of H_3PO_2 requires 22.50 mL of 0.1250 M NaOH for complete neutralization. What is the molarity of the H_3PO_2 solution?



9.129 An ionic compound has the following composition (by mass): Mg, 10.9%; Cl, 31.8%; O, 57.3%. What are the formula and name of the compound? Write the Lewis formulas for the ions.

9.130 An ionic compound has the following composition (by mass): Ca, 30.3%; N, 21.2%; O, 48.5%. What are the

formula and name of the compound? Write the Lewis formulas for the ions.

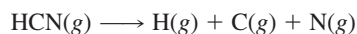
9.131 A gaseous compound has the following composition by mass: C, 25.0%; H, 2.1%; F, 39.6%; O, 33.3%. Its molecular mass is 48.0 amu. Write the Lewis formula for the molecule.

9.132 A liquid compound used in dry cleaning contains 14.5% C and 85.5% Cl by mass and has a molecular mass of 166 amu. Write the Lewis formula for the molecule.

9.133 A compound of tin and chlorine is a colorless liquid. The vapor has a density of 7.49 g/L at 151°C and 1.00 atm. What is the molecular mass of the compound? Why do you think the compound is molecular and not ionic? Write the Lewis formula for the molecule.

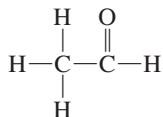
9.134 A compound of arsenic and fluorine is a gas. A sample weighing 0.100 g occupies 14.2 mL at 23°C and 765 mmHg. What is the molecular mass of the compound? Write the Lewis formula for the molecule.

9.135 Calculate the enthalpy of reaction for



from enthalpies of formation (see Appendix C). Given that the C—H bond energy is 411 kJ/mol, obtain a value for the C≡N bond energy. Compare your result with the value given in Table 9.5.

9.136 Assume the values of the C—H and C—C bond energies given in Table 9.5. Then, using data given in Appendix C, calculate the C=O bond energy in acetaldehyde,



Compare your result with the value given in Table 9.5.

9.137 According to Pauling, the A—B bond energy is equal to the average of the A—A and B—B bond energies plus an energy contribution from the polar character of the bond:

$$BE(\text{A}-\text{B}) = \frac{1}{2} [BE(\text{A}-\text{A}) + BE(\text{B}-\text{B})] + k(X_{\text{A}} - X_{\text{B}})^2$$

Here X_{A} and X_{B} are the electronegativities of atoms A and B, and k is a constant equal to 98.6 kJ. Assume that the electronegativity of H is 2.1. Use the formula to calculate the electronegativity of oxygen.

9.138 Because known compounds with N—I bonds tend to be unstable, there are no thermodynamic data available with which to calculate the N—I bond energy. However, we can estimate a value from Pauling's formula relating electronegativities and bond energies (see Problem 9.137). Using Pauling's electronegativities and the bond energies given in Table 9.5, calculate the N—I bond energy.

9.139 Using Mulliken's formula, calculate a value for the electronegativity of chlorine. Use values of the ionization energy from Figure 8.18 and values of the electron affinity from Table 8.4. Divide this result (in kJ/mol) by 230 to get a value comparable to Pauling's scale.

9.140 Using Mulliken's formula, calculate a value for the electronegativity of oxygen. Convert the result to a value on Pauling's scale. See Problem 9.139.

10

Molecular Geometry and Chemical Bonding Theory



Humans are one of the few animals unable to produce vitamin C (ascorbic acid) naturally and must obtain it through the diet (such as citrus fruits) or from supplements. The space-filling model shows the three-dimensional shape of the ascorbic acid molecule.

Contents and Concepts

Molecular Geometry and Directional Bonding

- 10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model
- 10.2 Dipole Moment and Molecular Geometry
- 10.3 Valence Bond Theory
- 10.4 Description of Multiple Bonding

We can predict the molecular geometry of a molecule, its general shape as determined by the relative positions of atomic nuclei, with a simple model: the valence-shell electron-pair repulsion model. After exploring molecular geometry, we explain chemical bonding by means of valence bond theory, which gives us insight into why bonds form and why they have definite directions in space, giving particular molecular geometries.

Molecular Orbital Theory

- 10.5 Principles of Molecular Orbital Theory
- 10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements
- 10.7 Molecular Orbitals and Delocalized Bonding

Although valence bond theory satisfactorily describes most molecules, it has trouble explaining the bonding in a molecule such as oxygen, O_2 , which has even numbers of electrons but is paramagnetic. Molecular orbital theory is an alternative theory that views the electronic structure of molecules much the way we think of atoms: in terms of orbitals that are successively occupied by electrons.

We know from various experiments that molecules have definite structures; that is, the atoms of a molecule have definite positions relative to one another in three-dimensional space. Consider two molecules: boron trifluoride, BF_3 , and phosphorus trifluoride, PF_3 . Both have the same general formula, AX_3 , but their molecular structures are very different (Figure 10.1). Boron trifluoride is a planar, or flat, molecule. The angle between any two B—F bonds is 120° . The geometry or general shape of the BF_3 molecule is said to be *trigonal planar* (trigonal because the figure described by imaginary lines connecting the F atoms has three sides). Phosphorus trifluoride is nonplanar, and the angle between any two P—F bonds is 96° . If you imagine lines connecting the fluorine atoms, these lines and those of the P—F bonds describe a pyramid with the phosphorus atom at its apex. The geometry of the PF_3 molecule is said to be *trigonal pyramidal*. How do you explain such different molecular geometries?

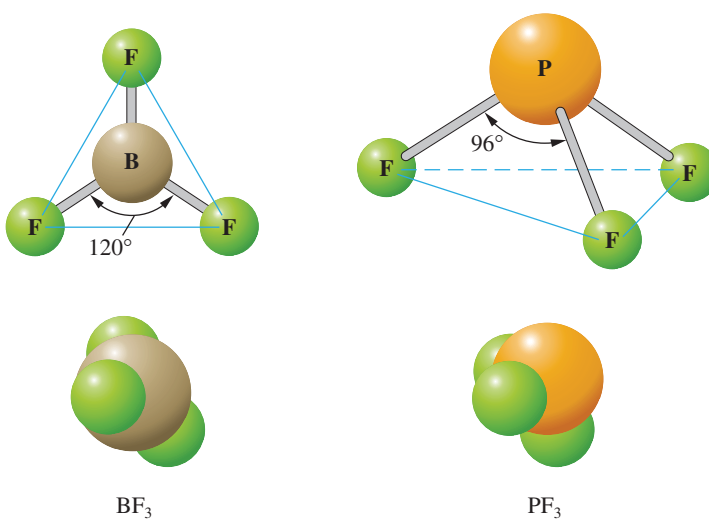
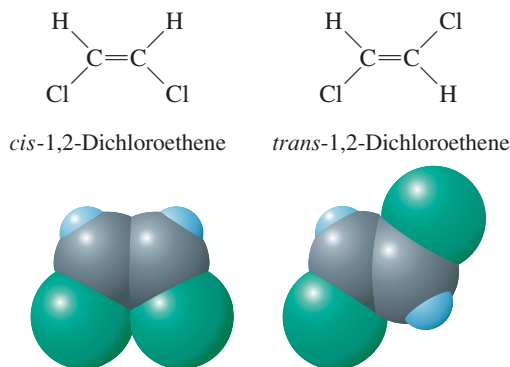


FIGURE 10.1 ▲

Molecular models of BF_3 and PF_3

Although both molecules have the general formula AX_3 , boron trifluoride is planar (flat), whereas phosphorus trifluoride is pyramidal (pyramid shaped).

Subtle differences in structure are also possible. Consider the following molecular structures, which differ only in the arrangement of the atoms about the $\text{C}=\text{C}$ bond; such molecules are referred to as *isomers*.



In the *cis* compound, both H atoms are on the same side of the $\text{C}=\text{C}$ bond; in the *trans* compound, they are on opposite sides. These structural formulas represent entirely different compounds, as their boiling points clearly demonstrate. *Cis*-1,2-dichloroethene boils at 60°C ; *trans*-1,2-dichloroethene boils at 48°C . The differences between such *cis* and *trans* compounds can be quite important. The central molecular event in the detection of light by the human eye involves the transformation of a *cis* compound to its corresponding *trans* compound after the absorption of a photon of light. How do you explain the existence of *cis* and *trans* compounds?

In this chapter we discuss how to explain the geometries of molecules in terms of their electronic structures. We also explore two theories of chemical bonding: valence bond theory and molecular orbital theory.

■ See page 410 for the Media Summary.

Molecular Geometry and Directional Bonding

Molecular geometry is the general shape of a molecule, as determined by the relative positions of the atomic nuclei. There is a simple model that allows you to predict molecular geometries, or shapes, from Lewis formulas. This valence-shell electron-pair model usually predicts the correct general shape of a molecule. It does not explain chemical bonding, however. For this you must look at a theory, such as valence bond theory, that is based on quantum mechanics. Valence bond theory provides further insight into why bonds form and, at the same time, reveals that bonds have definite directions in space, resulting in particular molecular geometries.

10.1

The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

The acronym VSEPR is pronounced “vesper.”

The **valence-shell electron-pair repulsion (VSEPR) model** predicts the shapes of molecules and ions by assuming that the valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing electron-pair repulsions. The possible arrangements assumed by different numbers of electron pairs about an atom are shown in Figure 10.2. (If you tie various numbers of similar balloons together, they assume these same arrangements; see Figure 10.3.)

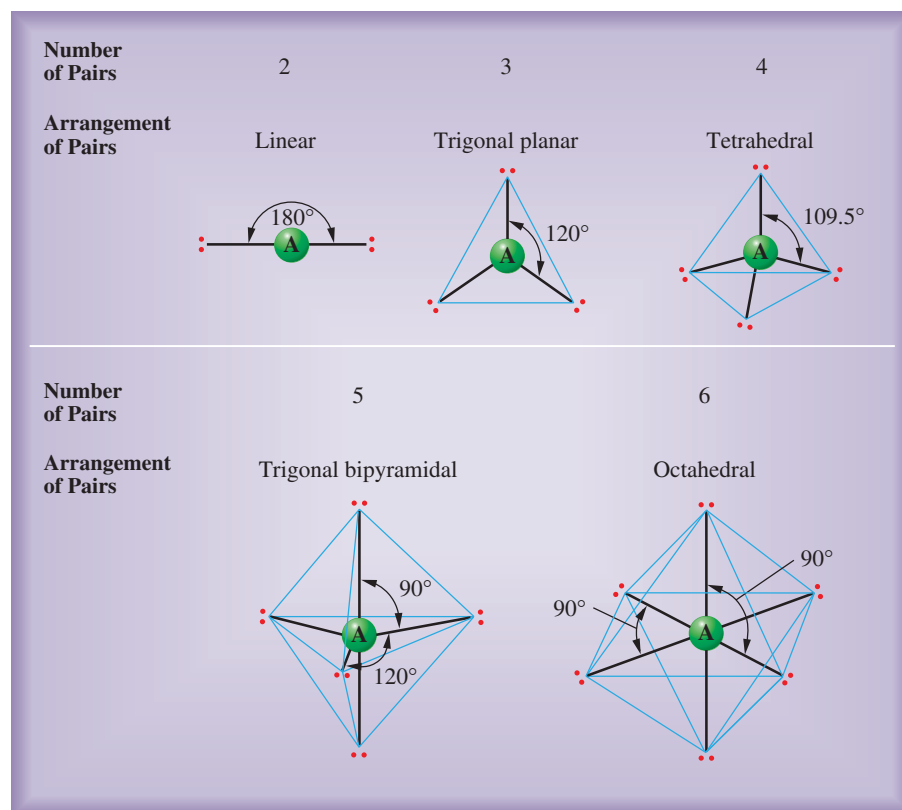
For example, if there are only two electron pairs in the valence shell of an atom, these pairs tend to be at opposite sides of the nucleus, so that repulsion is minimized. This gives a *linear* arrangement of electron pairs; that is, the electron pairs mainly occupy regions of space at an angle of 180° to one another (Figure 10.2).

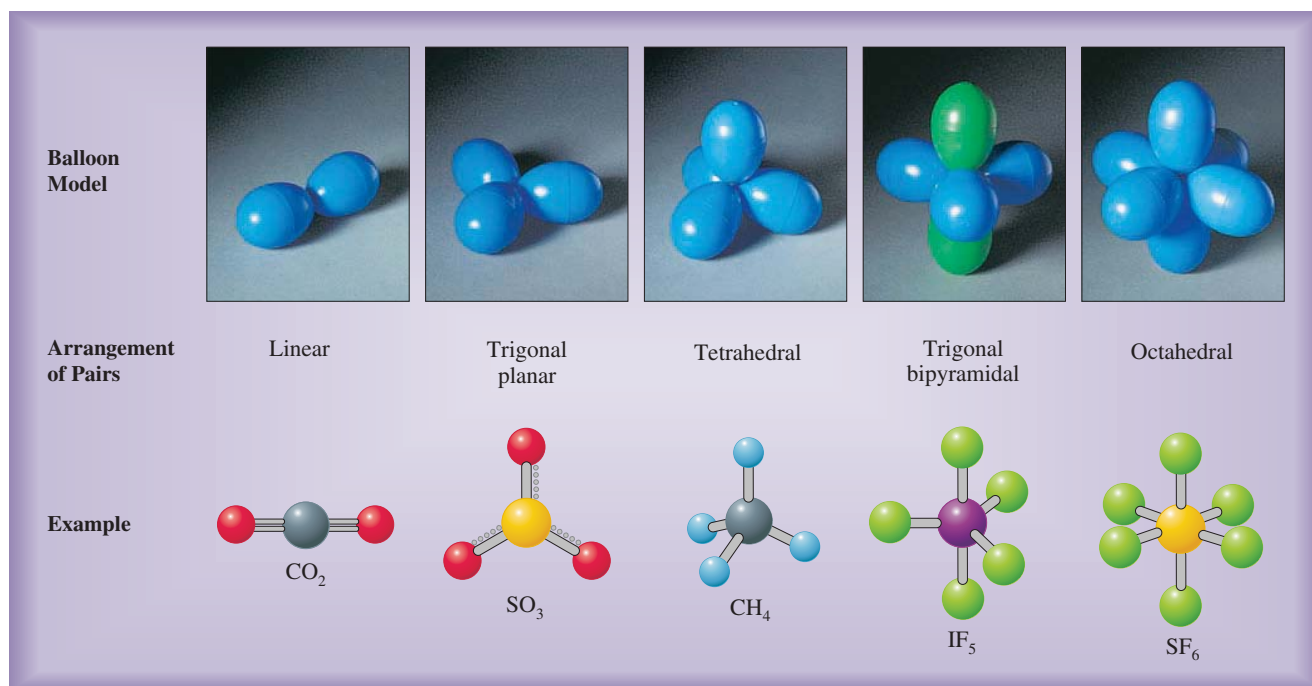
If three electron pairs are in the valence shell of an atom, they tend to be arranged in a plane directed toward the corners of a triangle of equal sides (equilateral triangle). This arrangement is *trigonal planar*, in which the regions of space occupied by electron pairs are directed at 120° angles to one another (Figure 10.2).

FIGURE 10.2

Arrangement of electron pairs about an atom

Black lines give the directions of electron pairs about atom A. The blue lines merely help depict the geometric arrangement of electron pairs.



**FIGURE 10.3** ▲**Balloon models of electron-pair arrangements**

When you tie similar balloons together, they assume the arrangements shown. These arrangements are the same as those assumed by valence electron pairs about an atom, as in the examples.

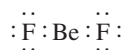
Four electron pairs in the valence shell of an atom tend to have a *tetrahedral* arrangement. That is, if you imagine the atom at the center of a regular tetrahedron, each region of space in which an electron pair mainly lies extends toward a corner, or vertex (Figure 10.2). (A regular tetrahedron is a geometrical shape with four faces, each an equilateral triangle. Thus, it has the form of a triangular pyramid.) The regions of space mainly occupied by electron pairs are directed at approximately 109.5° angles to one another.

When you determine the geometry of a molecule experimentally, you locate the positions of the atoms, not the electron pairs. To predict the relative positions of atoms around a given atom using the VSEPR model, you first note the arrangement of valence-shell electron pairs around that central atom. Some of these electron pairs are bonding pairs and some are lone pairs. *The direction in space of the bonding pairs gives you the molecular geometry.* To consider examples of the method, we will first look at molecules AX_n in which the central atom A is surrounded by two, three, or four valence-shell electron pairs. Later we will look at molecules in which A is surrounded by five or six valence-shell electron pairs.

Central Atom with Two, Three, or Four Valence-Shell Electron Pairs

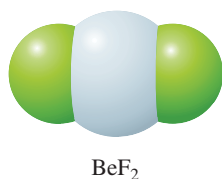
Examples of geometries in which two, three, or four valence-shell electron pairs surround a central atom are shown in Figure 10.4.

Two Electron Pairs (Linear Arrangement) To find the geometry of the molecule AX_n, you first determine the number of valence-shell electron pairs around atom A. You can get this information from the electron-dot formula. For example, following the rules given in Section 9.6, you can find the electron-dot formula for the BeF₂ molecule. <



There are two electron pairs in the valence shell for beryllium, and the VSEPR model predicts that they will have a linear arrangement (see Figure 10.2). Fluorine atoms are bonded in the same direction as the electron pairs. Hence, the geometry of the BeF₂ molecule is *linear*—that is, the atoms are arranged in a straight line (see Figure 10.4).

Beryllium fluoride, BeF₂, is normally a solid. The BeF₂ molecule exists in the vapor phase at high temperature.



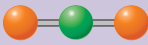
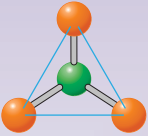
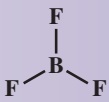
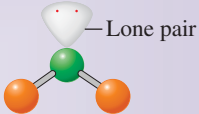
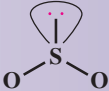
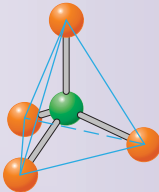
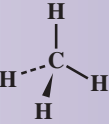
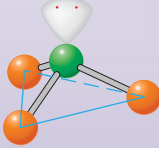
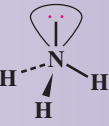
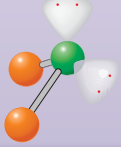
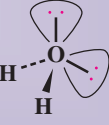
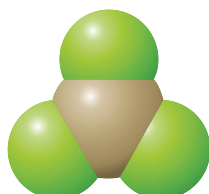
Electron Pairs			Arrangement of Pairs	Molecular Geometry	Example
Total	Bonding	Lone			
2	2	0	Linear	Linear AX_2	 BeF_2 $F-Be-F$
3	$\left\{ \begin{array}{l} 3 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 1 \end{array} \right.$	Trigonal planar	Trigonal planar AX_3	 BF_3 
				Bent (or angular) AX_2	 SO_2 
4	$\left\{ \begin{array}{l} 4 \\ 3 \\ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0 \\ 1 \\ 2 \end{array} \right.$	Tetrahedral	Tetrahedral AX_4	 CH_4 
				Trigonal pyramidal AX_3	 NH_3 
				Bent (or angular) AX_2	 H_2O 

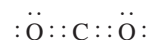
FIGURE 10.4 ▲

Molecular geometries

Central atom with two, three, or four valence-shell electron pairs. The notation in the column at the right provides a convenient way to represent the shape of a molecule drawn on a flat surface. A straight line represents a bond or electron pair in the plane of the page. A dashed line represents a bond or electron pair extending behind the page. A wedge represents a bond or electron pair extending above (in front of) the page.

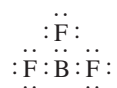
 BF_3

The VSEPR model can also be applied to molecules with multiple bonds. In this case, each multiple bond is treated as though it were a single electron pair. (All pairs of a multiple bond are required to be in approximately the same region.) To predict the geometry of carbon dioxide, for example, you first write the electron-dot formula.



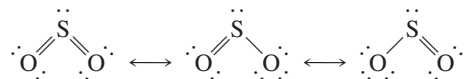
You have two double bonds, or two electron groups, about the carbon atom, and these are treated as though there were two pairs on carbon. Thus, according to the VSEPR model, the bonds are arranged linearly and the geometry of carbon dioxide is linear.

Three Electron Pairs (Trigonal Planar Arrangement) Let us now predict the geometry of the boron trifluoride molecule, BF_3 , introduced in the chapter opening. The electron-dot formula is



The three electron pairs on boron have a trigonal planar arrangement, and the molecular geometry, which is determined by the directions of the bonding pairs, is also *trigonal planar* (Figures 10.1 and 10.4).

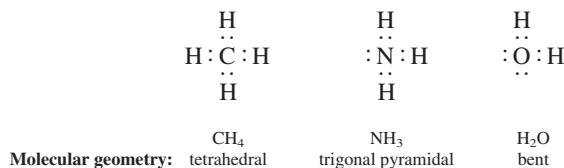
Sulfur dioxide, SO_2 , provides an example of a molecule with three electron groups about the S atom; one group is a lone pair. This molecule requires a resonance description, so it gives us a chance to see how the VSEPR model can be applied in such cases. The resonance description can be written



Whichever formula you consider, sulfur has three groups of electrons about it. These groups have a trigonal planar arrangement, so sulfur dioxide is a *bent*, or *angular*, molecule (Figure 10.4). In general, whenever you consider a resonance description, you can use any of the resonance formulas to predict the molecular geometry with the VSEPR model.

Note the difference between the *arrangement of electron pairs* and the *molecular geometry*, or the arrangement of nuclei. What you usually “see” by means of x-ray diffraction and similar methods are the nuclear positions—that is, the molecular geometry. Unseen, but nevertheless important, are the lone pairs, which occupy definite positions about an atom according to the VSEPR model.

Four Electron Pairs (Tetrahedral Arrangement) The common and most important case of four electron pairs about the central atom (the octet rule) leads to three different molecular geometries, depending on the number of bonds formed. Note the following examples.



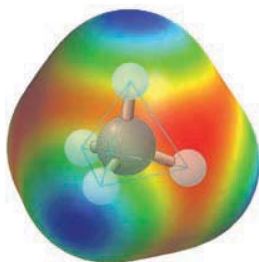
In each of these examples, the electron pairs are arranged tetrahedrally, and two or more atoms are bonded in these tetrahedral directions to give the different geometries (Figure 10.4).

When all electron pairs are bonding, as in methane, CH₄, the molecular geometry is *tetrahedral* (Figure 10.5). When three of the pairs are bonding and one pair is nonbonding, as in ammonia, NH₃, the molecular geometry is *trigonal pyramidal*. Note that the nitrogen atom is at the apex of the pyramid, and the three hydrogen atoms extend downward to form the triangular base of the pyramid.

Now you can answer the question raised in the chapter opening: Why is the BF₃ molecule trigonal planar and the PF₃ molecule trigonal pyramidal? The difference occurs because in BF₃ there are three pairs of electrons around boron, and in PF₃ there are four pairs of electrons around phosphorus. As in NH₃, there are three bonding pairs and one lone pair in PF₃, which give rise to the trigonal pyramidal geometry.

Steps in the Prediction of Geometry by the VSEPR Model Let us summarize the steps to follow in order to predict the geometry of an AX_n molecule or ion by the VSEPR method. (All X atoms of AX_n need not be identical.)

- Step 1:** Write the electron-dot formula from the molecular formula.
- Step 2:** Determine from the electron-dot formula the number of electron pairs around the central atom, including bonding and nonbonding pairs. (Count a multiple bond as one pair. If resonance occurs, use one resonance formula to determine this number.)
- Step 3:** Determine the arrangement of these electron pairs about the central atom (see Figure 10.2).
- Step 4:** Obtain the molecular geometry from the directions of the bonding pairs for this arrangement (see Figure 10.4).

CH₄NH₃H₂O**FIGURE 10.5** ▲**The methane molecule**

A ball-and-stick model shows the tetrahedral arrangement of bonds. This model is within an electrostatic-potential map, showing the electron density about the molecule by gradations of color. Thus, the red color means high density, which occurs in the C—H bonding regions.

Concept Check 10.1

An atom in a molecule is surrounded by four pairs of electrons: one lone pair and three bonding pairs. Describe how the four electron pairs are arranged about the atom. How are any three of these pairs arranged in space? What is the geometry about this central atom, taking into account just the bonded atoms?

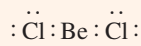
Example 10.1

Predicting Molecular Geometries (Two, Three, or Four Electron Pairs)

Predict the geometry of the following molecules or ions, using the VSEPR method: a. BeCl_2 ; b. NO_2^- ; c. SiCl_4 .

Problem Strategy After drawing the Lewis formula for a molecule, determine the number of electron groups about the central atom. This number determines the arrangement of the electron groups (Figure 10.2). The geometry is determined by the arrangement of bonds to the central atom (Figure 10.4).

Solution a. Following the steps outlined in Sections 9.6 and 9.8 for writing Lewis formulas, you distribute the valence electrons to the skeleton structure of BeCl_2 as follows:



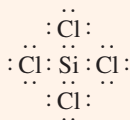
The two pairs on Be have a linear arrangement, indicating a **linear** molecular geometry for BeCl_2 . (See Figure 10.4; 2 electron pairs, 0 lone pairs.)

b. The nitrite ion, NO_2^- , has the following resonance description:



The N atom has three electron groups (one single bond, one double bond, and one lone pair) about it. Therefore the molecular geometry of the NO_2^- ion is **bent**. (See Figure 10.4; 2 bonding pairs, 1 lone pair.)

c. The electron-dot formula of SiCl_4 is



The molecular geometry is **tetrahedral**. (See Figure 10.4; 4 bonding pairs, 0 lone pairs.)

Answer Check Be careful not to confuse the name for the arrangement of valence electron pairs with the name for the molecular geometry. The geometry refers only to the arrangement of bonds. In this example, the nitrite ion, NO_2^- , has a trigonal planar arrangement of valence electron pairs and a bent geometry (arrangement of the bonds).

Exercise 10.1 Use the VSEPR method to predict the geometry of the following ion and molecules: a. ClO_3^- ; b. OF_2 ; c. SiF_4 .



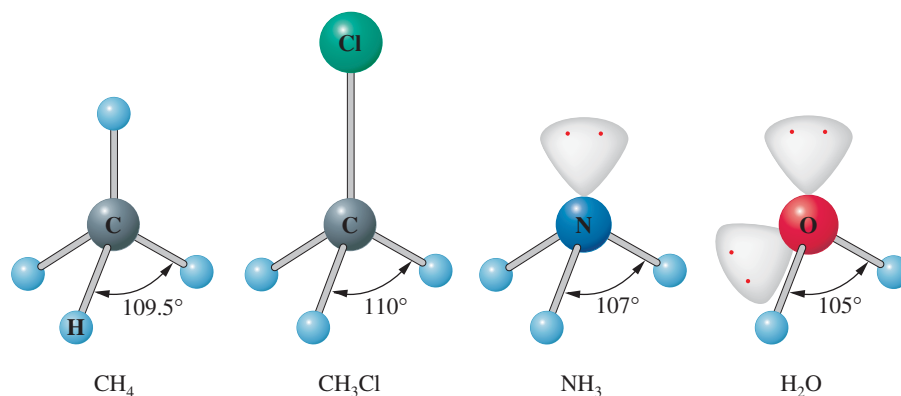
■ See Problems 10.33, 10.34, 10.35, and 10.36.

Bond Angles and the Effect of Lone Pairs

The VSEPR model allows you to predict the approximate angles between bonds in molecules. For example, it tells you that CH_4 should have a tetrahedral geometry and that the $\text{H}-\text{C}-\text{H}$ bond angles should be 109.5° (see Figure 10.2). Because all of the valence-shell electron pairs about the carbon atom are bonding and all of the bonds

FIGURE 10.6 ▶**H—A—H bond angles in some molecules**

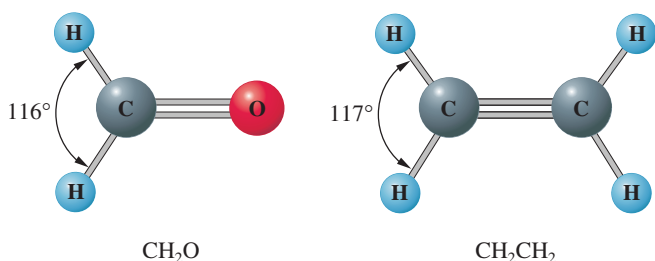
Experimentally determined bond angles are shown for CH_4 , CH_3Cl , NH_3 , and H_2O , represented here by models.



are alike, you expect the CH_4 molecule to have an exact tetrahedral geometry. However, if one or more of the electron pairs is nonbonding or if there are dissimilar bonds, all four valence-shell electron pairs will not be alike. Then you expect the bond angles to deviate from the 109.5° predicted by an exact tetrahedral geometry. This is indeed what you see. Experimentally determined H—A—H bond angles (A is the central atom) in CH_4 , CH_3Cl , NH_3 , and H_2O are shown in Figure 10.6.

The increase or decrease of bond angles from the ideal values is often predictable. A lone pair tends to require more space than a corresponding bonding pair. You can explain this as follows: A lone pair of electrons is attracted to only one atomic core, whereas a bonding pair is attracted to two. As a result, the lone pair is spatially more diffuse, while the bonding pair is drawn more tightly to the nuclei. Consider the trigonal pyramidal molecule NH_3 . The lone pair on the nitrogen atom requires more space than the bonding pairs. Therefore, the N—H bonds are effectively pushed away from the lone pair, and the H—N—H bond angles become smaller than the tetrahedral value of 109.5° . How much smaller, the VSEPR model cannot tell you. The experimental value of an H—N—H bond angle is a few degrees smaller (107°). But the trigonal pyramidal molecule PF_3 , mentioned in the chapter opening, has an F—P—F bond angle of 96° , which is significantly smaller than the exact tetrahedral value.

Multiple bonds require more space than single bonds because of the greater number of electrons. You therefore expect the C=O bond in the formaldehyde molecule, CH_2O , to require more space than the C—H bonds. You predict that the H—C—H bond angle will be smaller than the 120° seen in an exact trigonal planar geometry, such as the F—B—F angle in BF_3 . Similarly, you expect the H—C—H bond angles in the ethylene molecule, CH_2CH_2 , to be smaller than the trigonal planar value. Experimental values are shown in Figure 10.7.

**FIGURE 10.7** ▲**H—C—H bond angles in molecules with carbon double bond**

Bond angles are shown for formaldehyde, CH_2O , and ethylene, CH_2CH_2 , represented here by models.

Central Atom with Five or Six Valence-Shell Electron Pairs

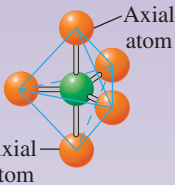
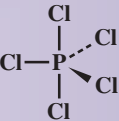
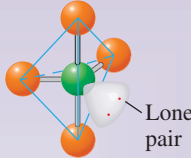

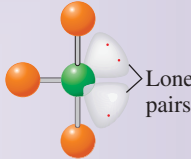
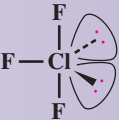
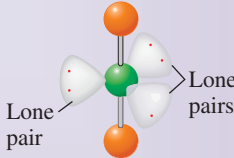
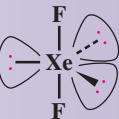
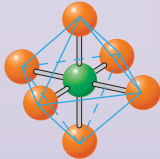

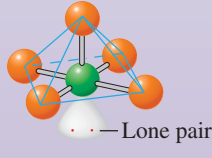

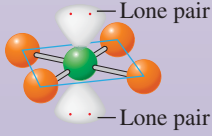
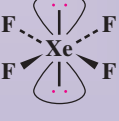
Five electron pairs tend to have a *trigonal bipyramidal arrangement*. The electron pairs tend to be directed to the corners of a trigonal bipyramid, a figure formed by placing the face of one tetrahedron onto the face of another tetrahedron (see Figure 10.2).

Six electron pairs tend to have an *octahedral arrangement*. The electron pairs tend to be directed to the corners of a regular octahedron, a figure that has eight triangular faces and six vertexes, or corners (see Figure 10.2).

FIGURE 10.8 ▼**Molecular geometries**

Central atom with five or six valence-shell electron pairs.

Five Electron Pairs (Trigonal Bipyramidal Arrangement) Large atoms like phosphorus can accommodate more than eight valence electrons. The phosphorus atom in phosphorus pentachloride, PCl_5 , has five electron pairs in its valence shell. With five electron pairs around phosphorus, all bonding, PCl_5 should have a *trigonal bipyramidal geometry* (Figure 10.8). Note, however, that the vertexes of the trigonal bipyramid are not all equivalent (that is, the angles between the electron pairs are not

Electron Pairs			Arrangement of Pairs	Molecular Geometry	Example
Total	Bonding	Lone			
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal AX_5 	PCl_5 
	4	1		Seesaw (or distorted tetrahedron) AX_4 	SF_4 
	3	2		T-shaped AX_3 	ClF_3 
	2	3		Linear AX_2 	XeF_2 
6	6	0	Octahedral	Octahedral AX_6 	SF_6 
	5	1		Square pyramidal AX_5 	IF_5 
	4	2		Square planar AX_4 	XeF_4 

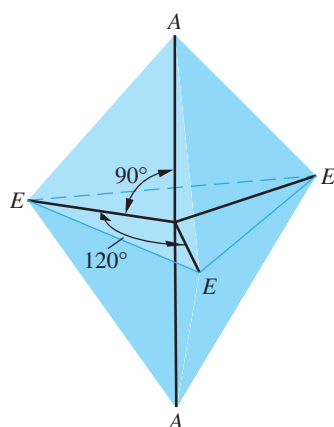


FIGURE 10.9 ▲

Trigonal bipyramidal arrangement of electron pairs

Electron pairs are directed along the black lines to the vertices of a trigonal bipyramid. Equatorial directions are labeled *E*, and axial directions are labeled *A*.

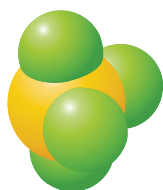


FIGURE 10.10 ▲

The sulfur tetrafluoride molecule
Molecular model.

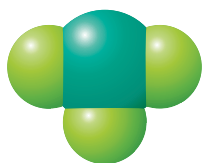


FIGURE 10.11 ▲

The chlorine trifluoride molecule
Molecular model.



FIGURE 10.12 ▲

The xenon difluoride molecule
Molecular model.

all the same). Thus, the directions to which the electron pairs point are not equivalent. Two of the directions, called *axial directions*, form an axis through the central atom (see Figure 10.9). They are 180° apart. The other three directions are called *equatorial directions*. These point toward the corners of the equilateral triangle that lies on a plane through the central atom, perpendicular (at 90°) to the axial directions. The equatorial directions are 120° from each other.

Molecular geometries other than trigonal bipyramidal are possible when one or more of the five electron pairs are lone pairs. Consider the sulfur tetrafluoride molecule, SF_4 . The Lewis electron-dot formula is



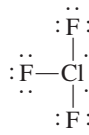
The five electron pairs about sulfur should have a trigonal bipyramidal arrangement. Because the axial and equatorial positions of the electron pairs are not equivalent, you must decide in which of these positions the lone pair appears.

The lone pair acts as though it is somewhat “larger” than a bonding pair. Therefore, the total repulsion between all pairs should be lower if the lone pair is in a position that puts it directly adjacent to the smallest number of other pairs.

An electron pair in an equatorial position is directly adjacent to only *two* other pairs—the two axial pairs at 90° . The other two equatorial pairs are farther away at 120° . An electron pair in an axial position is directly adjacent to *three* other pairs—the three equatorial pairs at 90° . The other axial pair is much farther away at 180° .

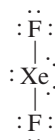
Thus you expect lone pairs to occupy equatorial positions in the trigonal bipyramidal arrangement. For sulfur tetrafluoride, this gives a *seesaw* (or *distorted tetrahedral*) geometry (Figure 10.10).

Chlorine trifluoride, ClF_3 , has the electron-dot formula



The lone pairs on chlorine occupy two of the equatorial positions of the trigonal bipyramidal arrangement, giving a *T-shaped geometry* (Figure 10.11). The four atoms of the molecule all lie in one plane, with the chlorine nucleus at the intersection of the “T.”

Xenon difluoride, XeF_2 , has the electron-dot formula



The three lone pairs on xenon occupy the equatorial positions of the trigonal bipyramidal arrangement, giving a *linear geometry* (Figure 10.12).

Six Electron Pairs (Octahedral Arrangement) There are six electron pairs (all bonding pairs) about sulfur in sulfur hexafluoride, SF_6 . Thus, it has an *octahedral geometry*, with sulfur at the center of the octahedron and fluorine atoms at the vertices (Figure 10.8).

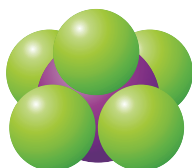


FIGURE 10.13 ▲
The iodine pentafluoride molecule
Molecular model.

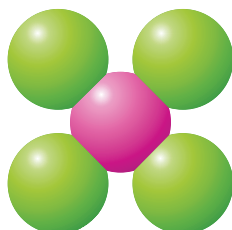
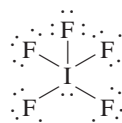


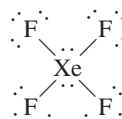
FIGURE 10.14 ▲
The xenon tetrafluoride molecule
Molecular model.

Iodine pentafluoride, IF_5 , has the electron-dot formula



The lone pair on iodine occupies one of the six equivalent positions in the octahedral arrangement, giving a *square pyramidal geometry* (Figure 10.13). The name derives from the shape formed by drawing lines between atoms.

Xenon tetrafluoride, XeF_4 , has the electron-dot formula



The two lone pairs on xenon occupy opposing positions in the octahedral arrangement to minimize their repulsion. The result is a *square planar geometry* (Figure 10.14).

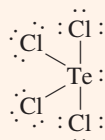
Example 10.2

Predicting Molecular Geometries (Five or Six Electron Pairs)

What do you expect for the geometry of tellurium tetrachloride, TeCl_4 ?

Problem Strategy After drawing the Lewis formula for a molecule, determine the number of electron groups about the central atom. This number determines the arrangement of the electron groups (Figure 10.2). The geometry is determined by the arrangement of bonds to the central atom (Figure 10.8).

Solution First you distribute the valence electrons to the Cl atoms to satisfy the octet rule. Then you allocate the remaining valence electrons to the central atom, Te (following the steps outlined in Section 9.6). The electron-dot formula is



There are five electron pairs in the valence shell of Te in TeCl_4 . Of these, four are bonding pairs and one is a lone pair. The arrangement of electron pairs is trigonal bipyramidal. You expect the lone pair to occupy an equatorial position, so TeCl_4 has a **seesaw** molecular geometry. (See Figure 10.8; 4 bonding pairs, 1 lone pair.)

Answer Check Again, be careful to distinguish the name for the arrangement of valence electron pairs from the name for the molecular geometry.

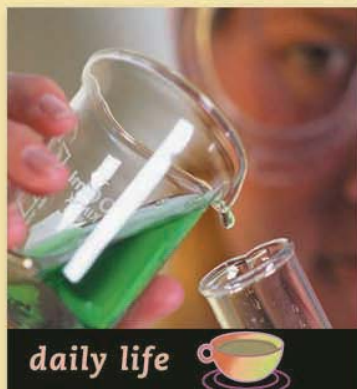
Exercise 10.2 According to the VSEPR model, what molecular geometry would you predict for iodine trichloride, ICl_3 ?

■ See Problems 10.39, 10.40, 10.41, and 10.42.

10.2 Dipole Moment and Molecular Geometry

The VSEPR model provides a simple procedure for predicting the geometry of a molecule. However, predictions must be verified by experiment. Information about the geometry of a molecule can sometimes be obtained from an experimental quantity

A Chemist Looks at . . .



Left-Handed and Right-Handed Molecules

This morning, half asleep, I (D. E.) tried to put my left glove on my right hand. Silly mistake, of course. A person's two hands are similar but not identical. If I look at my hands, say, with both palms toward me, the thumbs point in opposite directions. But, if I now hold the palm of my right hand toward a mirror and compare that image with my actual left hand, I see that the thumbs point in the same direction. A person's left hand looks like the mirror image of his or her right hand, and vice versa. You can mentally superimpose one hand onto the mirror image of the other hand. Yet the two hands are themselves nonsuperimposable. Some molecules have this "handedness" property too, and this possibility gives rise to a subtle kind of isomerism.

The presence of handedness in molecules depends on the fact that the atoms in the molecules occupy specific places in three-dimensional space. In most organic molecules, this property depends on the tetrahedral bonding of the carbon atom. Consider a carbon atom bonded to four different kinds of groups, say, —H , —OH , —CH_3 , and —COOH . (The resulting molecule is called lactic acid.) Two isomers are possible in which one isomer

is the mirror image of the other, but the two isomers are themselves not identical (they are nonsuperimposable) (see Figure 10.15). However, all four groups bonded to this carbon atom must be different to have this isomerism. If you replace the —OH group of lactic acid by, say, an H atom, the molecule and its mirror image become identical. There are no isomers; there is just one kind of molecule.

The two lactic acid isomers shown in Figure 10.15 are labeled D-lactic acid and L-lactic acid (D is for *dextro*, meaning right; L is for *levo*, meaning left). They might be expected to have quite similar properties, and they do. They have identical melting points, boiling points, and solubilities, for instance. And if we try to prepare lactic acid in the laboratory, we almost always get an equal molar mixture of the D and L isomers. But the biological origins of the molecules are different. Only D-lactic acid occurs in sour milk, whereas only L-lactic acid forms in muscle tissue after exercising. (If you overexercise, lactic acid accumulates in muscle tissue, causing soreness.)

Biological molecules frequently have the handedness character. The chemical substance responsible for the flavor of spearmint is L-carvone. The substance responsible for the flavor of caraway seeds, which you see in some rye bread, is D-carvone (see Figure 10.16). Here are two substances whose molecules differ only in being mirror images of one another. Yet, they have strikingly different flavors: one is minty; the other is pungent aromatic.

called the dipole moment, which is related to the polarity of the bonds in a molecule. The **dipole moment** is a quantitative measure of the degree of charge separation in a molecule. The polarity of a bond, such as that in HCl, is characterized by a separation of electric charge. We can represent this in HCl by indicating partial charges, δ^+ and δ^- , on the atoms.



Any molecule that has a net separation of charge, as in HCl, has a dipole moment. A molecule in which the distribution of electric charge is equivalent to charges $+\delta$ and $-\delta$ separated by a distance d has a dipole moment equal to δd . Dipole moments are

FIGURE 10.15 ►

Isomers of lactic acid

Note that the two molecules labeled D-lactic acid and L-lactic acid are mirror images and cannot be superimposed on one another. See Figure 10.4 for an explanation of the notation used to represent the tetrahedral geometry.

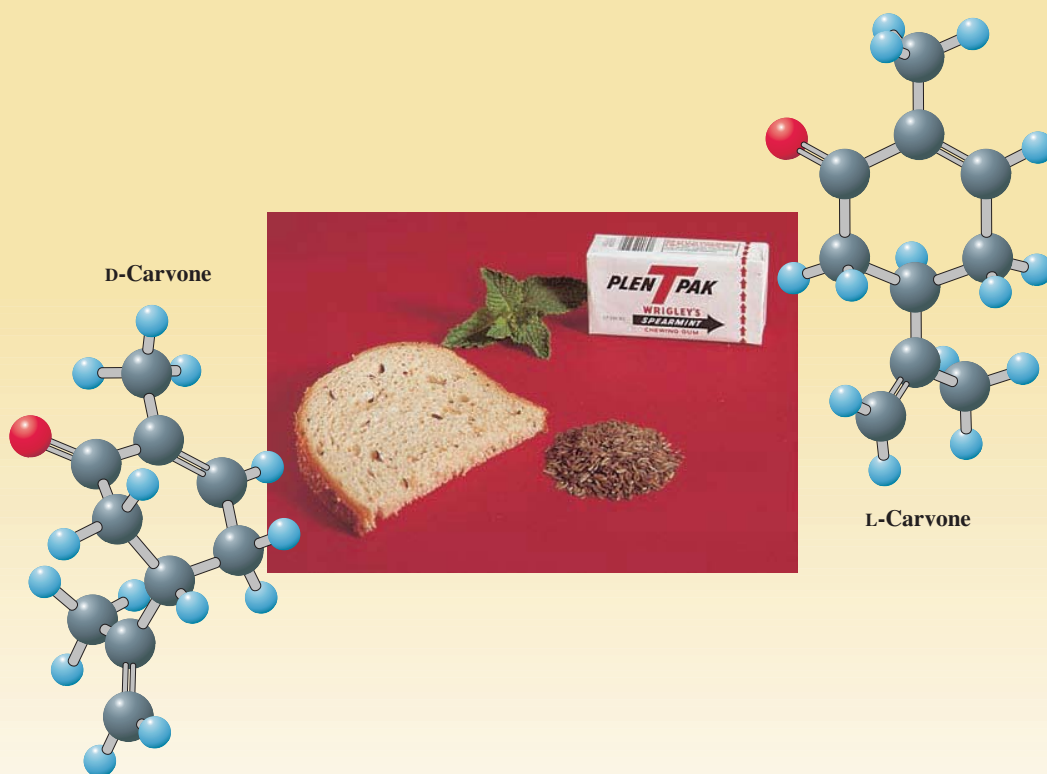
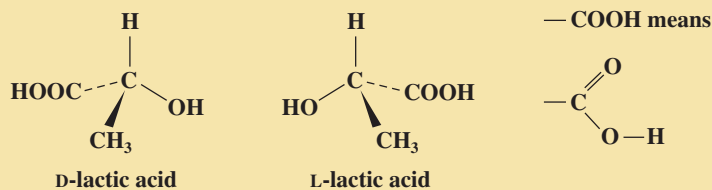


FIGURE 10.16 ▲

Spearmint and caraway

Spearmint leaves contain L-carvone; caraway seeds contain D-carvone.

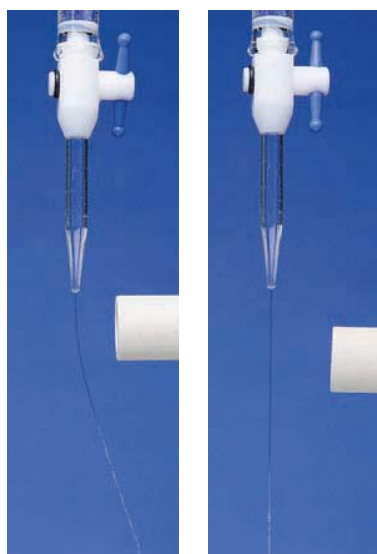
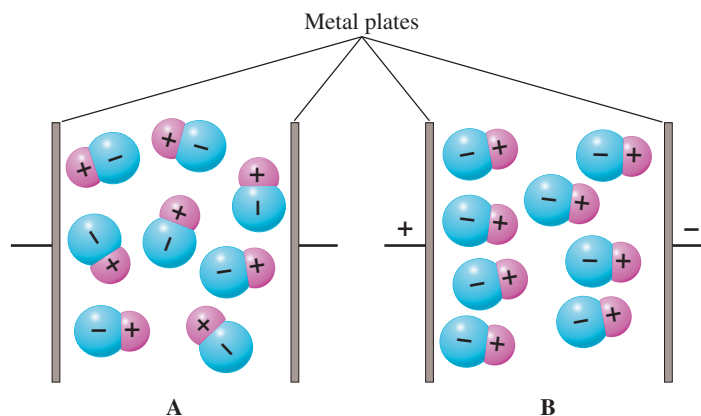
■ See Problems 10.83 and 10.84.

usually measured in units of *debyes* (D). In SI units, dipole moments are measured in coulomb-meters (C·m), and $1 \text{ D} = 3.34 \times 10^{-30} \text{ C}\cdot\text{m}$.

Measurements of dipole moments are based on the fact that polar molecules (molecules having a dipole moment) can be oriented by an electric field. Figure 10.17 shows an electric field generated by charged plates. Note that the polar molecules tend to align themselves so that the negative ends of the molecules point toward the positive plate, and the positive ends point toward the negative plate. This orientation of the molecules affects the *capacitance* of the charged plates (the capacity of the plates to hold a charge). Consequently, measurements of the capacitance of plates separated by different substances can be used to obtain the dipole moments of those substances. Figure 10.18 shows a simple demonstration that distinguishes between a polar liquid

FIGURE 10.17 ▶**Alignment of polar molecules by an electric field**

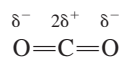
(A) A polar substance is placed between metal plates. (B) When the plates are connected to an electric voltage (whose direction is shown by the + and – signs), the polar molecules align so that their negative ends point toward the positive plate.

**FIGURE 10.18** ▲**Attraction of a polar liquid to an electrified rod**

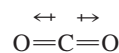
Left: Water is a polar liquid; it is attracted to the electrically charged rod. The capacitance of the polar liquid (due to the alignment of polar molecules) stabilizes a charge separation induced in the column of liquid by the charged rod. Charges of signs opposite to those on the rod form on the liquid surface near the rod, resulting in a net attraction. *Right:* Carbon tetrachloride, CCl_4 , is a nonpolar liquid; it is not attracted to the glass rod.

(one whose molecules have a dipole moment) and a nonpolar liquid. The polar liquid, but not the nonpolar one, is attracted to a charged rod.

You can sometimes relate the presence or absence of a dipole moment in a molecule to its molecular geometry. For example, consider the carbon dioxide molecule. Each carbon–oxygen bond has a polarity in which the more electronegative oxygen atom has a partial negative charge.



We will denote the dipole-moment contribution from each bond (the bond dipole) by an arrow with a positive sign at one end (\leftrightarrow). The dipole-moment arrow points from the positive partial charge toward the negative partial charge. Thus, you can rewrite the formula for carbon dioxide as



Each bond dipole, like a force, is a *vector* quantity; that is, it has both magnitude and direction. Like forces, two bond dipoles of equal magnitude but opposite direction cancel each other. (Think of two groups of people in a tug of war. As long as each group pulls on the rope with the same force but in the opposite direction, there is no movement—the net force is zero.) Because the two carbon–oxygen bonds in CO_2 are equal but point in opposite directions, they give a net dipole moment of zero for the molecule.

For comparison, consider the water molecule. The bond dipoles point from the hydrogen atoms toward the more electronegative oxygen.



Here, the two bond dipoles do not point directly toward or away from each other. As a result, they add together to give a nonzero dipole moment for the molecule.



The dipole moment of H_2O has been observed to be 1.94 D.

The fact that the water molecule has a dipole moment is excellent experimental evidence for a bent geometry. If the H_2O molecule were linear, the dipole moment would be zero.

The analysis we have just made for two different geometries of AX_2 molecules can be extended to other AX_n molecules (in which all X atoms are identical). Table 10.1 summarizes the relationship between molecular geometry and dipole moment. Those geometries in which A–X bonds are directed symmetrically about the central atom

TABLE 10.1 Relationship Between Molecular Geometry and Dipole Moment		
Formula	Molecular Geometry	Dipole Moment*
AX	Linear	Can be nonzero
AX ₂	Linear	Zero
	Bent	Can be nonzero
AX ₃	Trigonal planar	Zero
	Trigonal pyramidal	Can be nonzero
	T-shaped	Can be nonzero
AX ₄	Tetrahedral	Zero
	Square planar	Zero
	Seesaw	Can be nonzero
AX ₅	Trigonal bipyramidal	Zero
	Square pyramidal	Can be nonzero
AX ₆	Octahedral	Zero

*All X atoms are assumed to be identical.

(for example, linear, trigonal planar, and tetrahedral) give molecules of zero dipole moment; that is, the molecules are *nonpolar*. Those geometries in which the X atoms tend to be on one side of the molecule (for example, bent and trigonal pyramidal) can have nonzero dipole moments; that is, they can give *polar* molecules.

Example 10.3

Relating Dipole Moment and Molecular Geometry

Each of the following molecules has a nonzero dipole moment. Select the molecular geometry that is consistent with this information. Explain your reasoning.

- a. SO₂ linear, bent
b. PH₃ trigonal planar, trigonal pyramidal

Problem Strategy Because the dipole moment is a *vector* quantity, it can happen that nonzero bond dipoles cancel one another to give a molecule with zero dipole moment. Look for bonds that are symmetrically arranged to oppose one another (think of a tug of war between bonds). Table 10.1 summarizes the relationship between geometry and dipole moment.

Solution a. In the linear geometry, the S—O bond contributions to the dipole moment would cancel, giving a zero dipole moment. That would not happen in the **bent** geometry; hence, this must be the geometry for the SO₂ molecule. b. In the trigonal planar geometry, the bond contributions to the dipole moment would cancel,

giving a zero dipole moment. That would not occur in the **trigonal pyramidal** geometry; hence, this is a possible molecular geometry for PH₃.

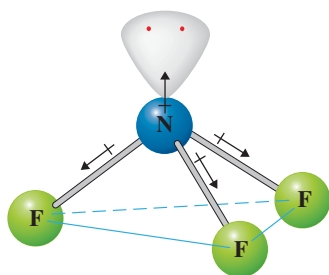
Answer Check Make sure that you have the correct geometry for the molecule, and note how the bonds either oppose one another, to give zero dipole moment, or else do not oppose and so give a dipole moment.

Exercise 10.3 Bromine trifluoride, BrF₃, has a nonzero dipole moment. Indicate which of the following geometries are consistent with this information: a. trigonal planar; b. trigonal pyramidal; c. T-shaped.

■ See Problems 10.43 and 10.44.

Exercise 10.4 Which of the following would be expected to have a dipole moment of zero on the basis of symmetry? Explain. a. SOCl₂; b. SiF₄; c. OF₂.

■ See Problems 10.45 and 10.46.

**FIGURE 10.19** ▲**Explanation of the small dipole moment of NF_3**

The lone-pair and bond contributions to the dipole moment of NF_3 tend to offset one another.

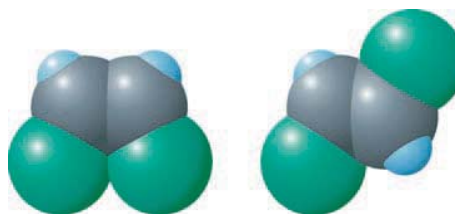
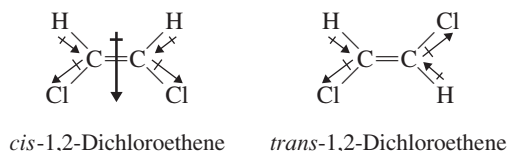
Can you explain why NH_3 has such a large dipole moment compared with NF_3 ?

In Example 10.3, the fact that certain molecular geometries necessarily imply a zero dipole moment allowed us to eliminate these geometries when considering a molecule with a nonzero dipole moment. The reverse argument does not follow, however. For example, suppose a molecule of the type AX_3 is found to have no measurable dipole moment. It may be that the geometry is trigonal planar. Another possibility, however, is that the geometry is trigonal pyramidal or T-shaped, but the lone pairs on the central atom offset the polarity of the bonds.

You can see this effect of lone pairs on the dipole moment of nitrogen trifluoride, NF_3 . Judging by the electronegativity difference, you would expect each $\text{N}-\text{F}$ bond to be quite polar. Yet the dipole moment of nitrogen trifluoride is only 0.2 D. (By contrast, ammonia has a dipole moment of 1.47 D.) The explanation for the small dipole moment in NF_3 appears in Figure 10.19. The lone pair on nitrogen has a dipole-moment contribution that is directed outward from the nucleus, because the electrons are offset from the nuclear center. This dipole-moment contribution thus opposes the $\text{N}-\text{F}$ bond moments. <

Effect of Polarity on Molecular Properties

Whether a molecule has a dipole moment (that is, whether it is polar or nonpolar) can affect its properties. We will explore this issue in detail in the next chapter (Section 11.5). Briefly, though, we can see why *cis*- and *trans*-1,2-dichloroethene, mentioned in the chapter opening, have different boiling points. The $\text{C}-\text{Cl}$ bonds are quite polar, because of the relatively large electronegativity difference between C and Cl atoms (0.9); the $\text{H}-\text{C}$ bonds have moderate polarity (electronegativity difference of 0.4). The bond dipoles (light arrows) add together in *cis*-1,2-dichloroethene to give a polar molecule (the total dipole moment is indicated by the heavy arrow). (Note that the electronegative Cl atoms are on the same side in the *cis* molecule.) In the *trans* molecule, the bond dipoles subtract to give a nonpolar molecule.



In a liquid, polar molecules tend to orient so that positive ends of molecules are attracted to negative ends. This results in an attractive force between molecules (an *intermolecular* force), which increases the energy required for the liquid to boil, and therefore increases the boiling point. Recall that the *trans* compound boils at 48°C , whereas the *cis* compound boils at a higher temperature, 60°C .

Concept Check 10.2

Two molecules, each with the general formula AX_3 , have different dipole moments. Molecule Y has a dipole moment of zero, whereas molecule Z has a nonzero dipole moment. From this information, what can you say about the geometries of Y and Z?

10.3 Valence Bond Theory

The VSEPR model is usually a satisfactory method for predicting molecular geometries. To understand bonding and electronic structure, however, you must look to quantum mechanics. We will consider two theories stemming from quantum mechanics: valence bond theory and molecular orbital theory. Both use the methods of quantum mechanics but make different simplifying assumptions. In this section, we will look in a qualitative way at the basic ideas involved in **valence bond theory**, *an approximate theory to explain the electron pair or covalent bond by quantum mechanics*.

Basic Theory

According to valence bond theory, a bond forms between two atoms when the following conditions are met:

1. An orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. The two orbitals are said to *overlap*.
2. The total number of electrons in both orbitals is no more than two.

As the orbital of one atom overlaps the orbital of another, the electrons in the orbitals begin to move about both atoms. Because the electrons are attracted to both nuclei at once, they pull the atoms together. Strength of bonding depends on the amount of overlap; the greater the overlap, the greater the bond strength. The two orbitals cannot contain more than two electrons because a given region of space can hold only two electrons with opposite spin.

For example, consider the formation of the H_2 molecule from atoms. Each atom has the electron configuration $1s^1$. As the H atoms approach each other, their $1s$ orbitals begin to overlap and a covalent bond forms (Figure 10.20). Valence bond theory also explains why two He atoms (each with electron configuration $1s^2$) do not bond. Suppose two He atoms approach one another and their $1s$ orbitals begin to overlap. Each orbital is doubly occupied, so the sharing of electrons between atoms would place the four valence electrons from the two atoms in the same region. This, of course, could not happen. As the orbitals begin to overlap, each electron pair strongly repels the other. The atoms come together, then fly apart.

Because the strength of bonding depends on orbital overlap, orbitals other than s orbitals bond only in given directions. *Orbitals bond in the directions in which they protrude or point, to obtain maximum overlap*. Consider the bonding between a hydrogen atom and a chlorine atom to give the HCl molecule. A chlorine atom has the electron configuration $[\text{Ne}]3s^23p^5$. Of the orbitals in the valence shell of the chlorine atom, three are doubly occupied by electrons and one (a $3p$ orbital) is singly occupied. The bonding of the hydrogen atom has to occur with the singly occupied $3p$ orbital of chlorine. For the strongest bonding to occur, the maximum overlap of orbitals is required. The $1s$ orbital of hydrogen must overlap along the axis of the singly occupied $3p$ orbital of chlorine (see Figure 10.21).

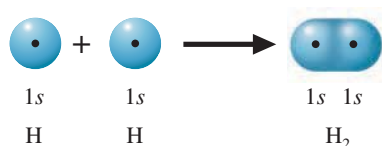


FIGURE 10.20 ▲

Formation of H_2

The $\text{H}-\text{H}$ bond forms when the $1s$ orbitals, one from each atom, overlap.

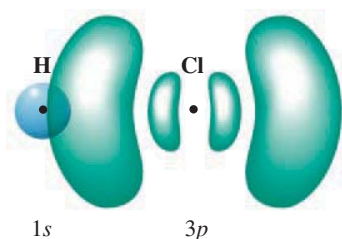


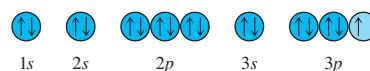
FIGURE 10.21 ▲

Bonding in HCl

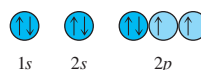
The bond forms by the overlap of a hydrogen $1s$ orbital (blue) along the axis of a chlorine $3p$ orbital (green).

Hybrid Orbitals

From what has been said, you might expect the number of bonds formed by a given atom to equal the number of unpaired electrons in its valence shell. Chlorine, whose orbital diagram is

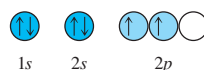


has one unpaired electron and forms one bond. Oxygen, whose orbital diagram is



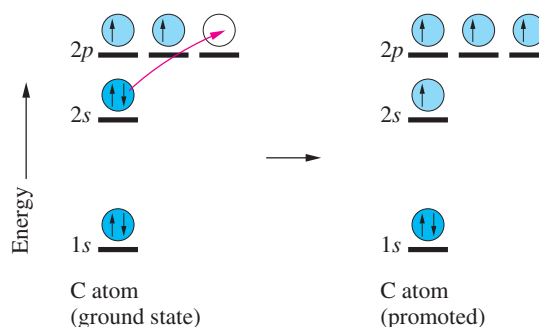
has two unpaired electrons and forms two bonds, as in H_2O .

However, consider the carbon atom, whose orbital diagram is



You might expect this atom to bond to two hydrogen atoms to form the CH_2 molecule. Although this molecule is known to be present momentarily during some reactions, it is very reactive and cannot be isolated. But methane, CH_4 , in which the carbon atom bonds to four hydrogen atoms, is well known. In fact, a carbon atom usually forms four bonds.

You might explain this as follows: Four unpaired electrons are formed when an electron from the $2s$ orbital of the carbon atom is *promoted* (excited) to the vacant $2p$ orbital.



It would require energy to promote the carbon atom this way, but more than enough energy would be obtained from the formation of two additional covalent bonds. One bond would form from the overlap of the carbon $2s$ orbital with a hydrogen $1s$ orbital. Each of the other three bonds would form from a carbon $2p$ orbital and a hydrogen $1s$ orbital.

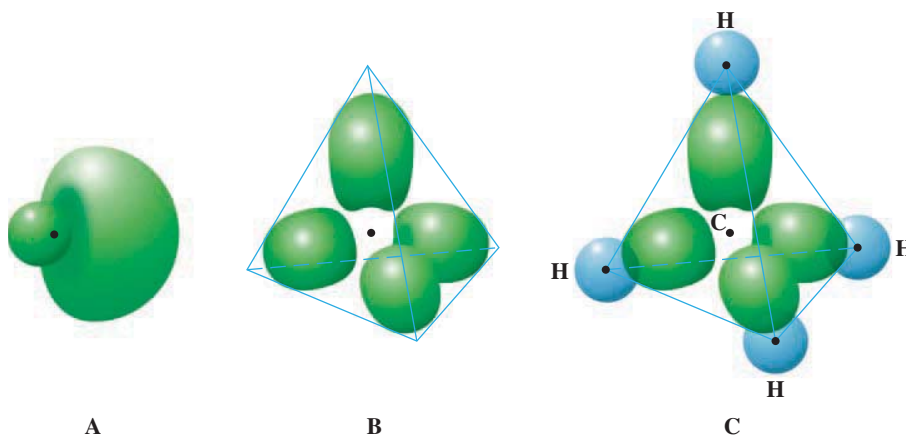
Experiment shows, however, that the four C—H bonds in methane are identical. < This implies that the carbon orbitals involved in bonding are also equivalent. For this reason, valence bond theory assumes that the four valence orbitals of the carbon atom combine during the bonding process to form four new, but equivalent, hybrid orbitals. **Hybrid orbitals** are orbitals used to describe bonding that are obtained by taking combinations of atomic orbitals of the isolated atoms. In this case, a set of hybrid orbitals is constructed from one s orbital and three p orbitals, so they are called sp^3 hybrid orbitals. Calculations from theory show that each sp^3 hybrid orbital has a large lobe pointing in one direction and a small lobe pointing in the opposite direction. The four sp^3 hybrid orbitals point in tetrahedral directions. Figure 10.22A shows the shape of

Nuclear magnetic resonance (page 296) and infrared spectroscopy (page 362) both show that CH_4 has four equivalent C—H bonds.

FIGURE 10.22 ▶

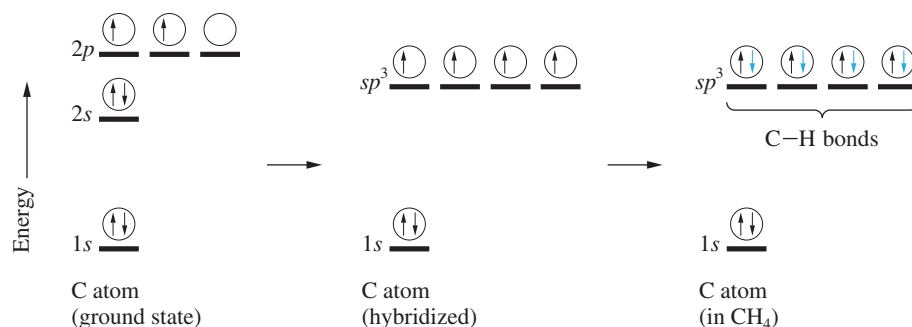
Spatial arrangement of sp^3 hybrid orbitals

(A) The shape of a single sp^3 hybrid orbital. Each orbital consists of two lobes. One lobe is small, but dense, and concentrated near the nucleus. The other lobe is large, but diffuse. Bonding occurs with the large lobe, since it extends farther from the nucleus. (B) The four hybrid orbitals are arranged tetrahedrally in space. (Small lobes are omitted here for clarity, and large lobes are stylized and greatly narrowed for ease in depicting the directional bonding.) (C) Bonding in CH_4 . Each C—H bond is formed by the overlap of a $1s$ orbital from a hydrogen atom and an sp^3 hybrid orbital of the carbon atom.



a single sp^3 orbital; Figure 10.22B shows a stylized set of four orbitals pointing in tetrahedral directions.

The C—H bonds in methane, CH_4 , are described by valence bond theory as the overlapping of each sp^3 hybrid orbital of the carbon atom with $1s$ orbitals of hydrogen atoms (see Figure 10.22C). Thus, the bonds are arranged tetrahedrally, which is predicted by the VSEPR model. You can represent the hybridization of carbon and the bonding of hydrogen to the carbon atom in methane as follows:



Here the blue arrows represent electrons originally belonging to hydrogen atoms.

Hybrid orbitals can be formed from various numbers of atomic orbitals. *The number of hybrid orbitals formed always equals the number of atomic orbitals used.* For example, if you combine an s orbital and two p orbitals to get a set of equivalent orbitals, you get three hybrid orbitals (called sp^2 hybrid orbitals). A set of hybrid orbitals always has definite directional characteristics. Here, all three sp^2 hybrid orbitals lie in a plane and are directed at 120° angles to one another; that is, they have a trigonal planar arrangement. Some possible hybrid orbitals and their geometric arrangements are listed in Table 10.2 and shown in Figure 10.23. Note that the geometric arrangements of hybrid orbitals are the same as those for electron pairs in the VSEPR model.

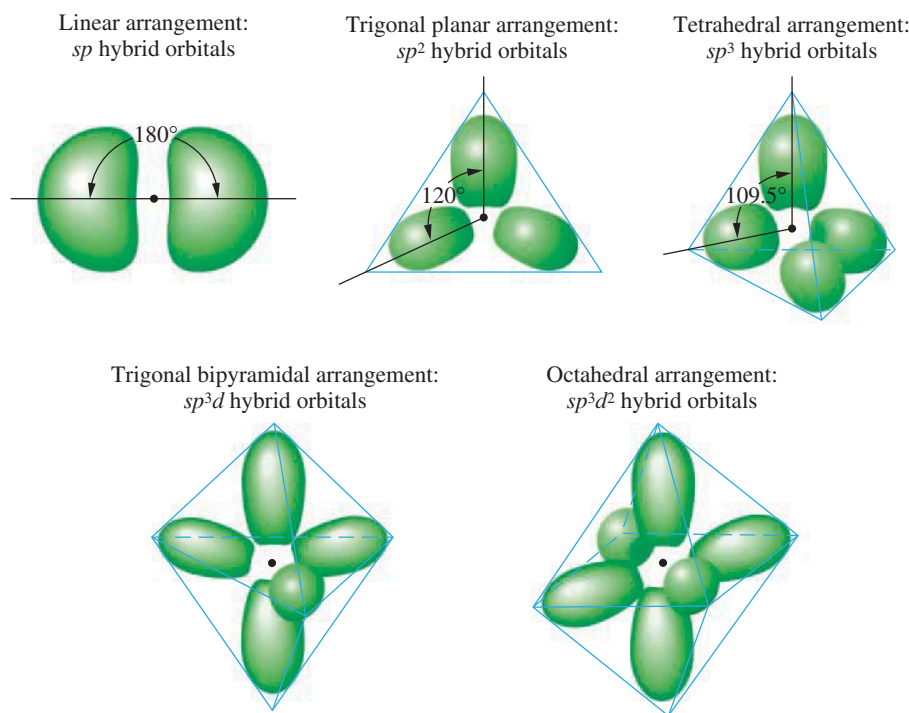
Only two of the three p orbitals are used to form sp^2 hybrid orbitals. The unhybridized p orbital is perpendicular to the plane of the sp^2 hybrid orbitals. Similarly, only one of the three p orbitals is used to form sp hybrid orbitals. The two unhybridized p orbitals are perpendicular to the axis of the sp hybrid orbitals and perpendicular to each other. We will use these facts when we discuss multiple bonding in the next section.

Now that you know something about hybrid orbitals, let us develop a general scheme for describing the bonding about any atom (we will call this the central atom). First, notice from Table 10.2 that there is a relationship between type of hybrid orbitals on an atom and the geometric arrangement of those orbitals. If you know one, you can infer the other. Thus, if you know the geometric arrangement, you know what hybrid orbitals to use in the bond description of the central atom. Your first task in describing

TABLE 10.2 Kinds of Hybrid Orbitals			
Hybrid Orbitals	Geometric Arrangement	Number of Orbitals	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4
sp^3d	Trigonal bipyramidal	5	P in PCl_5
sp^3d^2	Octahedral	6	S in SF_6

FIGURE 10.23**Diagrams of hybrid orbitals showing their spatial arrangements**

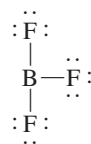
Each lobe shown is one hybrid orbital (small lobes are omitted for clarity).



the bonding, then, is to obtain the geometric arrangement about the central atom. In lieu of experimental information about the geometry, you can use the VSEPR model, since it proves to be a fairly good predictor of molecular geometry. To obtain the bonding description about any atom in a molecule, you proceed as follows:

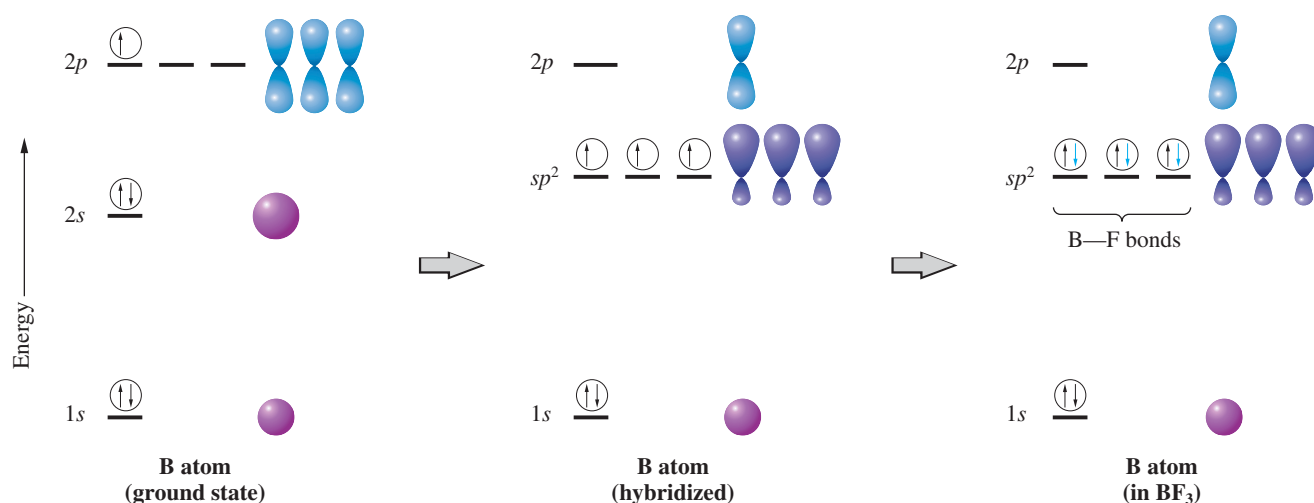
- Step 1:** Write the Lewis electron-dot formula of the molecule.
- Step 2:** From the Lewis formula, use the VSEPR model to obtain the arrangement of electron pairs about this atom.
- Step 3:** From the geometric arrangement of the electron pairs, deduce the type of hybrid orbitals on this atom required for the bonding description (see Table 10.2).
- Step 4:** Assign valence electrons to the hybrid orbitals of this atom one at a time, pairing them only when necessary.
- Step 5:** Form bonds to this atom by overlapping singly occupied orbitals of other atoms with the singly occupied hybrid orbitals of this atom.

As an application of this scheme, let us look at the BF_3 molecule and obtain the bond description of the boron atom. Following Step 1, you write the Lewis formula of BF_3 .



Now you apply the VSEPR model to the boron atom (Step 2). There are three electron pairs about the boron atom, so they are expected to have a planar trigonal arrangement. Looking at Table 10.2 (Step 3), you note that the three sp^2 hybrid orbitals have a trigonal planar arrangement. In Step 4, you assign the valence electrons of the boron atom to the hybrid orbitals. Finally, in Step 5, you imagine three fluorine atoms approaching the boron atom. The singly occupied $2p$ orbital on a fluorine atom overlaps one of the sp^2 hybrid orbitals on boron, forming a covalent bond. Three such B—F bonds form. Note that one of the $2p$ orbitals of boron remains unhybridized and

is unoccupied by electrons. It is oriented perpendicular to the molecular plane. You can summarize these steps using orbital diagrams as follows:



The next example further illustrates how to describe the bonding about an atom in a molecule. To solve problems of this type, you need to know the geometric arrangements of the hybrid orbitals listed in Table 10.2.

Example 10.4

Applying Valence Bond Theory (Two, Three, or Four Electron Pairs)

Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR model.

Problem Strategy From the Lewis formula for a molecule, determine its geometry about the central atom using the VSEPR model. From this geometry, determine the hybrid orbitals on this atom, assigning its valence electrons to these orbitals one at a time. Finally, form bonds by overlapping these hybrid orbitals with orbitals of the other atoms.

Solution The Lewis formula for H_2O is



Note that there are four pairs of electrons about the oxygen atom. According to the VSEPR model, these are directed tetrahedrally, and from Table 10.2 you see that you should use sp^3 hybrid orbitals. Each O—H bond is formed by the overlap of a 1s orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the oxygen atom. You can represent the bonding to the oxygen atom in H_2O as follows (see also Figure 10.24):

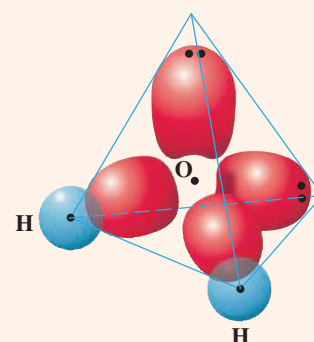
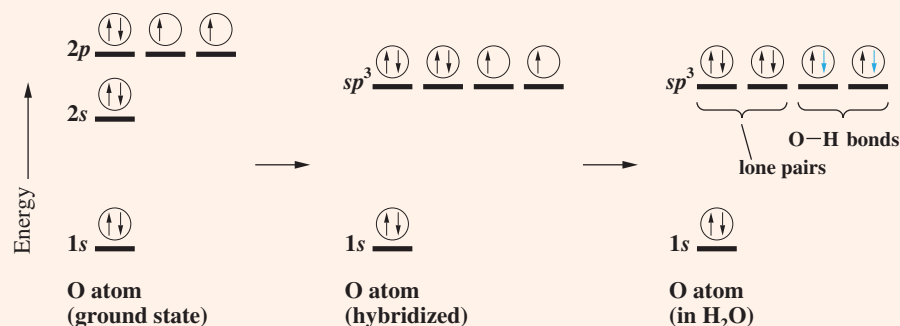


FIGURE 10.24

Bonding in H_2O

Orbitals on oxygen are sp^3 hybridized; bonding is tetrahedral.

(continued)

(continued)

Answer Check Check that you have the correct Lewis formula for the molecule and that you have the correct geometry about the central atom and the correct hybrid orbitals (Table 10.2).

Exercise 10.5 Using hybrid orbitals, describe the bonding in NH_3 according to valence bond theory.

■ See Problems 10.47, 10.48, 10.49, and 10.50.

The actual angle between O—H bonds in H_2O has been experimentally determined to be 104.5° . Because this is close to the tetrahedral angle (109.5°), the description of bonding given in Example 10.4 is essentially correct. To be more precise, you should note that the hybrid orbitals for bonds and lone pairs are not exactly equivalent. The lone pairs are somewhat larger than bonding pairs. Because they take up more space, the lone pairs push the bonding pairs closer together than they are in the exact tetrahedral case.

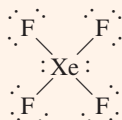
As the next example illustrates, hybrid orbitals are also useful for describing bonding when the central atom of a molecule is surrounded by more than eight valence electrons.

Example 10.5 Applying Valence Bond Theory (Five or Six Electron Pairs)

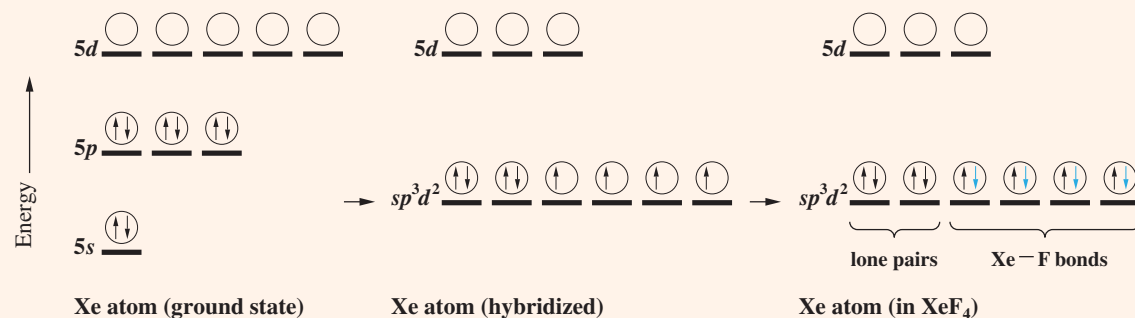
Describe the bonding in XeF_4 using hybrid orbitals.

Problem Strategy From the Lewis formula for a molecule, determine its geometry about the central atom using the VSEPR model. From this geometry, determine the hybrid orbitals on this atom, assigning its valence electrons to these orbitals one at a time. Finally, form bonds by overlapping these hybrid orbitals with orbitals of the other atoms.

Solution The Lewis formula of XeF_4 is



The xenon atom has four single bonds and two lone pairs. It will require six orbitals to describe the bonding. This suggests that you use sp^3d^2 hybrid orbitals on xenon (according to Table 10.2). Each fluorine atom (valence-shell configuration $2s^22p^5$) has one singly occupied orbital, so you assume that this orbital is used in bonding. Each Xe—F bond is formed by the overlap of a xenon sp^3d^2 hybrid orbital with a singly occupied fluorine $2p$ orbital. You can summarize this as follows:



(continued)

(continued)

Answer Check Check that you have the correct Lewis formula for the molecule and that you have the correct geometry about the central atom and the correct hybrid orbitals (Table 10.2).

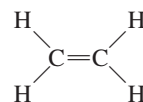
Exercise 10.6Describe the bonding in PCl_5 using hybrid orbitals.

■ See Problems 10.53, 10.54, 10.55, and 10.56.

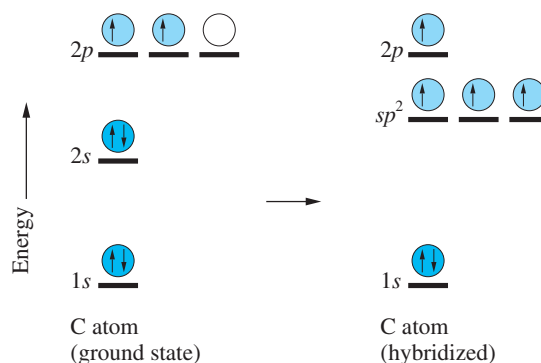
10.4 Description of Multiple Bonding

In the previous section, we described bonding as the overlap of *one* orbital from each of the bonding atoms. Now we consider the possibility that *more than one* orbital from each bonding atom might overlap, resulting in a multiple bond.

As an example, consider the ethylene molecule.



One hybrid orbital is needed for each bond (whether a single or a multiple bond) and for each lone pair. Because each carbon atom is bonded to three other atoms and there are no lone pairs, three hybrid orbitals are needed. This suggests the use of sp^2 hybrid orbitals on each carbon atom (there are three sp^2 hybrid orbitals; see Table 10.2). Thus, during bonding, the $2s$ orbital and two of the $2p$ orbitals of each carbon atom form three hybrid orbitals having trigonal planar orientation. A third $2p$ orbital on each carbon atom remains unhybridized and is perpendicular to the plane of the three sp^2 hybrid orbitals.

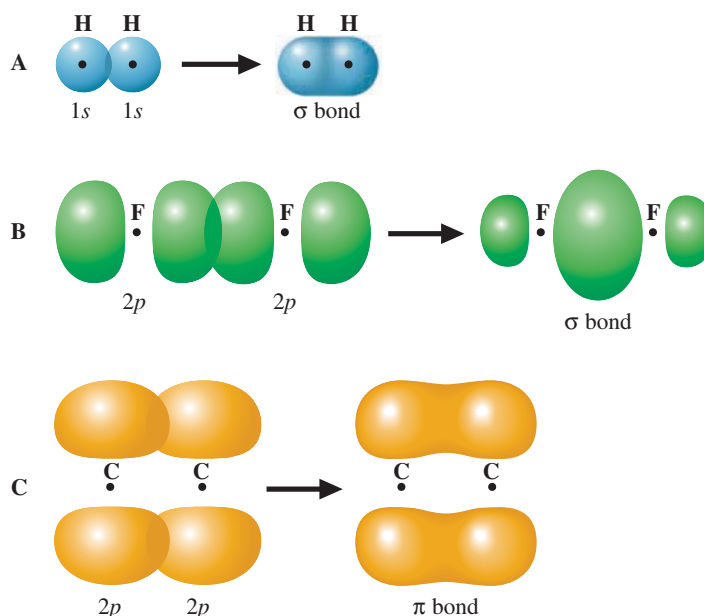


To describe the multiple bonding in ethylene, we must distinguish between two kinds of bonds. A **σ (sigma) bond** has a cylindrical shape about the bond axis. It is formed either when two s orbitals overlap, as in H_2 (Figure 10.25A), or when an orbital with directional character, such as a p orbital or a hybrid orbital, overlaps another orbital *along their axis* (Figure 10.25B). The bonds we discussed in the previous section are σ bonds.

A **π (pi) bond** has an electron distribution above and below the bond axis. It is formed by the *sideways* overlap of two parallel p orbitals (see Figure 10.25C). A sideways overlap will not give so strong a bond as an along-the-axis overlap of two p orbitals. A π bond occurs when two parallel orbitals are still available after strong σ bonds have formed.

FIGURE 10.25 ▶**Sigma and pi bonds**

(A) The formation of a σ bond by the overlap of two s orbitals. (B) A σ bond can also be formed by the overlap of two p orbitals along their axes. (C) When two p orbitals overlap sideways, a π bond is formed.



Now imagine that the separate atoms of ethylene move into their normal molecular positions. Each sp^2 hybrid carbon orbital overlaps a $1s$ orbital of a hydrogen atom or an sp^2 hybrid orbital of another carbon atom to form a σ bond (Figure 10.26A). Together, the σ bonds give the molecular framework of ethylene.

As you see from the orbital diagram for the hybridized C atom, a single $2p$ orbital still remains on each carbon atom. These orbitals are perpendicular to the plane of the hybrid orbitals; that is, they are perpendicular to the $-\text{CH}_2$ plane. Note that the two $-\text{CH}_2$ planes can rotate about the carbon–carbon axis without affecting the overlap of the hybrid orbitals. As these planes rotate, the $2p$ orbitals also rotate. When the $-\text{CH}_2$ planes rotate so that the $2p$ orbitals become parallel, the orbitals overlap to give a π bond (Figure 10.26B).

You therefore describe the carbon–carbon double bond as one σ bond and one π bond. Note that when the two $2p$ orbitals are parallel, the two $-\text{CH}_2$ ends of the molecule lie in the same plane. Thus, the formation of a π bond “locks” the two ends into a flat, rigid molecule.

FIGURE 10.26 ▼**Bonding in ethylene**

(A) The σ -bond framework in ethylene, formed by the overlap of sp^2 hybrid orbitals on C atoms and $1s$ orbitals on H atoms. (B) The formation of the π bonds in ethylene. When the $2p$ orbitals are perpendicular to one another, there is no overlap and no bond formation. When the two $-\text{CH}_2$ groups rotate so that the $2p$ orbitals are parallel, a π bond forms.

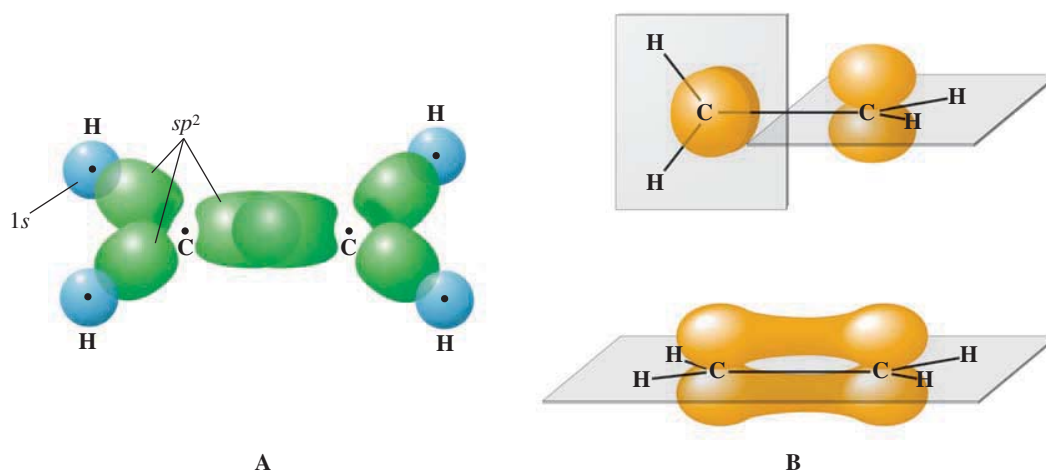
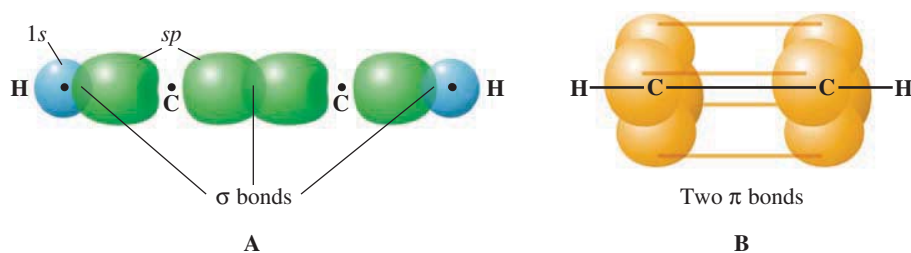
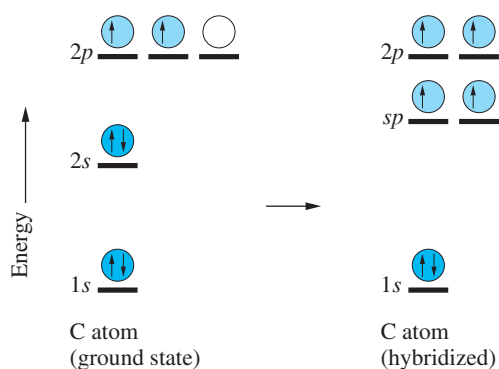


FIGURE 10.27**Bonding in acetylene**

(A) The σ -bond framework. (B) Two $2p$ orbitals on each carbon atom begin to overlap (symbolized by lines) to form two π bonds.



You can describe the triple bonding in acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$, in similar fashion. Because each carbon atom is bonded to two other atoms and there are no lone pairs, two hybrid orbitals are needed. This suggests sp hybridization (see Table 10.2).



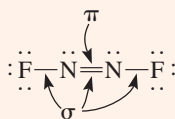
These sp hybrid orbitals have a linear arrangement, so the $\text{H}-\text{C}-\text{C}-\text{H}$ geometry is linear. Bonds formed by the overlap of these hybrid orbitals are σ bonds. The two $2p$ orbitals not used to construct hybrid orbitals are perpendicular to the bond axis and to each other. They are used to form two π bonds. Thus, the carbon–carbon triple bond consists of one σ bond and two π bonds (see Figure 10.27).

Example 10.6**Applying Valence Bond Theory (Multiple Bonding)**

Describe the bonding on a given N atom in dinitrogen difluoride, N_2F_2 , using valence bond theory.

Problem Strategy From the Lewis formula, determine the hybrid orbitals on the double-bonded atoms. Do this by counting the number of electron groups about each atom, and from this determine the kind of hybrid orbitals used. Form a σ bond between the double-bonded atoms by overlapping a hybrid orbital of one atom with a hybrid orbital of the other atom. Also, form σ bonds from these atoms to other atoms. Use any unhybridized p orbitals on the central atoms to form π bonds between them.

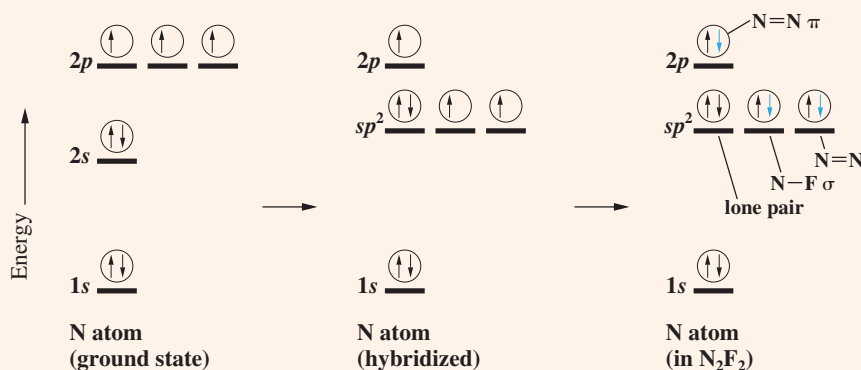
Solution The electron-dot formula of N_2F_2 is



(continued)

(continued)

Note that a double bond is described as a π bond plus a σ bond. Hybrid orbitals are needed to describe each σ bond and each lone pair (a total of three hybrid orbitals for each N atom). This suggests sp^2 hybridization (see Table 10.2). According to this description, one of the sp^2 hybrid orbitals is used to form the N—F bond, another to form the σ bond of N=N, and the third to hold the lone pair on the N atom. The $2p$ orbitals on each N atom overlap to form the π bond of N=N. Hybridization and bonding of the N atoms are shown as follows:



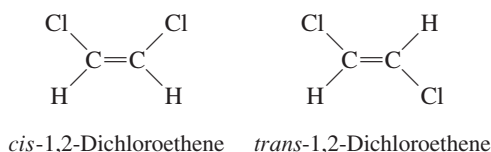
Answer Check Check that the number of hybrid orbitals on an atom of a multiple bond equals the number of sigma bonds plus lone pairs on that atom.

Exercise 10.7

Describe the bonding on the carbon atom in carbon dioxide, CO_2 , using valence bond theory.

■ See Problems 10.57 and 10.58.

The π -bond description of the double bond agrees well with experiment. The *geometric*, or *cis-trans*, *isomers* of the compound 1,2-dichloroethene (described in the chapter opening) illustrate this. *Isomers* are compounds of the same molecular formula but with different arrangements of the atoms. (The numbers in the name 1,2-dichloroethene refer to the positions of the chlorine atoms; one chlorine atom is attached to carbon atom 1 and the other to carbon atom 2.) The structures of these isomers of 1,2-dichloroethene are

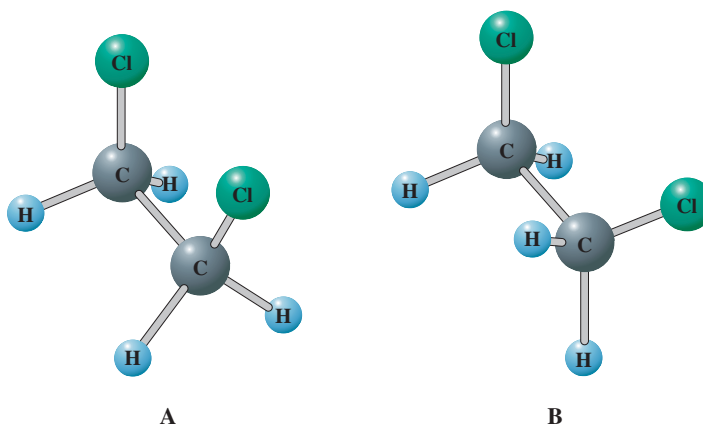


To transform one isomer into the other, one end of the molecule must be rotated as the other remains fixed. For this to happen, the π bond must be broken. Breaking the π bond requires considerable energy, so the *cis* and *trans* compounds are not easily interconverted. Contrast this with 1,2-dichloroethane (Figure 10.28), in which the two ends of the molecule can rotate without breaking any bonds. Here isomers corresponding to different spatial orientations of the two chlorine atoms cannot be prepared, because the two ends rotate freely with respect to one another. There is only one compound.

As we noted in the chapter opening, *cis* and *trans* isomers have different properties. The *cis* isomer of 1,2-dichloroethene boils at 60°C , the *trans* compound at 48°C .

FIGURE 10.28 ▶**Lack of geometric isomers in 1,2-dichloroethane**

Because of rotation about the carbon–carbon bond in 1,2-dichloroethane, geometric isomers are not possible. Note that the molecule pictured in (A) can be twisted easily to give the molecule pictured in (B).



These isomers can also be differentiated on the basis of dipole moment. The *trans* compound has no dipole moment because it is symmetrical (the polar C—Cl bonds point in opposite directions and so cancel). However, the *cis* compound has a dipole moment of 1.85 D.

It is possible to convert one isomer to another if sufficient energy is supplied—say by chemical reaction. The role of the conversion of a *cis* isomer to its *trans* isomer in human vision is discussed in the essay at the end of Section 10.7.

Exercise 10.8

Dinitrogen difluoride (see Example 10.6) exists as *cis* and *trans* isomers. Write structural formulas for these isomers and explain (in terms of the valence bond theory of the double bond) why they exist.

■ See Problems 10.59 and 10.60.

Concept Check 10.3

An atom in a molecule has one single bond and one triple bond to other atoms. What hybrid orbitals do you expect for this atom? Describe how you arrive at your answer.

Molecular Orbital Theory

In the preceding sections, we looked at a simple version of valence bond theory. Although simple valence bond theory satisfactorily describes most of the molecules we encounter, it does not apply to all molecules. For example, according to this theory any molecule with an even number of electrons should be diamagnetic (not attracted to a magnet), because we assume the electrons to be paired and to have opposite spins. In fact, a few molecules with an even number of electrons are paramagnetic (attracted to a magnet), indicating that some of the electrons are not paired. The best-known example of such a paramagnetic molecule is O_2 . Because of the paramagnetism of O_2 , liquid oxygen sticks to a magnet when poured over it

(Figure 10.29). Although valence bond theory can be extended to explain the electronic structure of O_2 , molecular orbital theory (an alternative bonding theory) provides a straightforward explanation of the paramagnetism of O_2 .

Molecular orbital theory is a theory of the electronic structure of molecules in terms of molecular orbitals, which may spread over several atoms or the entire molecule. This theory views the electronic structure of molecules to be much like the electronic structure of atoms. Each molecular orbital has a definite energy. To obtain the ground state of a molecule, electrons are put into orbitals of lowest energy, consistent with the Pauli exclusion principle, just as in atoms.

10.5

Principles of Molecular Orbital Theory

You can think of a molecular orbital as being formed from a combination of atomic orbitals. As atoms approach each other and their atomic orbitals overlap, molecular orbitals are formed.

Bonding and Antibonding Orbitals

Consider the H_2 molecule. As the atoms approach to form the molecule, their $1s$ orbitals overlap. One molecular orbital is obtained by adding the two $1s$ orbitals (see Figure 10.30). Note that where the atomic orbitals overlap, their values sum to give a larger result. This means that in this molecular orbital, electrons are often found in the region between the two nuclei where the electrons can hold the nuclei together. *Molecular orbitals that are concentrated in regions between nuclei are called **bonding orbitals**.* The bonding orbital in H_2 , which we have just described, is denoted σ_{1s} . The σ (sigma) means that the molecular orbital has a cylindrical shape about the bond axis. The subscript $1s$ tells us that the molecular orbital was obtained from $1s$ atomic orbitals.

Another molecular orbital is obtained by subtracting the $1s$ orbital on one atom from the $1s$ orbital on the other (Figure 10.30). When the orbitals are subtracted, the resulting values in the region of the overlap are close to zero. This means that in this molecular orbital, the electrons spend little time between the nuclei. *Molecular orbitals having zero values in the region between two nuclei and therefore concentrated in other regions are called **antibonding orbitals**.* The antibonding orbital in H_2 , which we have just described, is denoted σ_{1s}^* . The asterisk, which you read as “star,” tells us that the molecular orbital is antibonding.

Figure 10.31 shows the energies of the molecular orbitals σ_{1s} and σ_{1s}^* relative to the atomic orbitals. Energies of the separate atomic orbitals are represented by heavy

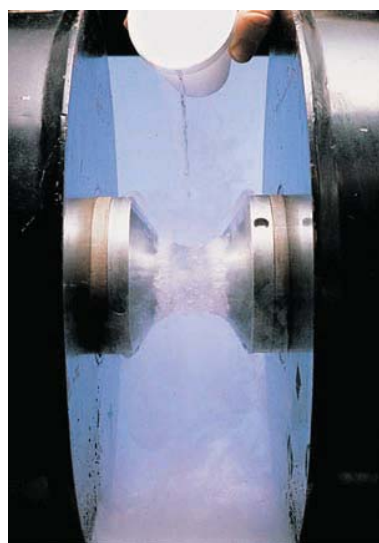


FIGURE 10.29 ▲

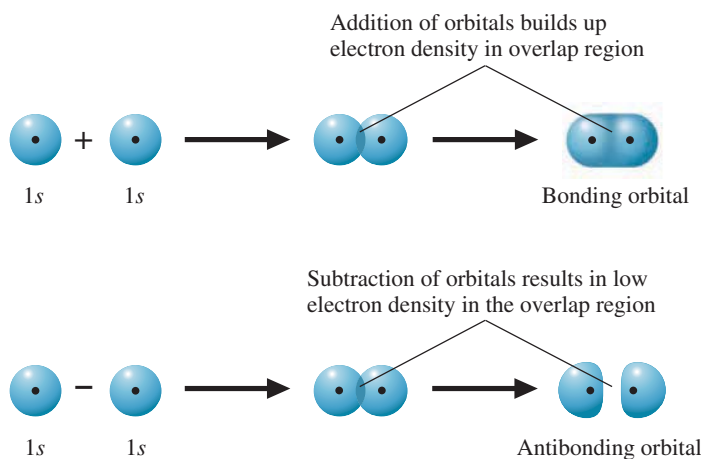
Paramagnetism of oxygen, O_2

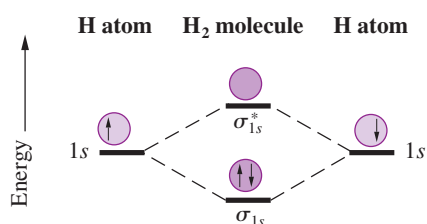
Liquid oxygen is poured between the poles of a strong magnet. Oxygen adheres to the poles, showing that it is paramagnetic.

FIGURE 10.30 ►

Formation of bonding and antibonding orbitals from $1s$ orbitals of hydrogen atoms

When the two $1s$ orbitals overlap, they can either add to give a bonding molecular orbital or subtract to give an antibonding molecular orbital.



**FIGURE 10.31** ▲

Relative energies of the 1s orbital of the H atom and the σ_{1s} and σ_{1s}^* molecular orbitals of H_2

Arrows denote occupation of the σ_{1s} orbital by electrons in the ground state of H_2 .

black lines at the far left and right. The energies of the molecular orbitals are shown by heavy black lines in the center. (These are connected by dashed lines to show which atomic orbitals were used to obtain the molecular orbitals.) Note that the energy of a bonding orbital is less than that of the separate atomic orbitals, whereas the energy of an antibonding orbital is higher.

You obtain the electron configuration for the ground state of H_2 by placing the two electrons (one from each atom) into the lower-energy orbital (see Figure 10.31). The orbital diagram is



and the electron configuration is $(\sigma_{1s})^2$. Because the energy of the two electrons is lower than their energies in the isolated atoms, the H_2 molecule is stable.

Configurations involving the σ_{1s}^* orbital describe excited states of the molecule. As an example of an excited state, you can write the orbital diagram



The corresponding electron configuration is $(\sigma_{1s})^1(\sigma_{1s}^*)^1$.

You obtain a similar set of orbitals when you consider the approach of two helium atoms. To obtain the ground state of He_2 , you note that there are four electrons, two from each atom, that would fill the molecular orbitals. Two electrons go into the σ_{1s} orbital and two go into the σ_{1s}^* orbital. The orbital diagram is



and the configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^2$. The energy decrease from the bonding electrons is offset by the energy increase from the antibonding electrons. Hence, He_2 is not a stable molecule. Molecular orbital theory therefore explains why the element helium exists as a monatomic gas, whereas hydrogen is diatomic.

Bond Order

The term *bond order* refers to the number of bonds that exist between two atoms. In molecular orbital theory, the bond order of a diatomic molecule is defined as one-half the difference between the number of electrons in bonding orbitals, n_b , and the number of electrons in antibonding orbitals, n_a . <

$$\text{Bond order} = \frac{1}{2}(n_b - n_a)$$

For H_2 , which has two bonding electrons,

$$\text{Bond order} = \frac{1}{2}(2 - 0) = 1$$

That is, H_2 has a single bond. For He_2 , which has two bonding and two antibonding electrons,

$$\text{Bond order} = \frac{1}{2}(2 - 2) = 0$$

Bond orders need not be whole numbers; half-integral bond orders of $\frac{1}{2}$, $\frac{3}{2}$, and so forth are also possible. For example, the H_2^+ molecular ion, which is formed in mass spectrometers, has the configuration $(\sigma_{1s})^1$ and a bond order of $\frac{1}{2}(1 - 0) = \frac{1}{2}$.

Factors That Determine Orbital Interaction

The H_2 and He_2 molecules are relatively simple. A 1s orbital on one atom interacts with the 1s orbital on the other atom. But now let us consider the Li_2 molecule. Each Li atom has 1s and 2s orbitals. Which orbitals interact to form molecular orbitals? To find out, you need to understand the factors that determine orbital interaction.

For a Lewis formula, the bond order equals the number of electron pairs shared between two atoms (see Section 9.10).

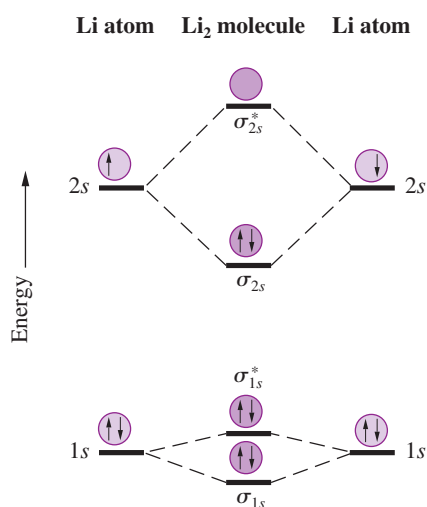


FIGURE 10.32 ▲
The energies of the molecular orbitals of Li_2

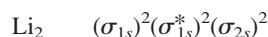
Arrows indicate the occupation of these orbitals by electrons in the ground state.

However, small shifts in the energy of the core electrons due to bonding can be measured by x-ray photoelectron spectroscopy (page 304).

The strength of the interaction between two atomic orbitals to form molecular orbitals is determined by two factors: (1) the energy difference between the interacting orbitals and (2) the magnitude of their overlap. *For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large.*

From this last statement, you see that when two Li atoms approach one another to form Li_2 , only like orbitals on the two atoms interact appreciably. The $2s$ orbital of one lithium atom interacts with the $2s$ orbital of the other atom, but the $2s$ orbital from one atom does not interact with the $1s$ orbital of the other atom, because their energies are quite different. Also, because the $2s$ orbitals are outer orbitals, they are able to overlap and interact strongly when the atoms approach. As in H_2 , these atomic orbitals interact to give a bonding orbital (denoted σ_{2s}) and an antibonding orbital (denoted σ_{2s}^*). However, even though the $1s$ orbitals of the two atoms have the same energy, they do not overlap appreciably and so interact weakly. (The difference in energy between σ_{1s} and σ_{1s}^* is very small.) Figure 10.32 gives the relative energies of the orbitals.

You obtain the ground-state configuration of Li_2 by putting six electrons (three from each atom) into the molecular orbitals of lowest energy. The configuration of the diatomic molecule Li_2 is



The $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ part of the configuration is often abbreviated KK (which denotes the K shells, or inner shells, of the two atoms). These electrons do not have a significant effect on bonding. <



In calculating bond order, we can ignore KK (it includes two bonding and two antibonding electrons). Thus, the bond order is 1, as in H_2 .

In Be_2 , the energy diagram is similar to that in Figure 10.32. You have eight electrons to distribute (four from each Be atom). The ground-state configuration of Be_2 is



Note that the configuration has two bonding and two antibonding electrons outside the K shells. Thus, the bond order is $\frac{1}{2}(2 - 2) = 0$. No bond is formed, so the Be_2 molecule, like the He_2 molecule, is unstable.

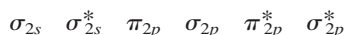
10.6

Electron Configurations of Diatomic Molecules of the Second-Period Elements

The previous section looked at the electron configurations of some simple molecules: H_2 , He_2 , Li_2 , and Be_2 . These are **homonuclear diatomic molecules**—that is, *molecules composed of two like nuclei*. (**Heteronuclear diatomic molecules** are *molecules composed of two different nuclei*—for example, CO and NO.) To find the electron configurations of other homonuclear diatomic molecules, we need to have additional molecular orbitals.

We have already looked at the formation of molecular orbitals from s atomic orbitals. Now we need to consider the formation of molecular orbitals from p atomic orbitals. There are two different ways in which $2p$ atomic orbitals can interact. One set of $2p$ orbitals can overlap along their axes to give one bonding and one antibonding σ orbital (σ_{2p} and σ_{2p}^*). The other two sets of $2p$ orbitals then overlap sideways to give two bonding and two antibonding π orbitals (π_{2p} and π_{2p}^*). (See Figure 10.33.)

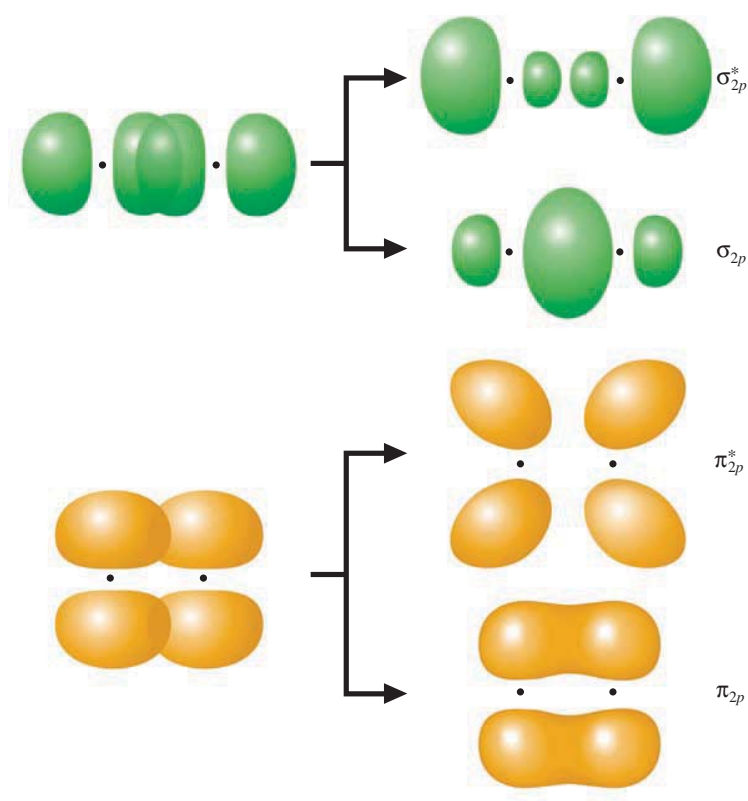
Figure 10.34 shows the relative energies of the molecular orbitals obtained from $2s$ and $2p$ atomic orbitals. This order of molecular orbitals reproduces the known electron configurations of homonuclear diatomic molecules composed of elements in the second row of the periodic table. < The order of filling is



This order gives the correct number of electrons in subshells, even though in O_2 and F_2 the energy of σ_{2p} is below π_{2p} .

FIGURE 10.33 ▶**The different ways in which 2p orbitals can interact**

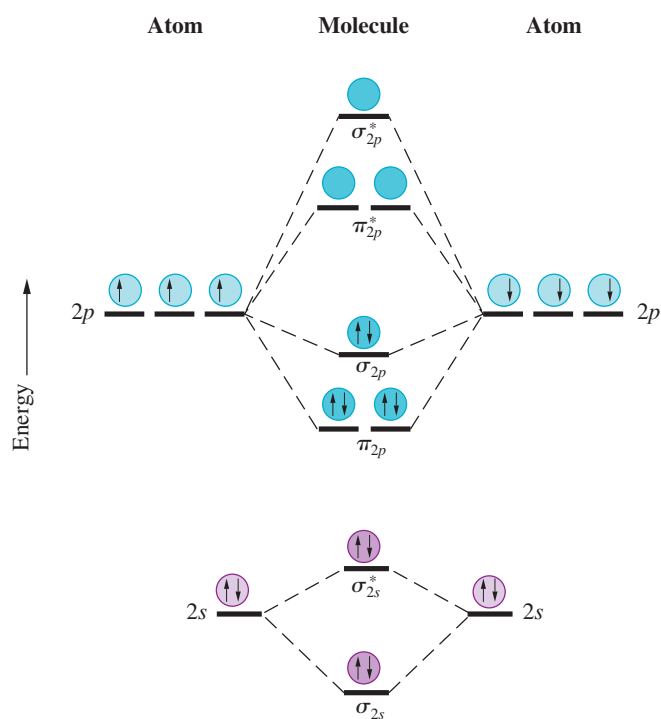
When the 2p orbitals overlap along their axes, they form σ_{2p} and σ_{2p}^* molecular orbitals. When they overlap sideways, they form π_{2p} and π_{2p}^* molecular orbitals.



Note that there are two orbitals in the π subshell and two orbitals in the π^* subshell. Because each orbital can hold two electrons, a π or π^* subshell can hold four electrons. The next example shows how you can use the order of filling to obtain the orbital diagram, magnetic character, electron configuration, and bond order of a homonuclear diatomic molecule.

FIGURE 10.34 ▶**Relative energies of molecular orbitals of homonuclear diatomic molecules (excluding K shells)**

The arrows show the occupation of molecular orbitals by the valence electrons of N_2 .



Example 10.7**Describing Molecular Orbital Configurations (Homonuclear Diatomic Molecules)**

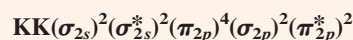
Give the orbital diagram of the O_2 molecule. Is the molecular substance diamagnetic or paramagnetic? What is the electron configuration? What is the bond order of O_2 ?

Problem Strategy Note the order of filling of molecular orbitals for the second-row homonuclear diatomic molecules (given just before this example). Now assign the valence electrons to these orbitals in this order. Pay attention to both the Pauli exclusion principle (no more than two electrons to an orbital, and then only with opposed spins) and Hund's rule (fill all orbitals of a subshell with one electron each—and with the same spins—before pairing electrons in any orbital). Decide whether the substance is diamagnetic (all electrons paired) or paramagnetic (unpaired electrons). Then calculate the bond order equal to $\frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$.

Solution There are 12 valence electrons in O_2 (six from each atom), which occupy the molecular orbitals as shown in the following orbital diagram:



Note that the two electrons in the π_{2p}^* subshell must go into different orbitals with their spins in the same direction (Hund's rule). Because there are two unpaired electrons, the molecular substance is **paramagnetic**. The electron configuration is



There are eight bonding electrons and four antibonding electrons. Therefore,

$$\text{Bond order} = \frac{1}{2}(8 - 4) = 2$$

Answer Check Check that the number of electrons assigned to orbitals equals the number of valence electrons of the two atoms. Make sure that the Pauli exclusion principle and Hund's rule have been properly applied.

Exercise 10.9 The C_2 molecule exists in the vapor phase over carbon at high temperature. Describe the molecular orbital structure of this molecule; that is, give the orbital diagram and electron configuration. Would you expect the molecular substance to be diamagnetic or paramagnetic? What is the bond order for C_2 ?

■ See Problems 10.61 and 10.62.

Table 10.3 compares experimentally determined bond lengths, bond dissociation energies, and magnetic character of the second-period homonuclear diatomic molecules with the bond order calculated from molecular orbital theory, as in the preceding example. Note that as the bond order increases, bond length tends to decrease and bond dissociation energy tends to increase. You should be able to verify that the

TABLE 10.3**Theoretical Bond Orders and Experimental Data for the Second-Period Homonuclear Diatomic Molecules**

Molecule	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Magnetic Character
Li_2	1	267	110	Diamagnetic
Be_2	0	*	*	*
B_2	1	159	290	Paramagnetic
C_2	2	124	602	Diamagnetic
N_2	3	110	942	Diamagnetic
O_2	2	121	494	Paramagnetic
F_2	1	142	155	Diamagnetic
Ne_2	0	*	*	*

The symbol * means that no stable molecule has been observed.

experimentally determined magnetic character of the molecule, given in the last column of the table, is correctly predicted by molecular orbital theory.

When the atoms in a heteronuclear diatomic molecule are close to one another in a row of the periodic table, the molecular orbitals have the same relative order of energies as those for homonuclear diatomic molecules. In this case you can obtain the electron configurations in the same way, as the next example illustrates.

Example 10.8**Describing Molecular Orbital Configurations (Heteronuclear Diatomic Molecules)**

Write the orbital diagram for nitrogen monoxide (nitric oxide), NO. What is the bond order of NO?

Problem Strategy If the two different atoms of the molecule are close to one another in the periodic table, then you can assume that the order of filling is the same as that for homonuclear diatomic molecules. After that, the procedure is similar to that for a homonuclear molecule (see Example 10.7).

Solution You assume that the order of filling of orbitals is the same as for homonuclear diatomic molecules. There are 11 valence electrons in NO. Thus, the orbital diagram is



Because there are eight bonding and three antibonding electrons,

$$\text{Bond order} = \frac{1}{2}(8 - 3) = \frac{5}{2}$$

Answer Check Check that the number of electrons assigned to orbitals equals the number of valence electrons of the two atoms. Make sure that the Pauli exclusion principle and Hund's rule have been properly applied.

Exercise 10.10 Give the orbital diagram and electron configuration for the carbon monoxide molecule, CO. What is the bond order of CO? Is the molecule diamagnetic or paramagnetic?

■ See Problems 10.63 and 10.64.

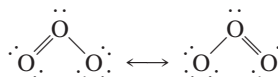
When the two atoms in a heteronuclear diatomic molecule differ appreciably, you can no longer use the scheme appropriate for homonuclear diatomic molecules. The HF molecule is an example. Figure 10.35 (on page 406) shows the relative energies of the molecular orbitals that form. Sigma bonding and antibonding orbitals are formed by combining the 1s orbital on the H atom with the 2p orbital on the F atom that lies along the bond axis. The 2s orbital and the other 2p orbitals on fluorine remain as *nonbonding* orbitals (neither bonding nor antibonding). Note that the energy of the 2p subshell in fluorine is lower than the energy of the 1s orbital in hydrogen, because the fluorine electrons are more tightly held. As a result, the bonding orbital is made up of a greater percentage of the 2p fluorine orbital than of the 1s hydrogen orbital. This means that electrons in the bonding molecular orbital spend more time in the vicinity of the fluorine atom; that is, the H—F bond is polar, with the F atom having a small negative charge.

10.7

Molecular Orbitals and Delocalized Bonding

One of the advantages of using molecular orbital theory is the simple way in which it describes molecules with delocalized bonding. Whereas valence bond theory requires two or more resonance formulas, molecular orbital theory describes the bonding in terms of a single electron configuration.

Consider the ozone molecule as an example. In the previous chapter, we described this molecule in terms of resonance as follows:



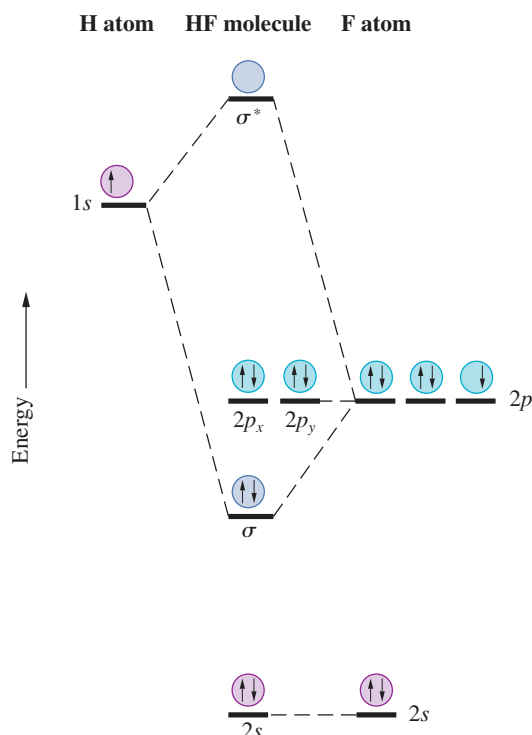


FIGURE 10.35 ▲
Relative energies of molecular orbitals in the valence shell of HF

Arrows show the occupation of orbitals by electrons.

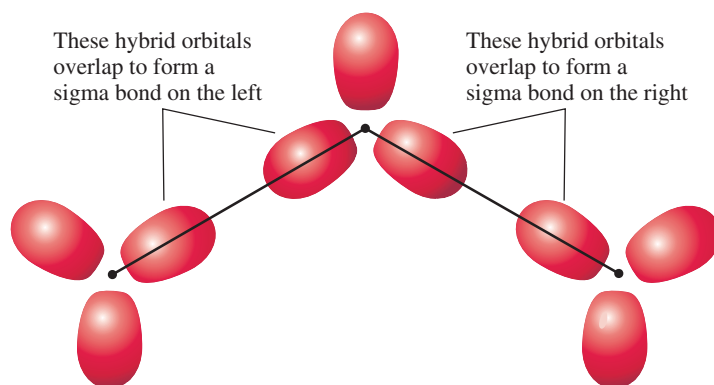


FIGURE 10.36 ▲

Hybrid orbitals on oxygen atoms of ozone, O_3

Each oxygen atom has sp^2 hybrid orbitals. One hybrid orbital on the center atom and one hybrid orbital on the left atom overlap to form a single bond at the left. Similar orbitals at the right form another single bond. Each atom has a π orbital perpendicular to the plane of these hybrid orbitals.

Some of these electrons are localized either on one atom or between an oxygen–oxygen bond (these are printed in black). The other electrons are delocalized (these are printed in blue). They are the electron pairs that change position in going from one resonance formula to the other.

Each O atom has three localized electron pairs about it, which suggests that each atom uses sp^2 hybrid orbitals (see Table 10.2). The overlap of one hybrid orbital on the center O atom with a hybrid orbital on the end O atom at the left forms the left O—O bond (Figure 10.36). The overlap of another hybrid orbital on the center O atom with a hybrid orbital on the end O atom at the right forms the other O—O bond. This leaves one hybrid orbital on the center O atom and two on each of the end O atoms for lone pairs.

After the hybrid orbitals are formed, one unhybridized p orbital remains on each O atom. These three p orbitals are perpendicular to the plane of the molecule and parallel to one another. They can overlap sideways to give three π molecular orbitals. (Three interacting atomic orbitals produce three molecular orbitals.) All three will span the entire molecule (Figure 10.37). One of these orbitals turns out to be antibonding; one is nonbonding (that is, it has an energy equal to that of the isolated atoms); and the third is bonding.

The bonding and nonbonding π orbitals are both doubly occupied. This agrees with the resonance description, in which one delocalized pair is bonding and the other is a lone (nonbonding) pair on the end oxygen atoms.

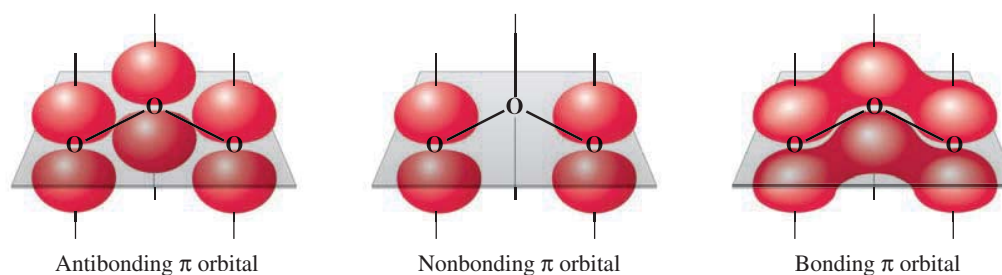
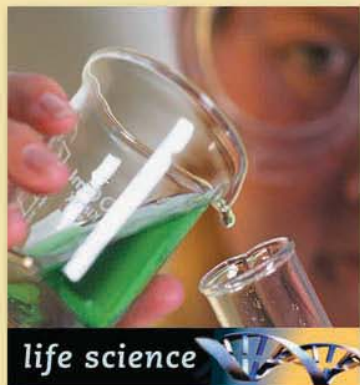


FIGURE 10.37 ▲

The electron distributions of the π molecular orbitals of O_3

Note that one molecular orbital is nonbonding. It describes a lone pair of electrons that can be on either end-oxygen atom.

A Chemist Looks at . . .



Human Vision

Human vision, as well as the detection of light by other organisms, is known to involve a compound called 11-*cis*-retinal. The structural formula is shown on the left side of Figure 10.38. This compound, which is derived from

vitamin A, is contained in two kinds of cells—rod cells and cone cells—located in the retina of the eye. Rod cells are responsible for vision in dim light. They give the sensation of light or dark but no sensation of color. Cone cells are responsible for color vision, but they require bright light. Color vision is possible because three types of cone cells exist: one type absorbs light in the red region of the spectrum, another absorbs in the green region, and a third absorbs in the blue region. In each of these different cells, 11-*cis*-retinal is attached to a different protein molecule, which affects the region of light that is absorbed by retinal.

When a photon of light is absorbed by 11-*cis*-retinal, it is transformed to 11-*trans*-retinal (see Figure 10.38). This small change at one carbon–carbon double bond results in a large movement of one end of the molecule with respect to the other. In other words, the absorption of a single photon results in a significant change in molecular geometry. This change in shape of retinal also affects the shape of the protein molecule to which it is attached, and this change results in a sequence of events, not completely understood, in which an electrical signal is generated.

To understand the *cis*–*trans* conversion when a photon is absorbed, consider the similar, but simpler, molecule

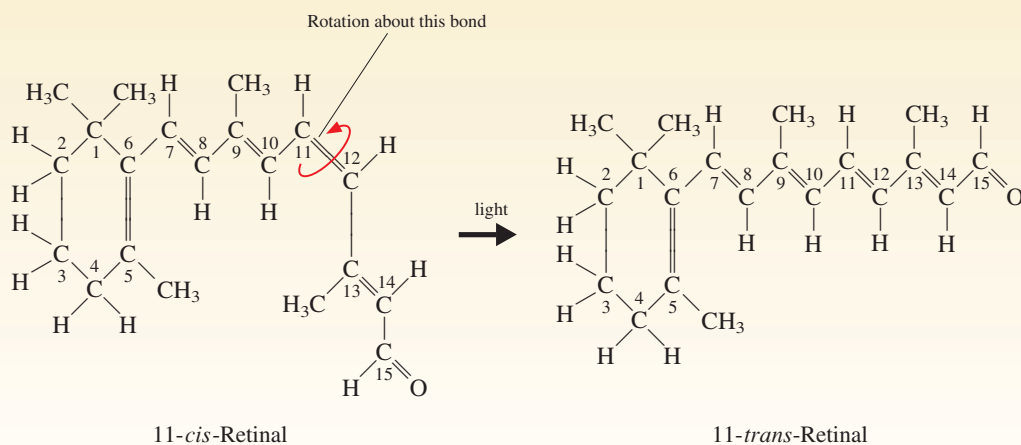
cis-1,2-dichloroethene (see structural formula on page 374). The double bond consists of a σ bond and a π bond. The π bond results from two electrons in a π -type molecular orbital. A corresponding antibonding orbital, π^* , has higher energy than the π orbital and is unoccupied in the ground state. When a photon of light in the ultraviolet region (near 180 nm) is absorbed by *cis*-1,2-dichloroethene, an electron in the π orbital undergoes a transition to the π^* orbital. Whereas there were previously two electrons in the bonding π orbital (contributing one bond), there is now one electron in the bonding orbital and one in the antibonding orbital (with zero net bonding). As a result of the absorption of a photon, the double bond becomes a single bond and rotation about the bond is now possible. The *cis* isomer tends to rotate to the *trans* isomer, which is more stable. Then energy is lost as heat, and the electron in the π^* orbital undergoes a transition back to the π orbital; the single bond becomes a double bond again. The net result is the conversion of the *cis* isomer to the *trans* isomer.

Retinal differs from dichloroethene in having six double bonds alternating with single bonds instead of only one double bond. The alternating double and single bonds give a rigid structure, and when the middle double bond undergoes the *cis*-to-*trans* change, a large movement of atoms occurs. Another result of a long chain of alternating double and single bonds is a change in the wavelength of light absorbed in the π -to- π^* transition. Dichloroethene absorbs in the ultraviolet region, but retinal attached to its protein absorbs in the visible region. (The attached protein also alters the wavelength of absorbed light.) Many biological compounds that are colored consist of long chains of alternating double and single bonds. β -Carotene, a yellow pigment in carrots, has this structure. It is broken down in the body to give vitamin A, from which retinal is derived.

FIGURE 10.38 ►

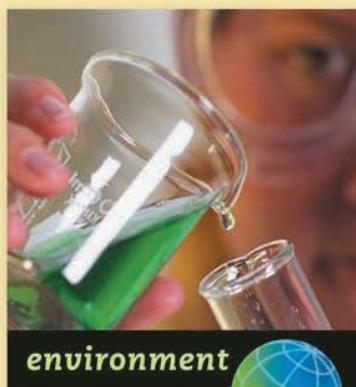
The *cis*–*trans* conversion of retinal on absorption of light

Note the large movement of atoms caused by the rotation about the double bond between carbon atoms 11 and 12.



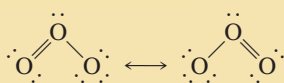
■ See Problems 10.85 and 10.86.

A Chemist Looks at . . .



Stratospheric Ozone (An Absorber of Ultraviolet Rays)

Ozone (also known as trioxygen, O_3) is a reactive form of oxygen having a bent molecular geometry, as you would predict from its resonance formulas:



Ozone forms in the atmosphere whenever O_2 is irradiated by ultraviolet light or subjected to electrical discharges. On bright sunny days, you might notice the fresh-air smell of

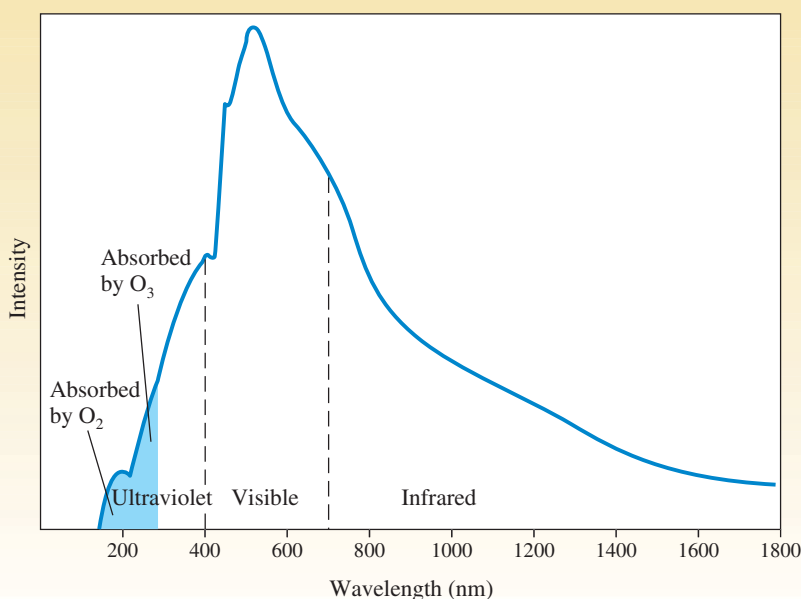
dilute ozone (trioxygen, O_3). Around electrical equipment, however, ozone often occurs in higher concentrations and has a disagreeable odor.

Although ozone occurs at ground level and is an ingredient of *photochemical smog*, it is an essential component of the *stratosphere*, which occurs at about 10 to 15 km above ground level. Ozone in the stratosphere absorbs ultraviolet radiation between 200 and 300 nm, which is vitally important to life on earth. Radiation from the sun contains ultraviolet rays that are harmful to the DNA of biological organisms. Oxygen, O_2 , absorbs the most energetic of these ultraviolet rays in the earth's upper atmosphere, but only ozone in the stratosphere absorbs the remaining ultraviolet radiation that is destructive to life on earth (Figure 10.39).

FIGURE 10.39 ►

The solar spectrum

Radiation below 200 nm is absorbed in the upper atmosphere by O_2 . Ultraviolet radiation between 200 and 300 nm is absorbed by O_3 in the stratosphere.



A Checklist for Review

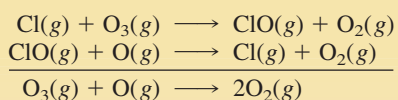
Important Terms

molecular geometry (10.1)
valence-shell electron-pair repulsion (VSEPR) model (10.1)
dipole moment (10.2)
valence bond theory (10.3)

hybrid orbitals (10.3)
 σ (sigma) bond (10.4)
 π (pi) bond (10.4)
molecular orbital theory (10.5)
bonding orbitals (10.5)
antibonding orbitals (10.5)

homonuclear diatomic molecules (10.6)
heteronuclear diatomic molecules (10.6)

In 1974, Mario J. Molina and F. Sherwood Rowland expressed concern that chlorofluorocarbons (CFCs), such as CClF_3 and CCl_2F_2 , would be a source of chlorine atoms that could catalyze the decomposition of ozone in the stratosphere, so that the ozone would be destroyed faster than it could be produced. The chlorofluorocarbons are relatively inert compounds used as refrigerants, spray-can propellants, and blowing agents (substances used to produce plastic foams). As a result of their inertness, however, CFCs concentrate in the atmosphere, where they steadily rise into the stratosphere. Once they are in the stratosphere, ultraviolet light decomposes them to form chlorine atoms, which react with ozone to form ClO and O_2 . The ClO molecules react with oxygen atoms in the stratosphere to regenerate Cl atoms.



The net result is the decomposition of ozone to dioxygen. Chlorine atoms are consumed in the first step but regenerated in the second. Thus, chlorine atoms are not used up, so they function as a catalyst.

In 1985, British researchers reported that the ozone over the Antarctic had been declining precipitously each spring for several years, although it returned the following winter. Then in August 1987, an expedition was assembled to begin flights through the “ozone hole” with instruments (Figure 10.40). Researchers found that wherever ozone is depleted in the stratosphere, chlorine monoxide (ClO) appears, as expected if chlorine atoms are catalyzing the depletion (see the previous reactions). The chlorofluorocarbons are the suspected source of these chlorine atoms, and by international treaty they are being phased out of production. Refrigerators and air conditioners, for example, now use hydrofluorocarbons (HFCs), such as R410A , which is a mixture of CH_2F_2 and CF_3CHF_2 .

In October 1995, Sherwood Rowland (University of California, Irvine), Mario Molina (Massachusetts Institute of Technology), and Paul Crutzen (Max Planck Institute, Mainz, Germany) were awarded the Nobel Prize in chemistry for their work on stratospheric ozone depletion. Crutzen studied the effect of nitrogen oxides in catalyzing the decomposition of ozone.

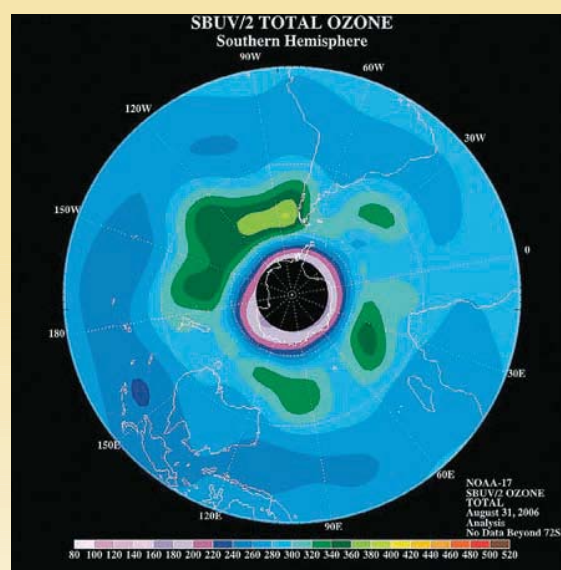


FIGURE 10.40 ▲
Total stratospheric ozone over the Southern Hemisphere

This computer image shows the total quantity of ozone over the Southern Hemisphere in Dobson units (equivalent to the thickness, in units of 10^{-2} mm, of total ozone, assuming it to be compressed to 1 atm at 0°C). The ozone depletion is shown near the South Pole (pink color; black color indicates no data). The data are from the SBUV/2 instrument on board the National Oceanic and Atmospheric Administration's polar orbiting satellite.

■ See Problems 10.87 and 10.88.

Summary of Facts and Concepts

Molecular geometry refers to the spatial arrangement of atoms in a molecule. The *valence-shell electron-pair repulsion (VSEPR) model* is a simple model for predicting molecular geometries. It is based on the idea that the valence-shell electron pairs are arranged symmetrically about an atom to minimize electron-pair repulsion. The geometry about an atom is then determined by the directions of the bonding pairs. Information about the geometry of a molecule can sometimes be obtained from the experimentally determined presence or absence of a *dipole moment*.

The bonding and geometry in a molecule can be described in terms of *valence bond theory*. In this theory, a bond is formed by the overlap of orbitals from two atoms. *Hybrid orbitals*, a set of equivalent orbitals formed by combining atomic orbitals, are often needed to describe this bond. Multiple bonds occur via the overlap of atomic orbitals to give σ bonds and π bonds. *Cis-trans* isomers result from the molecular rigidity imposed by a π bond.

Molecular orbital theory can also be used to explain bonding in molecules. According to this theory, electrons in a molecule occupy orbitals that may spread over the entire molecule.

You can think of these molecular orbitals as constructed from atomic orbitals. Thus, when two atoms approach to form a diatomic molecule, the atomic orbitals interact to form *bonding* and *antibonding* molecular orbitals. The electron configuration

of a diatomic molecule such as O_2 can be predicted from the order of filling of the molecular orbitals. From this configuration, you can predict the bond order and whether the molecular substance is diamagnetic or paramagnetic.

Media Summary

Visit the **student website at college.hmco.com/pic/ebbing9e** to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:



Prepare for Class

Video Lessons *Mini lectures from chemistry experts*

Valence-Shell Electron-Pair Repulsion Theory
Molecular Shapes for Steric Numbers 2–4
Predicting Molecular Characteristics Using VSEPR Theory
Molecular Shapes for Steric Numbers 5 and 6
Valence Bond Theory
An Introduction to Hybrid Orbitals
Pi Bonds
CIA Demonstration: The Paramagnetism of Oxygen
Molecular Orbital Theory
Applications of the Molecular Orbital Theory
Beyond Homonuclear Diatomics



Improve Your Grade

Visualizations *Molecular-level animations and lab demonstration videos*

VSEPR
VSEPR: Two Electron Pair
VSEPR: Four Electron Pair
VSEPR: Three Electron Pair
VSEPR: Iodine Pentafluoride

Polar Molecules

Hybridization: sp
Hybridization: sp^2
Hybridization: sp^3
Formation of C—C Double Bond in Ethylene
The Magnetic Properties of Liquid Nitrogen and Oxygen
Sigma Bonding and Antibonding Orbitals
Pi Bonding and Antibonding Orbitals
Molecular Orbital Diagram (N_2)
Delocalized Pi Bonding in the Nitrate Ion

Tutorials *Animated examples and interactive activities*

VSEPR Theory
Hybridization

Flashcards *Key terms and definitions*

Online Flashcards

Self-Assessment Questions *Additional questions with full worked-out solutions*

6 Self-Assessment Questions



ACE the Test

Multiple-choice quizzes
3 ACE Practice Tests

Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

10.1 The Valence-Shell Electron-Pair Repulsion (VSEPR) Model

- Define *molecular geometry*.
- Define *valence-shell electron-pair repulsion model*.
- Note the difference between the arrangement of electron pairs about a central atom and molecular geometry.
- Note the four steps in the prediction of geometry by the VSEPR model.
- Predict the molecular geometry (two, three, or four electron pairs). **Example 10.1**
- Note that a lone pair tends to require more space than a corresponding bonding pair and that a multiple bond requires more space than a single bond.
- Predict the molecular geometry (five or six electron pairs). **Example 10.2**

10.2 Dipole Moment and Molecular Geometry

- Define *dipole moment*.
- Explain the relationship between dipole moment and molecular geometry. **Example 10.3**
- Note that the polarity of a molecule can affect certain properties, such as a boiling point.

10.3 Valence Bond Theory

- Define *valence bond theory*.
- State the two conditions needed for bond formation, according to valence bond theory.
- Define *hybrid orbitals*.
- State the five steps in describing bonding, following the valence bond theory.

- Apply valence bond theory (two, three, or four electron pairs). **Example 10.4**
- Apply valence bond theory (five or six electron pairs). **Example 10.5**

10.4 Description of Multiple Bonding

- Define σ (sigma) bond.
- Define π (pi) bond.
- Apply valence bond theory (multiple bonding). **Example 10.6**
- Explain geometric, or *cis-trans*, isomers in terms of the π -bond description of a double bond.

10.5 Principles of Molecular Orbital Theory

- Define *molecular orbital theory*.
- Define *bonding orbitals* and *antibonding orbitals*.
- Define *bond order*.

- State the two factors that determine the strength of interaction between two atomic orbitals.
- Describe the electron configurations of H_2 , He_2 , Li_2 , and Be_2 .

10.6 Electron Configurations of Diatomic Molecules of the Second-Period Elements

- Define *homonuclear diatomic molecules* and *heteronuclear diatomic molecules*.
- Describe molecular orbital configurations (homonuclear diatomic molecules). **Example 10.7**
- Describe molecular orbital configurations (heteronuclear diatomic molecules). **Example 10.8**

10.7 Molecular Orbitals and Delocalized Bonding

- Describe the delocalized bonding in molecules such as O_3 .

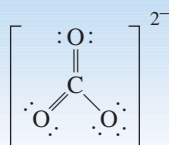
Self-Assessment and Review Questions

- 10.1** Describe the main features of the VSEPR model.
- 10.2** According to the VSEPR model, what are the arrangements of two, three, four, five, and six valence-shell electron pairs about an atom?
- 10.3** Why is a lone pair expected to occupy an equatorial position instead of an axial position in the trigonal bipyramidal arrangement?
- 10.4** Why is it possible for a molecule to have polar bonds, yet have a dipole moment of zero?
- 10.5** Explain why nitrogen trifluoride has a small dipole moment even though it has polar bonds in a trigonal pyramidal arrangement.
- 10.6** Explain in terms of valence bond theory why the orbitals used on an atom give rise to a particular geometry about that atom.
- 10.7** What is the angle between two sp^3 hybrid orbitals?
- 10.8** What is the difference between a sigma bond and a pi bond?
- 10.9** Describe the bonding in ethylene, C_2H_4 , in terms of valence bond theory.
- 10.10** How does the valence bond description of a carbon-carbon double bond account for *cis-trans* isomers?
- 10.11** What are the differences between a bonding and an antibonding molecular orbital of a diatomic molecule?
- 10.12** What factors determine the strength of interaction between two atomic orbitals to form a molecular orbital?
- 10.13** Describe the formation of bonding and antibonding molecular orbitals resulting from the interaction of two $2s$ orbitals.
- 10.14** Describe the formation of molecular orbitals resulting from the interaction of two $2p$ orbitals.
- 10.15** How does molecular orbital theory describe the bonding in the HF molecule?
- 10.16** Describe the bonding in O_3 , using molecular orbital theory. Compare this with the resonance description.
- 10.17** According to the VSEPR model, the H—P—H bond angle in PH_3 is
 a. 120° b. 109.5° c. 90°
 d. a little less than 120° e. a little less than 109.5°
- 10.18** Which of the following molecular geometries does the XeF_5^+ cation exhibit?
 a. tetradral
 b. T-shaped
 c. octahedral
 d. square pyramidal
 e. trigonal bipyramidal
- 10.19** Which of the following would be a polar molecule?
 a. CO_2 b. H_2S c. CH_4 d. SF_6 e. BeF_2
- 10.20** What is the bond order of NO?
 a. $\frac{1}{2}$ b. 1 c. $\frac{3}{2}$ d. 3 e. $\frac{5}{2}$

Concept Explorations

10.21 Best Lewis Formula and Molecular Geometry

A student writes the Lewis electron-dot formula for the carbonate anion, CO_3^{2-} , as



- a. Does this Lewis formula obey the octet rule? Explain. What are the formal charges on the atoms? Try describing the bonding for this formula in valence bond terms. Do you have any difficulty doing this?
- b. Does this Lewis formula give a reasonable description of the electron structure, or is there a better one? If there is a better Lewis formula, write it down and explain why it is better.

- c. The same student writes the following resonance description for CO_2 :

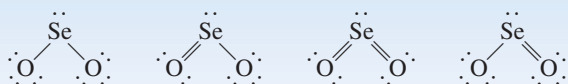


Is there something wrong with this description? (What would you predict as the geometries of these formulas?)

- d. Is one or the other formula a better description? Could a value for the dipole moment help you decide?
- e. Can you write a Lewis formula that gives an even better description of CO_2 ? Explain your answer.

10.22 Molecular Geometry and Bonding

- a. Shown here are several potential Lewis electron-dot formulas for the SeO_2 molecule.



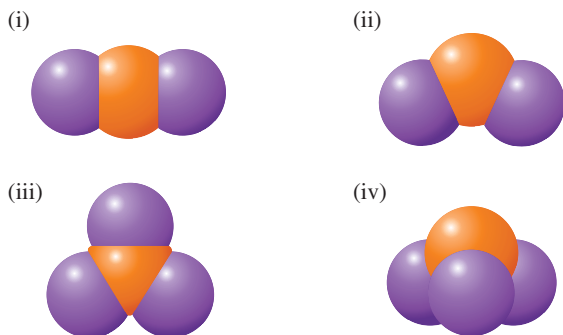
Are there any electron-dot formulas that you expect to give the best description? How would you describe the bonding in terms of electron-dot formulas?

- b. Describe the bonding in SeO_2 in valence bond terms. If there is delocalized bonding, note this in your description and explain how molecular orbital theory can be useful here.
- c. Determine the arrangement of electron pairs about Se in the SeO_2 molecule. What would you expect for the molecular geometry of the SeO_2 molecule?
- d. Would you expect the $\text{O}-\text{Se}-\text{O}$ angle in the SeO_2 molecule to be greater than, equal to, or less than 120° . Explain your answer.
- e. Draw an electron-dot formula for the H_2Se molecule and determine its molecular geometry.
- f. Compare the $\text{H}-\text{Se}-\text{H}$ bond angle to the $\text{O}-\text{Se}-\text{O}$ bond angle. Is it larger or smaller? Explain.
- g. Determine whether the H_2Se and SeO_2 molecules have dipole moments. Describe how you arrived at your answer.

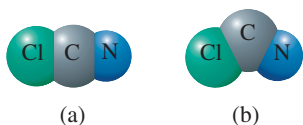
Conceptual Problems

10.23 Match the following molecular substances with one of the molecular models (i) to (iv) that correctly depicts the geometry of the corresponding molecule.

- a. SeO_2 b. BeCl_2 c. PBr_3 d. BCl_3



10.24 Which of the following molecular models correctly depicts the geometry of ClCN ?



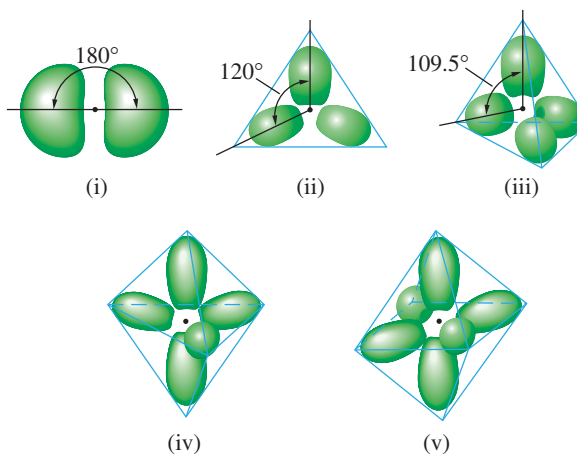
10.25 Suppose that an ethane molecule, CH_3CH_3 , is broken into two CH_3 molecules in such a way that one $:\text{CH}_3$ molecule retains the electron pair that was originally the one making up the $\text{C}-\text{C}$ bond. The other CH_3 molecule has two fewer

electrons. Imagine that momentarily this CH_3 molecule has the geometry it had in the ethane molecule. Describe the electron repulsions present in this molecule, and indicate how they would be expected to rearrange its geometry.

10.26 Suppose that a BF_3 molecule approaches the lone pair on the N atom of an $:\text{NH}_3$ molecule, and that a bond forms between the B atom and the N atom. Consider the arrangement of electron pairs about the B atom at the moment of this bond formation, and describe the repulsions among the electron pairs and how they might be expected to change the geometry about the B atom.

10.27 Indicate what hybrid orbital depicted below is expected for the central atom of each of the following:

- a. BeF_2 b. SiF_4 c. SeF_4 d. RnF_4

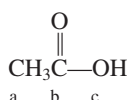


10.28 An atom in a molecule has two bonds to other atoms and one lone pair. What kind of hybrid orbitals do you expect for this atom? Describe how you arrived at your answer.

10.29 Two compounds have the same molecular formula, $C_2H_2Br_2$. One has a dipole moment; the other does not. Both compounds react with bromine, Br_2 , to produce the same compound. This reaction is a generally accepted test for double bonds, and each bromine atom of Br_2 adds to a different atom of the double bond. What is the identity of the original compounds? Describe the argument you use.

10.30 A neutral molecule is identified as a tetrafluoride, XF_4 , where X is an unknown atom. If the molecule has a dipole moment of 0.63 D, can you give some possibilities for the identity of X?

10.31 Acetic acid, the sour constituent of vinegar, has the following structure:



Indicate what geometry given below is expected to be found about each of the atoms labeled a, b, and c.

Practice Problems

The VSEPR Model

10.33 Predict the shape or geometry of the following molecules, using the VSEPR model.

- a. SiF_4 b. SF_2 c. COF_2 d. PCl_3

10.34 Use the electron-pair repulsion model to predict the geometry of the following molecules:

- a. GeCl_2 b. NF_3 c. SCl_2 d. XeO_4

10.35 Predict the geometry of the following ions, using the electron-pair repulsion model.

- a. ClO_3^- b. PO_4^{3-} c. SCN^- d. H_3O^+

10.36 Use the VSEPR model to predict the geometry of the following ions:

- a. N_3^- b. BH_4^- c. SO_3^{2-} d. NO_2^-

10.37 For each of the following molecules, state the bond angle (or bond angles, as appropriate) that you would expect to see on the central atom based on the simple VSEPR model. Would you expect the actual bond angles to be greater or less than this?

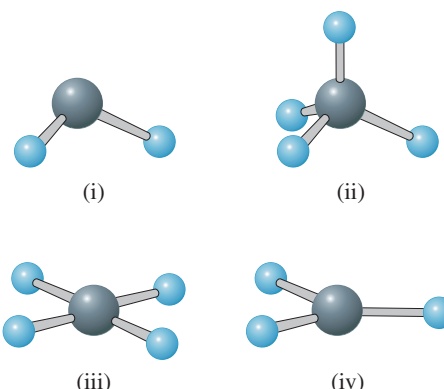
- a. CCl_4 b. SCl_2 c. COCl_2 d. AsH_3

10.38 For each of the following molecules, state the bond angle (or bond angles, as appropriate) that you would expect to see on the central atom based on the simple VSEPR model. Would you expect the actual bond angles to be greater or less than this?

- a. NCl_3 b. CF_2CF_2 c. GeF_4 d. OF_2

10.39 What geometry is expected for the following molecules, according to the VSEPR model?

- a. PF_5 b. BrF_3 c. BrF_5 d. SCl_4



10.32 What are the bond angles predicted by the VSEPR model about the carbon atom in the formate ion, HCO_2^- ? Considering that the bonds to this atom are not identical, would you expect the experimental values to agree precisely with the VSEPR values? How might they differ?

10.40 From the electron-pair repulsion model, predict the geometry of the following molecules:

- a. ClF_5 b. SbF_5 c. SeF_4 d. TeF_6

10.41 Predict the geometries of the following ions, using the VSEPR model.

- a. SnCl_5^- b. PF_6^- c. ClF_2^- d. IF_4^-

10.42 Name the geometries expected for the following ions, according to the electron-pair repulsion model.

- a. ICl_2^- b. BrF_4^- c. ClF_6^+ d. ClF_4^+

Dipole Moment and Molecular Geometry

10.43 (a) The molecule AsF_3 has a dipole moment of 2.59 D. Which of the following geometries are possible: trigonal planar, trigonal pyramidal, or T-shaped? (b) The molecule H_2S has a dipole moment of 0.97 D. Is the geometry linear or bent?

10.44 (a) The molecule BrF_3 has a dipole moment of 1.19 D. Which of the following geometries are possible: trigonal planar, trigonal pyramidal, or T-shaped? (b) The molecule TeCl_4 has a dipole moment of 2.54 D. Is the geometry tetrahedral, seesaw, or square planar?

10.45 Which of the following molecules would be expected to have zero dipole moment on the basis of their geometry?

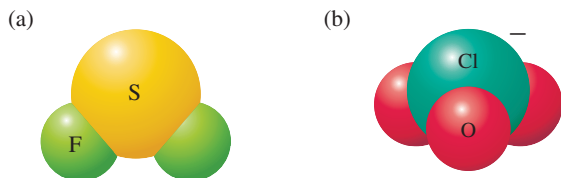
- a. CS_2 b. TeF_2 c. SeCl_4 d. XeF_4

10.46 Which of the following molecules would be expected to have a dipole moment of zero because of symmetry?

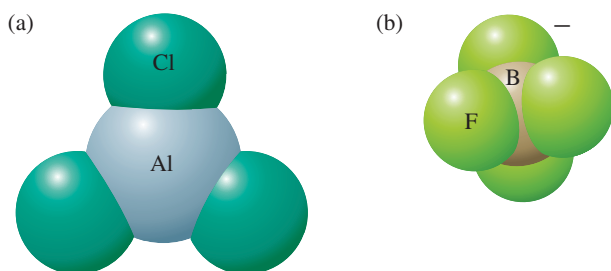
- a. SeF_2
b. BeI_2
c. TeF_6
d. TeF_4

Valence Bond Theory

10.47 What hybrid orbitals would be expected for the central atom in each of the following molecules or ions?



10.48 What hybrid orbitals would be expected for the central atom in each of the following molecules or ions?



10.49 What hybrid orbitals would be expected for the central atom in each of the following molecules or ions?

- a. SeCl_2 b. NO_2^- c. CO_2 d. COF_2

10.50 What hybrid orbitals would be expected for the central atom in each of the following molecules or ions?

- a. GeCl_4 b. PBr_3 c. BeF_2 d. SO_2

10.51 (a) Mercury(II) chloride dissolves in water to give poorly conducting solutions, indicating that the compound is largely nonionized in solution—it dissolves as HgCl_2 molecules. Describe the bonding of the HgCl_2 molecule, using valence bond theory. (b) Phosphorus trichloride, PCl_3 , is a colorless liquid with a highly irritating vapor. Describe the bonding in the PCl_3 molecule, using valence bond theory. Use hybrid orbitals.

10.52 (a) Nitrogen trifluoride, NF_3 , is a relatively unreactive, colorless gas. How would you describe the bonding in the NF_3 molecule in terms of valence bond theory? Use hybrid orbitals. (b) Silicon tetrafluoride, SiF_4 , is a colorless gas formed when hydrofluoric acid attacks silica (SiO_2) or glass. Describe the bonding in the SiF_4 molecule, using valence bond theory.

10.53 What hybrid orbitals would be expected for the central atom in each of the following?

- a. XeF_2
b. BrF_5
c. PCl_5
d. ClF_4^+

10.54 What hybrid orbitals would be expected for the central atom in each of the following?

- a. BrF_3 b. TeF_4 c. XeF_4 d. IF_4^-

10.55 Phosphorus pentachloride is normally a white solid. It exists in this state as the ionic compound $[\text{PCl}_4^+][\text{PCl}_6^-]$.

Describe the electron structure of the PCl_6^- ion in terms of valence bond theory.

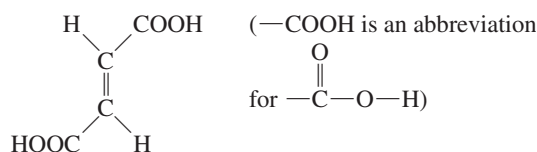
10.56 Iodine, I_2 , dissolves in an aqueous solution of iodide ion, I^- , to give the triiodide ion, I_3^- . This ion consists of one iodine atom bonded to two others. Describe the bonding of I_3^- in terms of valence bond theory.

10.57 (a) Formaldehyde, H_2CO , is a colorless, pungent gas used to make plastics. Give the valence bond description of the formaldehyde molecule. (Both hydrogen atoms are attached to the carbon atom.) (b) Nitrogen, N_2 , makes up about 80% of the earth's atmosphere. Give the valence bond description of this molecule.

10.58 (a) The molecule $\text{HN}=\text{NH}$ exists as a transient species in certain reactions. Give the valence bond description of this species. (b) Hydrogen cyanide, HCN , is a very poisonous gas or liquid with the odor of bitter almonds. Give the valence bond description of HCN . (Carbon is the central atom.)

10.59 The hyponitrite ion, $^-\text{O}-\text{N}=\text{N}-\text{O}^-$, exists in solid compounds as the *trans* isomer. Using valence bond theory, explain why *cis-trans* isomers might be expected for this ion. Draw structural formulas of the *cis-trans* isomers.

10.60 Fumaric acid, $\text{C}_4\text{H}_4\text{O}_4$, occurs in the metabolism of glucose in the cells of plants and animals. It is used commercially in beverages. The structural formula of fumaric acid is



Maleic acid is the *cis* isomer of fumaric acid. Using valence bond theory, explain why these isomers are possible.

Molecular Orbital Theory

10.61 Describe the electronic structure of each of the following, using molecular orbital theory. Calculate the bond order of each and decide whether it should be stable. For each, state whether the substance is diamagnetic or paramagnetic.

- a. B_2 b. B_2^+ c. O_2^-

10.62 Use molecular orbital theory to describe the bonding in the following. For each one, find the bond order and decide whether it is stable. Is the substance diamagnetic or paramagnetic?

- a. Be_2^+
b. Ne_2
c. B_2^-

10.63 Assume that the cyanide ion, CN^- , has molecular orbitals similar to those of a homonuclear diatomic molecule. Write the configuration and bond order of CN^- . Is a substance of the ion diamagnetic or paramagnetic?

10.64 Write the molecular orbital configuration of the diatomic molecule BN . What is the bond order of BN ? Is the substance diamagnetic or paramagnetic? Use the order of energies that was given for homonuclear diatomic molecules.

General Problems

10.65 Predict the molecular geometry of the following:

- a. SnCl_2 b. COBr_2 c. ICl_2^- d. PCl_6^-

10.66 Predict the molecular geometry of the following:

- a. HOF b. NH_4^+ c. PF_5 d. ClF_4^+

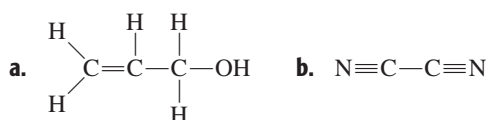
10.67 Which of the following molecules or ions are linear?

- a. SeF_2 b. CHCl_3 c. SeF_4 d. SnF_6^{2-}

10.68 Which of the following molecules or ions are trigonal planar?

- a. BBr_3 b. AsH_3 c. ClF_4^- d. TeF_5^-

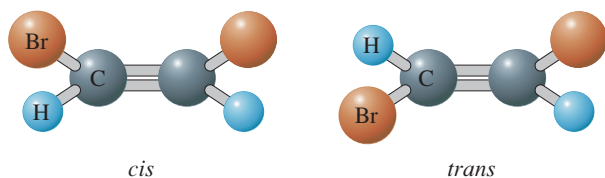
10.69 Describe the hybrid orbitals used by each carbon atom in the following molecules:



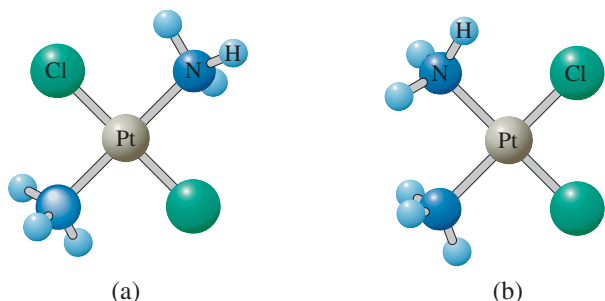
10.70 Describe the hybrid orbitals used by each nitrogen atom in the following molecules:



10.71 Explain how the dipole moment could be used to distinguish between the *cis* and *trans* isomers of 1,2-dibromoethene:



10.72 Two compounds have the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. (Compound B is *cisplatin*, mentioned in the opening to Chapter 1.) They have square planar structures. One is expected to have a dipole moment; the other is not. Which one would have a dipole moment?



10.73 Explain in terms of bonding theory why all four hydrogen atoms of allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, cannot lie in the same plane.

10.74 Explain in terms of bonding theory why all atoms of $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ must lie in the same plane.

10.75 What is the molecular orbital configuration of HeH^+ ? Do you expect the ion to be stable?

10.76 What is the molecular orbital configuration of He_2^+ ? Do you expect the ion to be stable?

10.77 Calcium carbide, CaC_2 , consists of Ca^{2+} and C_2^{2-} (acetylide) ions. Write the molecular orbital configuration and bond order of the acetylide ion, C_2^{2-} .

10.78 Sodium peroxide, Na_2O_2 , consists of Na^+ and O_2^{2-} (peroxide) ions. Write the molecular orbital configuration and bond order of the peroxide ion, O_2^{2-} .

10.79 The oxygen–oxygen bond in O_2^+ is 112 pm and in O_2 is 121 pm. Explain why the bond length in O_2^+ is shorter than in O_2 . Would you expect the bond length in O_2^- to be longer or shorter than that in O_2 ? Why?

10.80 The nitrogen–nitrogen bond distance in N_2 is 109 pm. On the basis of bond orders, would you expect the bond distance in N_2^+ to be less than or greater than 109 pm? Answer the same question for N_2^- .

10.81 Using molecular orbital theory, determine the electronic structure of the first excited electronic state of N_2 . What differences are expected in the properties of the excited state of N_2 compared with the same properties of the ground state?

10.82 The ionization energy of O_2 is smaller than the ionization energy of atomic O; the opposite is true for the ionization energies of N_2 and atomic N. Explain this behavior in terms of the molecular orbital energy diagrams of O_2 and N_2 .

10.83 Describe the property of “handedness.” What is it about the bonding of atoms in molecules that can give rise to handedness in molecules?

10.84 Biological molecules frequently display handedness. Describe the difference between the molecule responsible for the flavor of spearmint and the molecule responsible for the flavor of caraway seeds. In which way are the molecules similar and in which way do they differ?

10.85 Color vision results from the absorption of light by the cone cells of the retina. Briefly describe how different types of cone cells give rise to color vision. What is the chemical substance primarily responsible for human vision? How can its color absorption be changed?

10.86 Describe the *cis–trans* conversion that occurs in the ultraviolet absorption of *cis*-1,2-dichloroethene.

10.87 What is the biological importance of stratospheric ozone? Explain.

10.88 In 1995, Sherwood Rowland and Mario Molina received the Nobel Prize in chemistry. Explain in some detail the work they did for which they were awarded this prize.

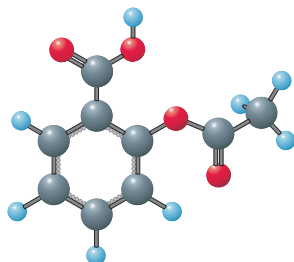
Strategy Problems

10.89 Calcium carbide, CaC_2 , has an ionic structure with ions Ca^{2+} and C_2^{2-} . Give the valence bond description of the bonding in the C_2^{2-} ion. Now write the MO configuration of this ion. What is the bond order according to this configuration? Compare the valence bond and molecular orbital descriptions.

10.90 Write Lewis formulas for the BF molecule (two with a single $\text{B}-\text{F}$ bond, two with a double $\text{B}=\text{F}$ bond, and one with a triple $\text{B}\equiv\text{F}$ bond) in which the octet rule is satisfied for at least one of the atoms. Obtain the formal charges of the atoms. Based on the information you have, is there one formula that you think best describes the molecule? Explain. For this best Lewis formula, give the valence bond description of the bonding.

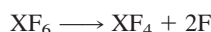
10.91 Boron trifluoride, BF_3 , reacts with ammonia, NH_3 , to form an addition compound, BF_3NH_3 . Describe the geometries about the B and the F atoms in this compound. Describe the hybridization on these two atoms. Now describe the bonding between the B and F atoms, using valence bond theory. Compare the geometries and hybridization of these atoms in this addition compound with that in the reactant molecules BF_3 and NH_3 .

10.92 Acetylsalicylic acid (aspirin) has the structure shown by the following molecular model:



Describe the geometry and bonding about the carbon atom shown at the top of the model, in which the carbon atom (in black) is bonded to two oxygen atoms (red) and to another carbon atom. One of the oxygen atoms is bonded to a hydrogen atom (blue).

10.93 A molecule XF_6 (having no lone pairs) has a dipole moment of zero. (X denotes an unidentified element.) When two atoms of fluorine have been taken away, you get the molecule XF_4 , which has dipole moment of 0.632 D.



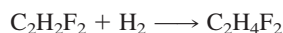
Describe the molecular geometry and bonding for each molecule. What are some possibilities for X?

Cumulative-Skills Problems

10.99 A molecular compound is composed of 60.4% Xe, 22.1% O, and 17.5% F, by mass. If the molecular weight is 217.3 amu, what is the molecular formula? What is the Lewis formula? Predict the molecular geometry using the VSEPR model. Describe the bonding, using valence bond theory.

10.100 A molecular compound is composed of 58.8% Xe, 7.2% O, and 34.0% F, by mass. If the molecular weight is 223 amu, what is the molecular formula? What is the Lewis formula? Predict the molecular geometry using the VSEPR model. Describe the bonding, using valence bond theory.

10.94 Three different compounds have the same molecular formula, $\text{C}_2\text{H}_2\text{F}_2$; call them A, B, and C. Compound A has a dipole moment of 2.42 D, compound B has a dipole moment of 1.38 D, and compound C has a dipole moment of 0 D. All three compounds react with hydrogen, H_2 :



Compound A gives product D (molecular formula $\text{C}_2\text{H}_4\text{F}_2$), compound B gives product E (same molecular formula, $\text{C}_2\text{H}_4\text{F}_2$, but different from product D), and compound C gives product D. Identify the structural formulas of compounds A, B, and C.

10.95 Obtain a Lewis formula of H_2N_2 . This molecule exhibits isomerism (it has two isomers). Sketch the electron-dot formulas of these isomers. Describe the bonding in terms of valence bond theory, and explain this isomerism in terms of this bonding description.

10.96 Dioxygen, O_2 , has sometimes been represented by the electron-dot formula



Note, however, that this formula implies that all electrons are paired. Give the molecular orbital description of the state of the O_2 molecule of lowest energy in which all electrons are paired in this way. Compare this configuration with that of the ground state of O_2 . In what way are they similar, and in what way are they different?

10.97 Solid sulfur normally consists of crystals of S_8 molecules, but when heated strongly, the solid vaporizes to give S_2 molecules (among other molecular species). Describe the bonding in S_2 in molecular orbital terms, assuming the orbitals are analogous to those of the preceding period. What would you expect to happen to the sulfur-sulfur bond length if two electrons were added to give the S_2^{2-} ion? What would you expect to happen to the bond length if, instead, two electrons were taken away to give S_2^{2+} ?

10.98 Formaldehyde has the formula H_2CO . Describe the bonding between the C and O atoms in VB terms. Formaldehyde absorbs UV light at about 270 nm. The absorption is described as a π to π^* transition. Explain in molecular orbital terms what is involved.

10.101 A compound of chlorine and fluorine, ClF_n , reacts at about 75°C with uranium metal to produce uranium hexafluoride, UF_6 , and chlorine monofluoride, $\text{ClF}(g)$. A quantity of uranium produced 3.53 g UF_6 and 343 mL ClF at 75°C and 2.50 atm. What is the formula (n) of the compound? Describe the bonding in the molecule, using valence bond theory.

10.102 Excess fluorine, $\text{F}_2(g)$, reacts at 150°C with bromine, $\text{Br}_2(g)$, to give a compound BrF_n . If 423 mL $\text{Br}_2(g)$ at 150°C and 748 mmHg produced 4.20 g BrF_n , what is n ? Describe the bonding in the molecule, using valence bond theory.

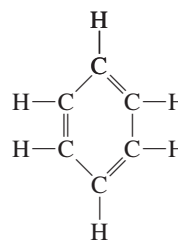
10.103 Each of the following compounds has a nitrogen–nitrogen bond: N_2 , N_2H_4 , N_2F_2 . Match each compound with one of the following bond lengths: 110 pm, 122 pm, 145 pm. Describe the geometry about one of the N atoms in each compound. What hybrid orbitals are needed to describe the bonding in valence bond theory?

10.104 The bond length in C_2 is 131 pm. Compare this with the bond lengths in C_2H_2 (120 pm), C_2H_4 (134 pm), and C_2H_6 (153 pm). What bond order would you predict for C_2 from its bond length? Does this agree with the molecular orbital configuration you would predict for C_2 ?

10.105 Draw resonance formulas of the nitric acid molecule, HNO_3 . What is the geometry about the N atom? What is the hybridization on N? Use bond energies and one Lewis formula for HNO_3 to estimate ΔH_f° for $\text{HNO}_3(\text{g})$. The actual value of ΔH_f° for $\text{HNO}_3(\text{g})$ is -135 kJ/mol , which is lower than the estimated value because of stabilization of HNO_3 by resonance. The

resonance energy is defined as $\Delta H_f^\circ(\text{estimated}) - \Delta H_f^\circ(\text{actual})$. What is the resonance energy of HNO_3 ?

10.106 One resonance formula of benzene, C_6H_6 , is



What is the other resonance formula? What is the geometry about a carbon atom? What hybridization would be used in valence bond theory to describe the bonding? The ΔH_f° for $\text{C}_6\text{H}_6(\text{g})$ is -83 kJ/mol ; ΔH_f° for $\text{C}(\text{g})$ is 715 kJ/mol . Obtain the resonance energy of benzene. (See Problem 10.105.)