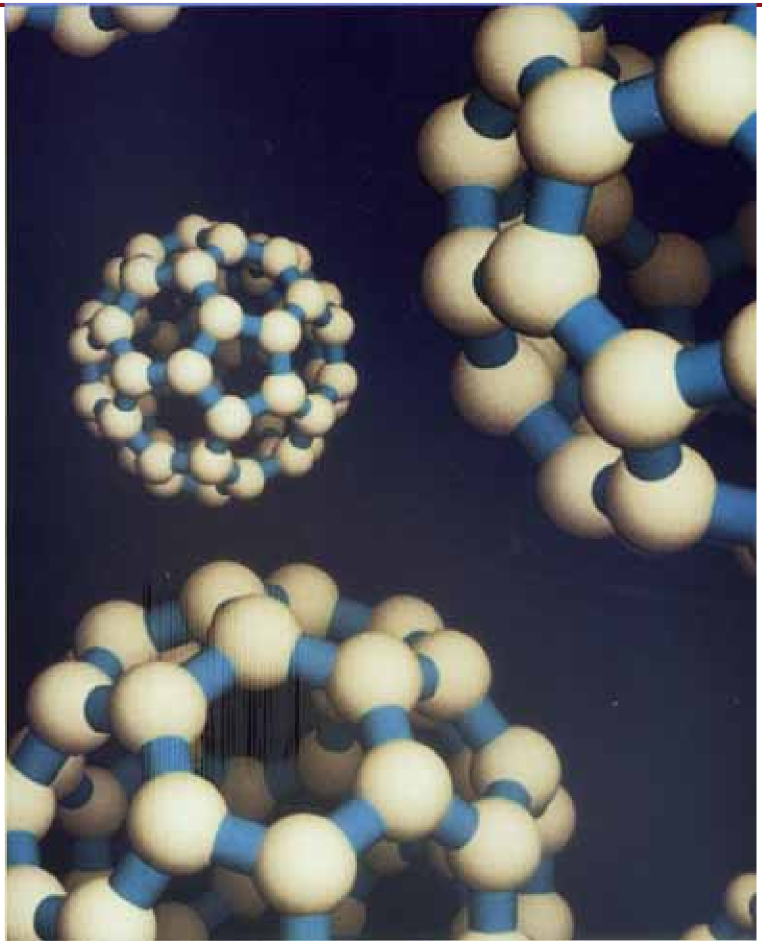
Chemistry

Zumdahl, 7th edition

歐亞書局

CH8 Bonding: General Concepts



Carbon forms very stable spherical C_{60} *molecules.*

Contents

Introduction

- As we examine the world around us, we find it to be composed almost entirely of, compounds and mixtures of compounds: Rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together.
- The manner in which atoms are bound together has a profound effect on chemical and physical properties.

8.1 Types of Chemical Bonds

- There are many types of experiments we can perform to determine the fundamental nature of materials.
- We can obtain information about the strength of a bonding interaction by measuring the **bond energy**, which is the energy required to break the bond.
- *The system can achieve the lowest possible energy by behaving in this way.*

- **ionic bonding**: The bonding forces that produce this great thermal stability result from the electrostatic attractions of the closely packed, oppositely charged ions.
- Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons.
- That is, an **ionic compound** results when a metal reacts with a nonmetal.

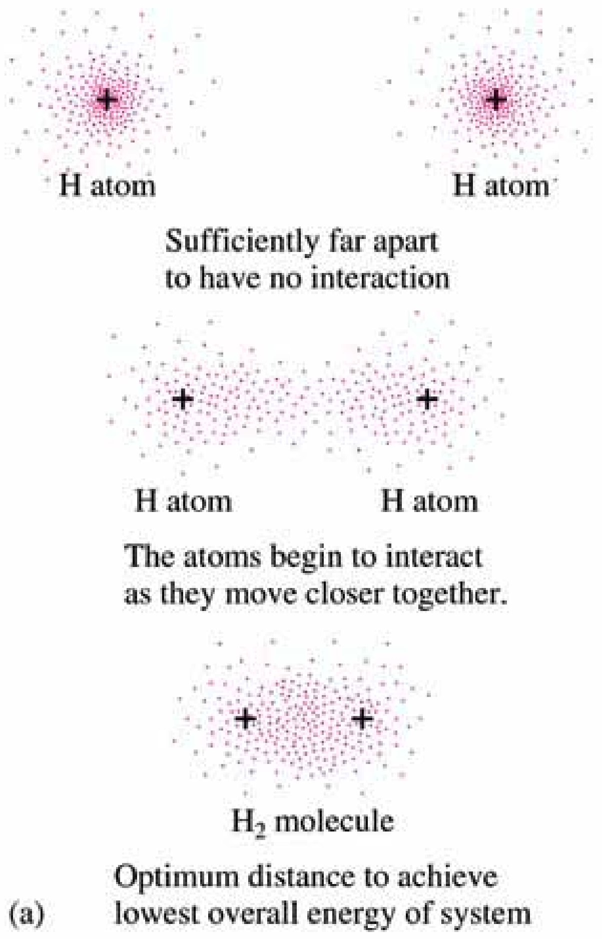
- The energy of interaction between a pair of ions can be calculated using **Coulomb's law** in the form

$$E = (2.31 \times 10^{-19}\ \mathrm{J \cdot nm})\left(\frac{Q_1 Q_2}{r}\right)$$

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

- A bonding force develops when two different types of atoms react to from oppositely charged ions.
- As shown in Fig. 8.1(a).
- The distance where the energy is minimal is called the **bond length**.
- The total energy of this system as a function of distance between the hydrogen nuclei is shown in Fig. 8.1(b).

Figure 8.1



(a) The interaction of two hydrogen atoms.

Figure 8.1

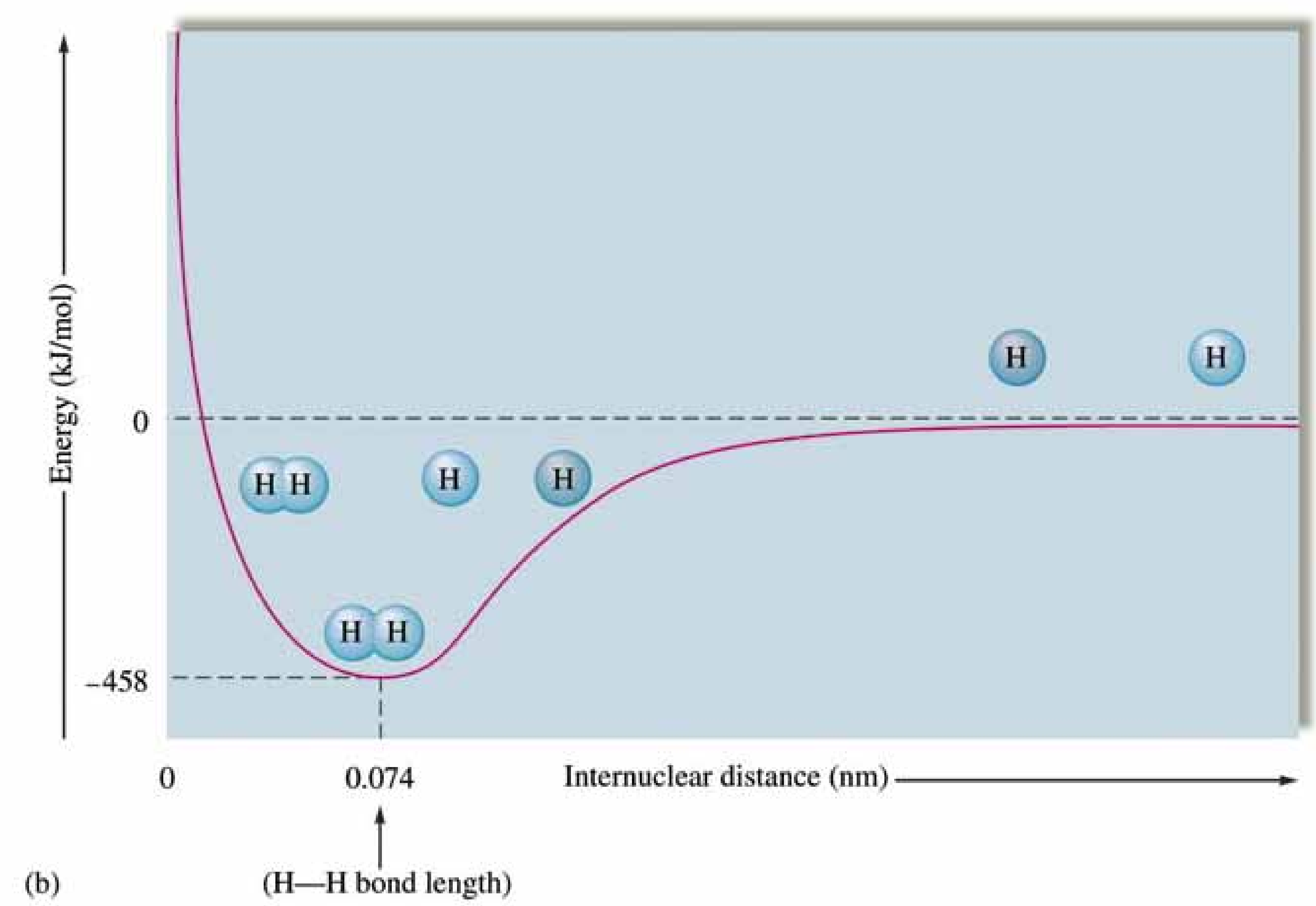

Energy (kJ/mol)
0
–458
H H
H
H
H
H
H H
0
0.074
Internuclear distance (nm)
(H—H bond length)
(b)

Figure 8.1

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

Note several important features of this diagram:

- The energy terms involved are the net potential energy that results from the attractions and repulsions among the charged particles and the kinetic energy due to the motions of the electrons.
- The zero point of energy is defined with the atoms at infinite separation.

- At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together.
- The bond length is the distance at which the system has minimum energy.

- The type of bonding we encounter in the hydrogen molecule and in many other molecules in which electrons are shared by nuclei is called **covalent bonding**.
- The bonding results from the mutual attraction of the two nuclei for the shared electrons.
- Between these extremes are intermediate cases in which the atoms are not so different that electrons are completely transferred but are different enough that unequal sharing results, forming what is called a **polar covalent bond**.

- When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves as shown in Fig. 8.2, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole.
- This result implies that the HF molecule has the following charge distribution:

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

- where δ (lowercase delta) is used to indicate a fractional charge.

8.2 Electronegativity

- The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity**: *the ability of an atom in a molecule to attract shared electrons to itself.*
- The most widely accepted method for determining values of electronegativity is that of Linus Pauling (1901-1995), an American scientist who won the Nobel Prizes for both chemistry and peace.

Figure 8.2

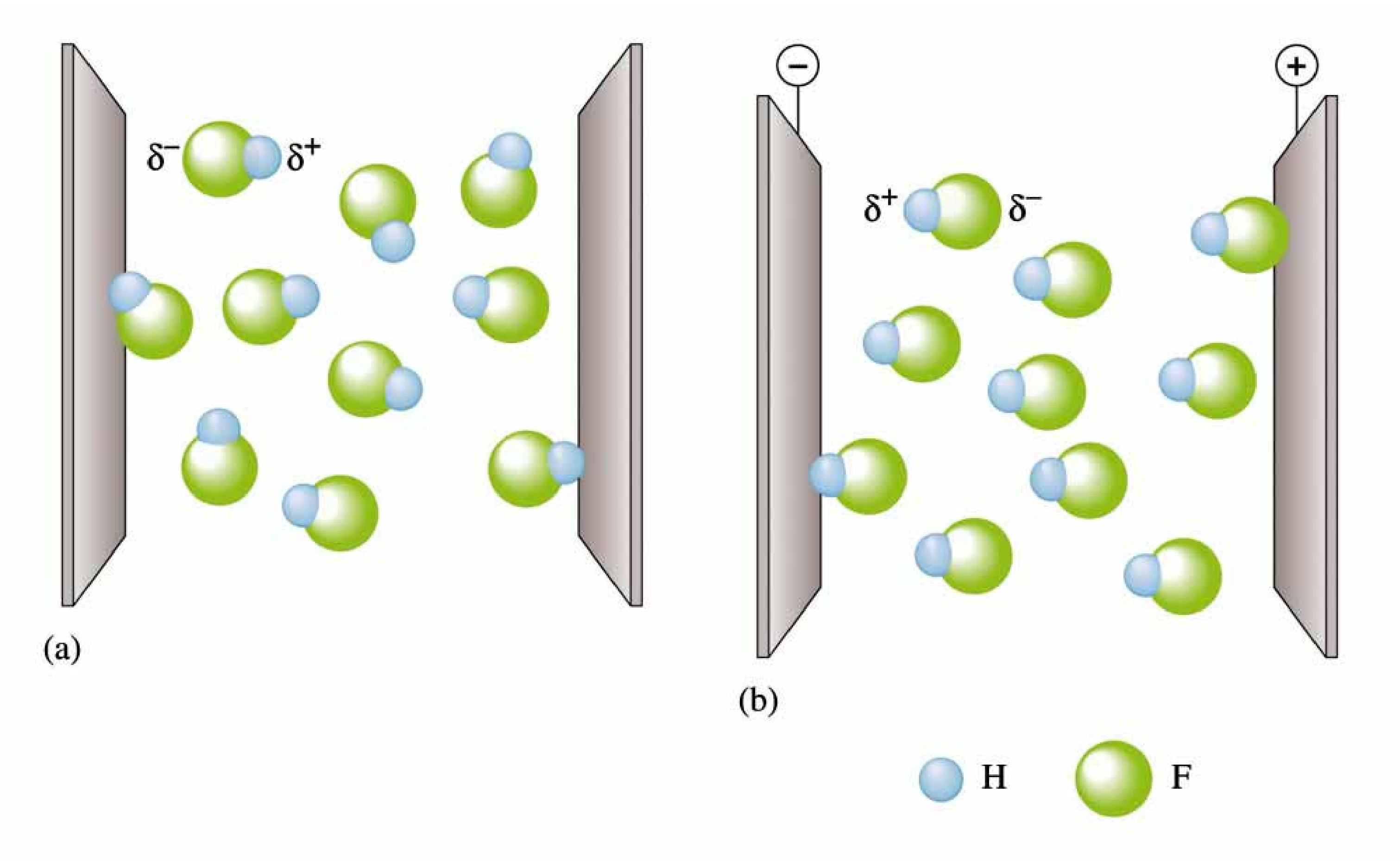


Figure 8.2

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

- The relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy with the “expected” H—X bond energy, which is an average of the H—X and X—X bond energies:

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

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

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

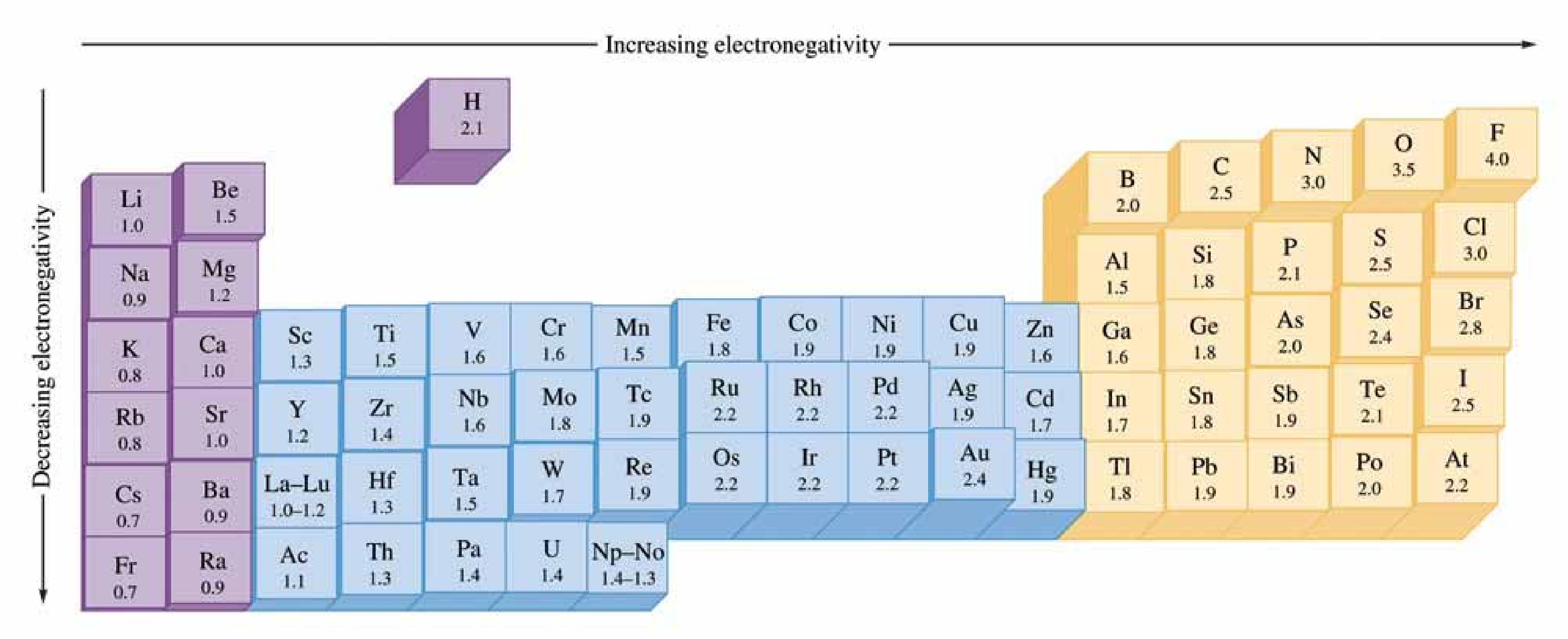
- The molecule will be polar, with the following charge distribution:

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

- Note that this bond can be viewed as having an ionic as well as a covalent component.

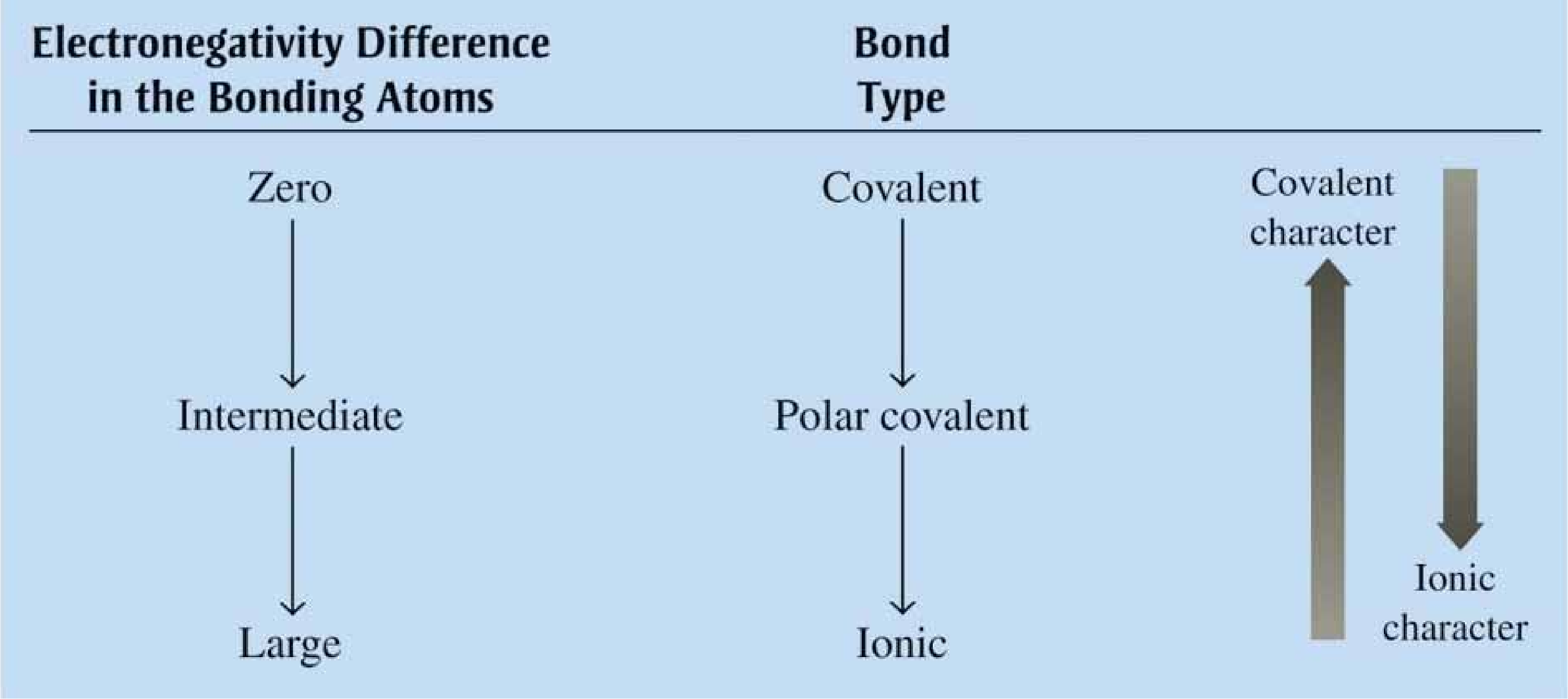
- Electronegativity values have been determined by this process for virtually all the elements: the results are given in Fig. 8.3.
- The relationship between electronegativity and bond type is shown in Table 8.1.

Figure 8.3



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

TABLE 8.1 The Relationship Between Electronegativity and Bond Type



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

Covalent character

Ionic character

Sample Exercise 8.1 Relative Bond Polarities

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

Solution

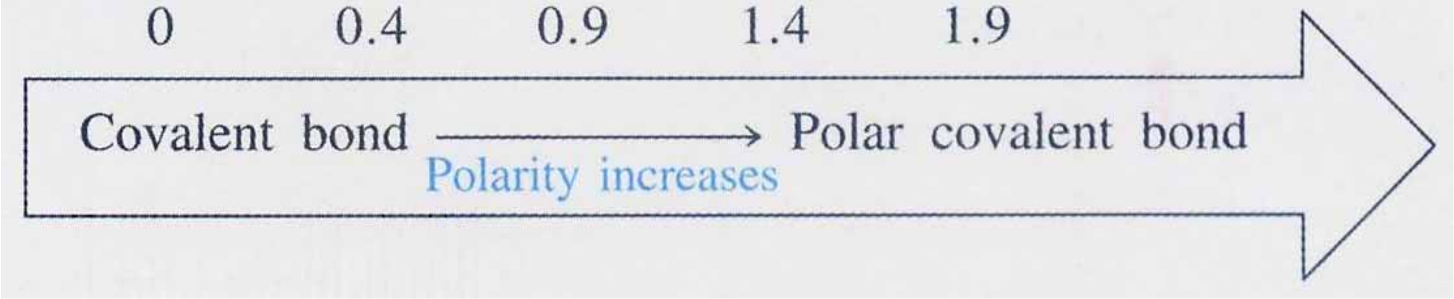
The polarity of the bond increases as the difference in electronegativity increases. From the eletronegativity values in Fig. 8.3, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):

H—H < S—H < Cl—H < O—H < F—H

(2.1)(2.1) (2.5)(2.1) (3.1)(2.1) (3.5)(2.1) (4.0)(2.1)

Sample Exercise 8.1

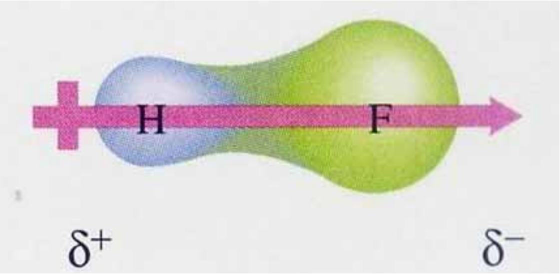
Electronegativity difference



See Exercises 8.31 and 8.32

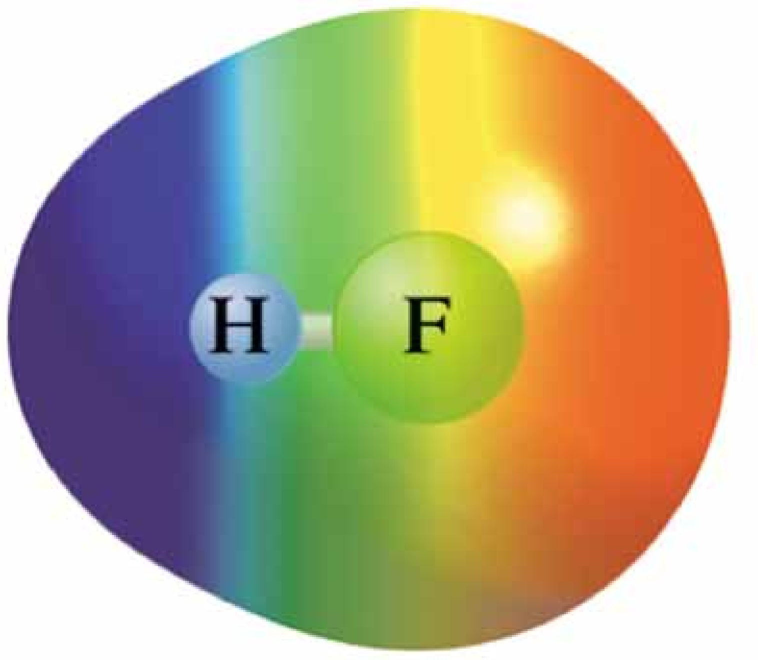
8.3 Bond Polarity and Dipole Moments

- A molecule such as HF that has a center of positive charge and a center of negative charge is said to be **dipolar**, or to have a **dipole moment**.
- The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge:



- Another way to represent the charge distribution in HF is by an electronstatic potential diagram(see Fig. 8.4).

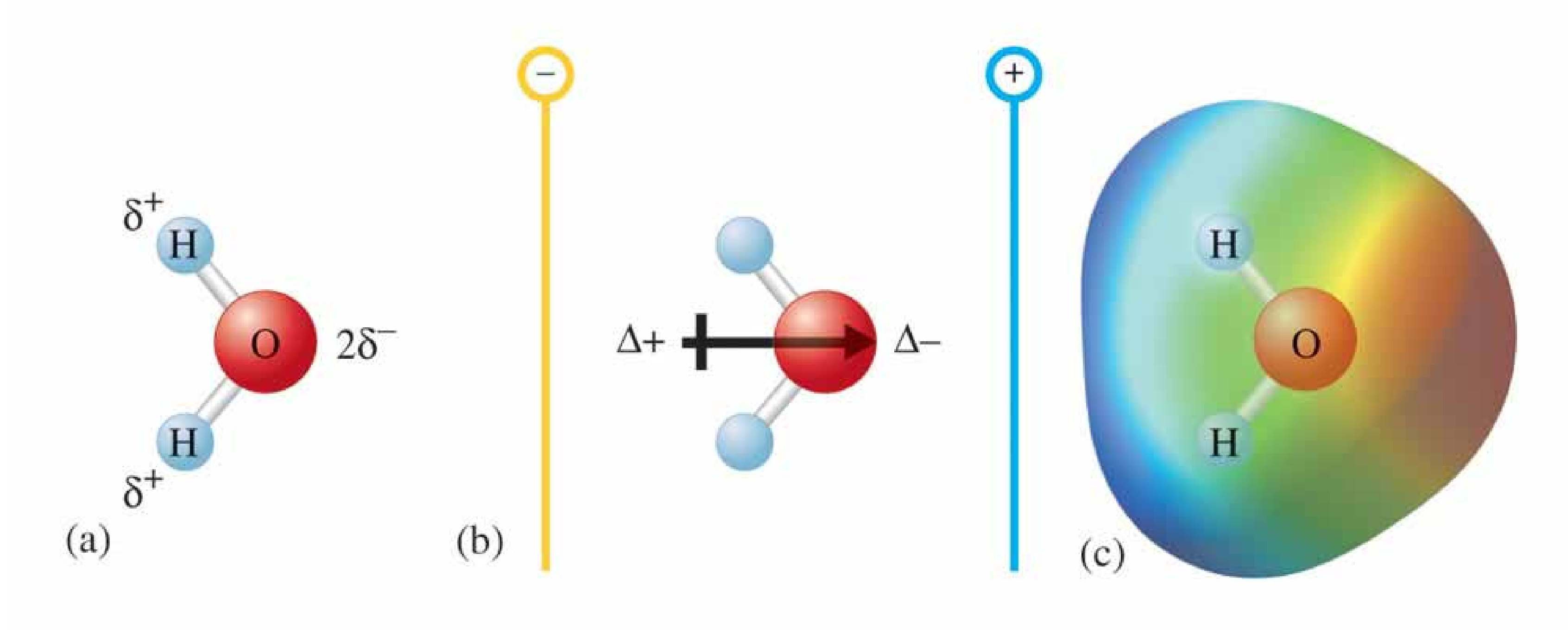
Figure 8.4



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

- Polyatomic molecules also can exhibit dipolar behavior.
- Because the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms, the molecular charge distribution is that shown in Fig. 8.5(a).
- Because of this charge distribution, the water molecule behaves in an electric field as if it had two centers of charge—one positive and one negative—as shown in Fig. 8.5(b). The water molecule has a dipole moment.

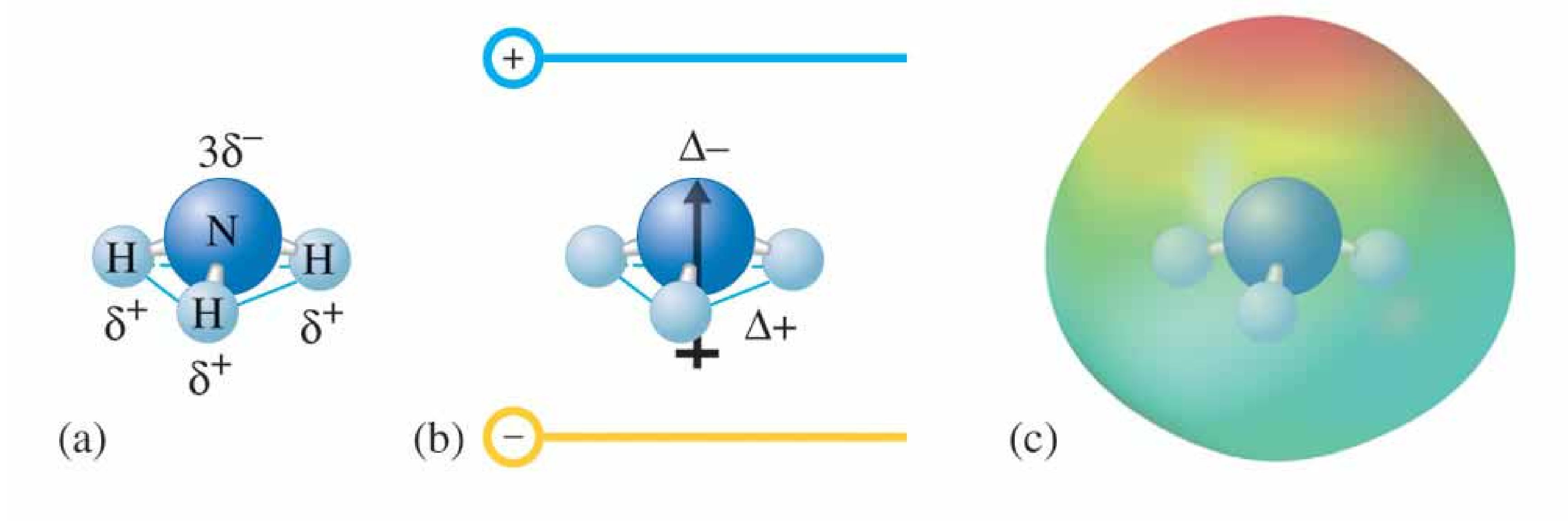
Figure 8.5



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

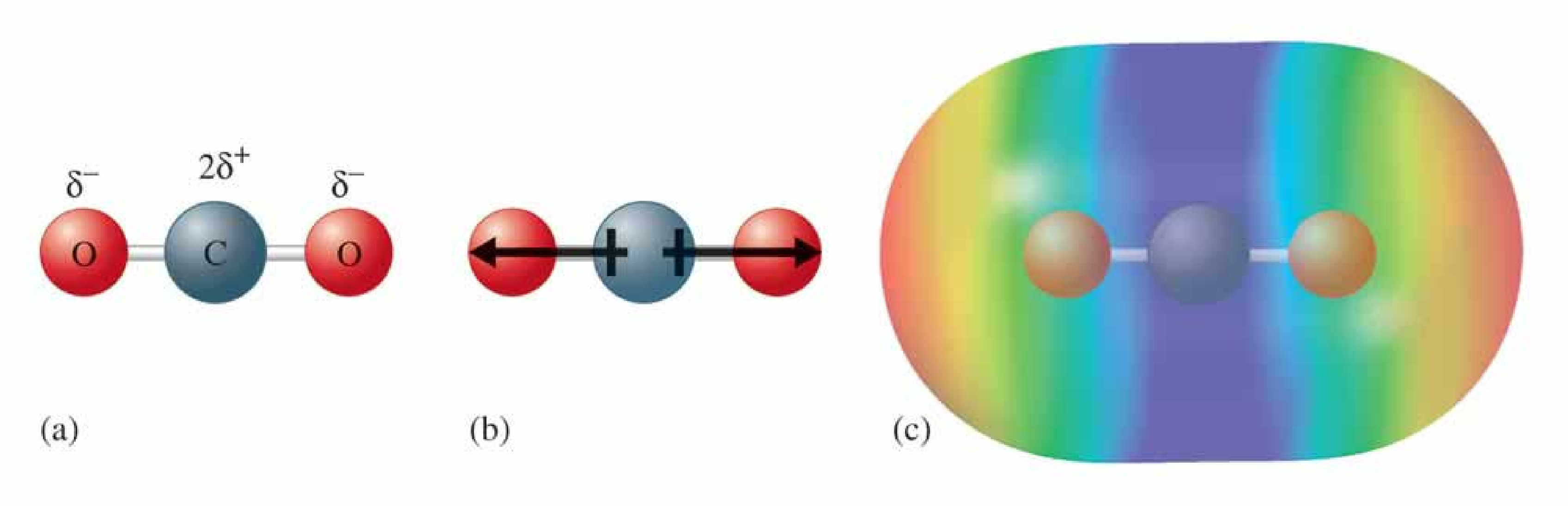
- The same type of behavior is observed for the NH_3 molecule (Fig. 8.6).
- An example is the CO_2 molecule, which is a linear molecule that has the charge distribution shown in Fig. 8.7.
- There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are shown in Table 8.2.

Figure 8.6



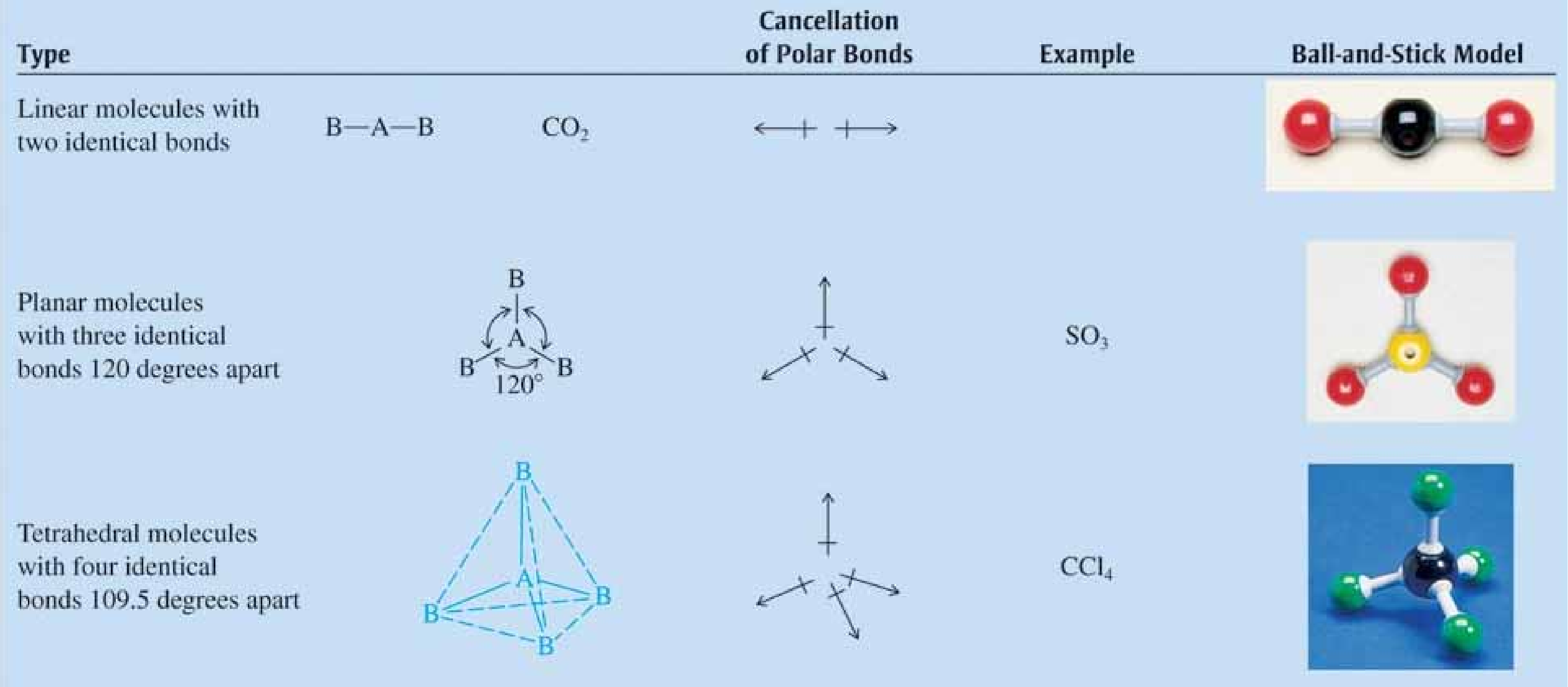
(a) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen. (b) The dipole moment of the ammonia molecule oriented in an electric field. (c) The electrostatic potential diagram for ammonia.

Figure 8.7



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

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



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

Sample Exercise 8.2

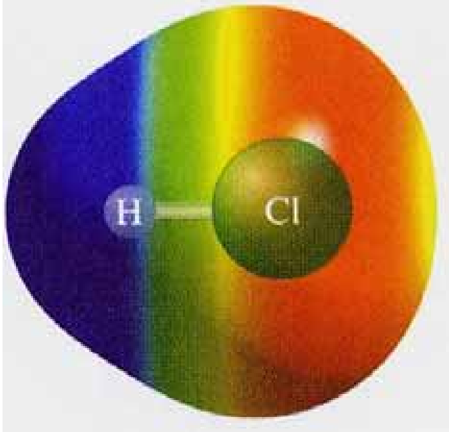
Bond Polarity and Dipole Moment

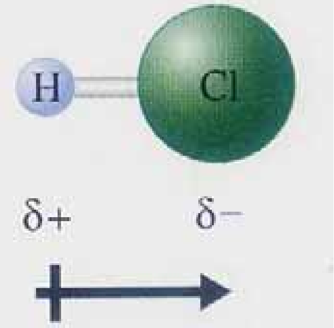
For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCl, Cl_2, SO_3 (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH_4 [tetrahedral (see Table 8.2) with the carbon atom at the center], and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

Sample Exercise 8.2

Solution

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

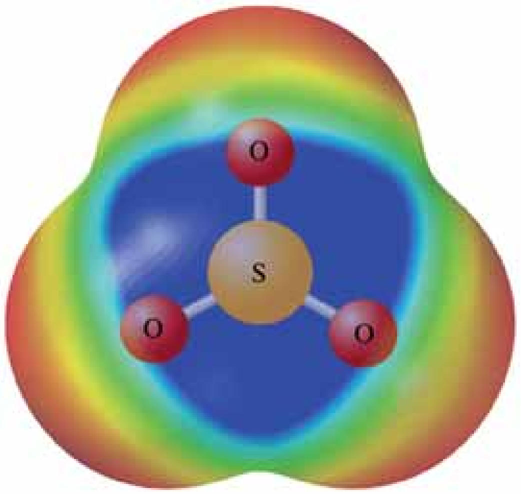




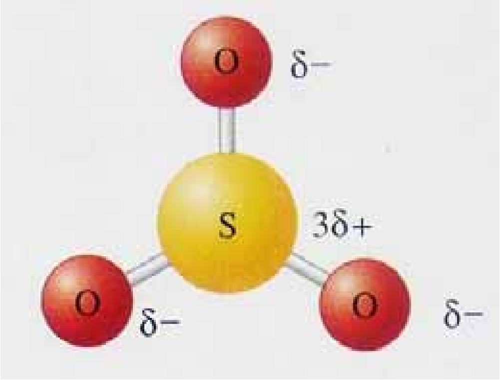
Sample Exercise 8.2

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

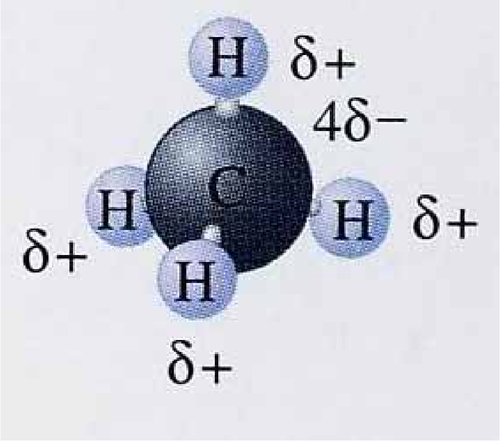
The SO_3 molecule: The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5). This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge:

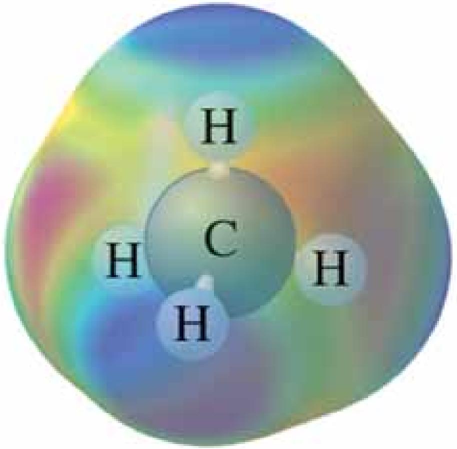


Sample Exercise 8.2



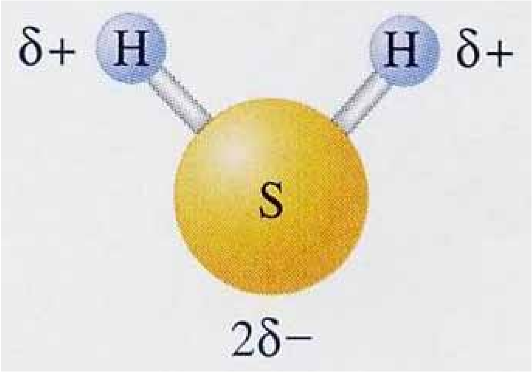
The CH_4 molecule:

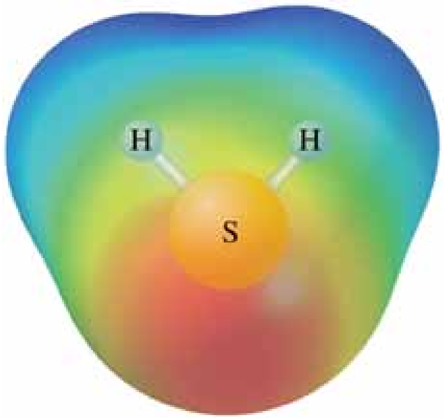




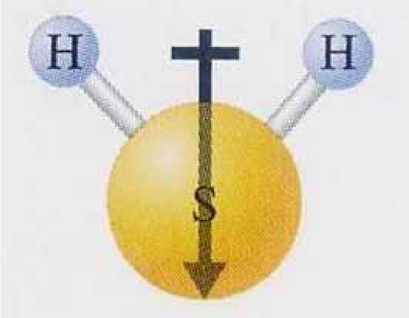
Sample Exercise 8.2

The H_2S molecule:





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



See Exercises 8.114

8.4 Ions: Electron Configurations and Sizes

- The generalizations that apply to electron configurations in stable compounds are as follows:

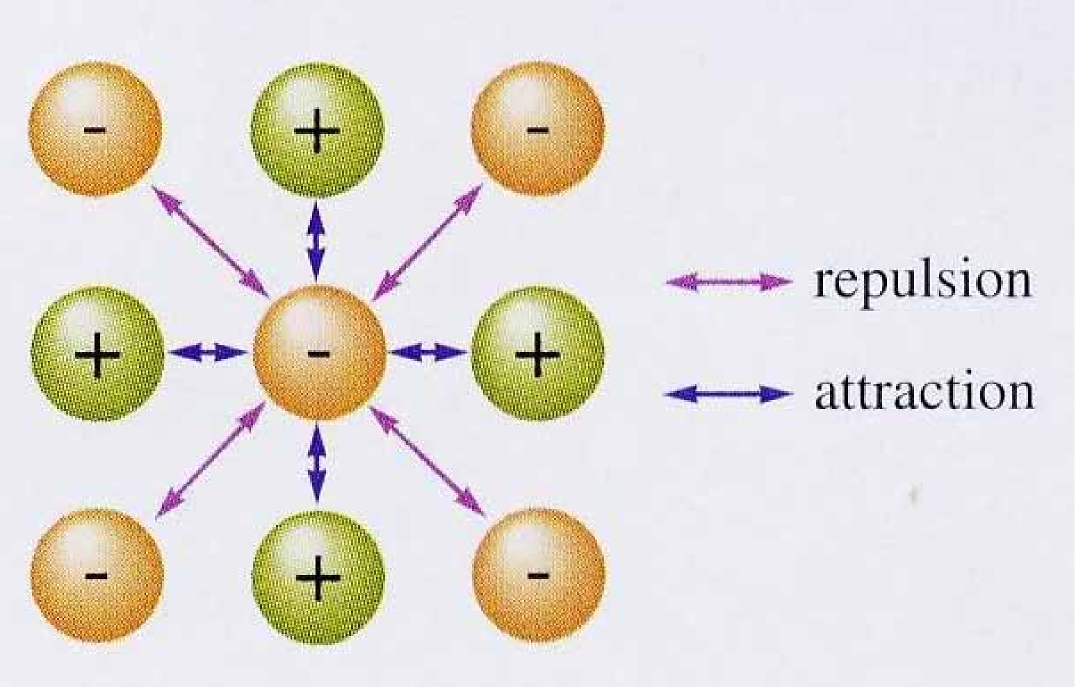
- When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is , both nonmetals attain noble gas electron configurations.
- When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal

achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied. In this way both ions achieve noble gas electron configurations.

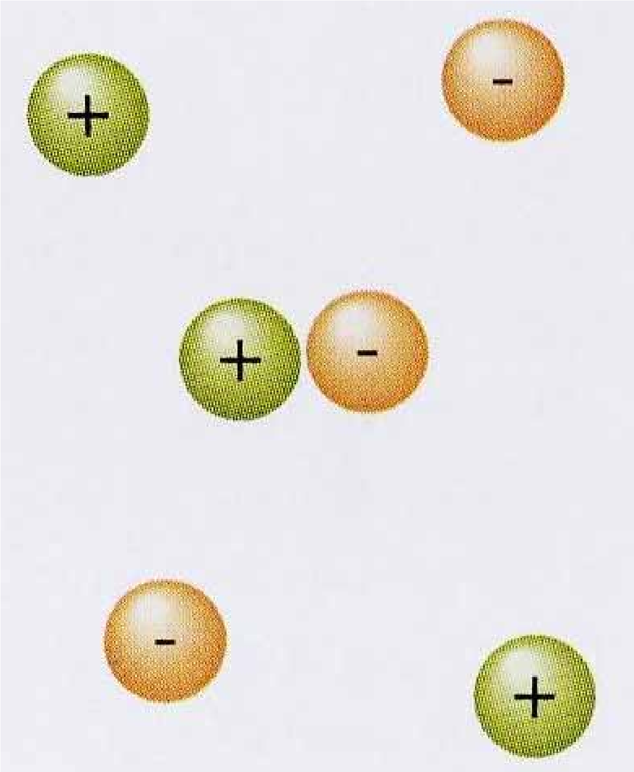
Predicting Formulas of Ionic Compounds

- At the beginning of this discussion it should be emphasized that when chemists use the term ionic compound, they are usually referring to the solid state of that compound.
- That is, solid ionic compounds contain a large collection of positive and negative ions packed together in a way that minimizes the ⊖ • • ⊖ and ⊕ • • ⊕ repulsions and maximizes the ⊕ • • ⊖ attractions.

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



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



- When we speak in this text of the stability of an ionic compound, we are referring to the solid state, where the largy attractive forces present among oppositely charged ions tend to stabilize the ions.
- To illustrate the principles of electron configurations in stable, solid ionic compounds, we will consider the formation of an ionic comopound from calcium and oxygen.

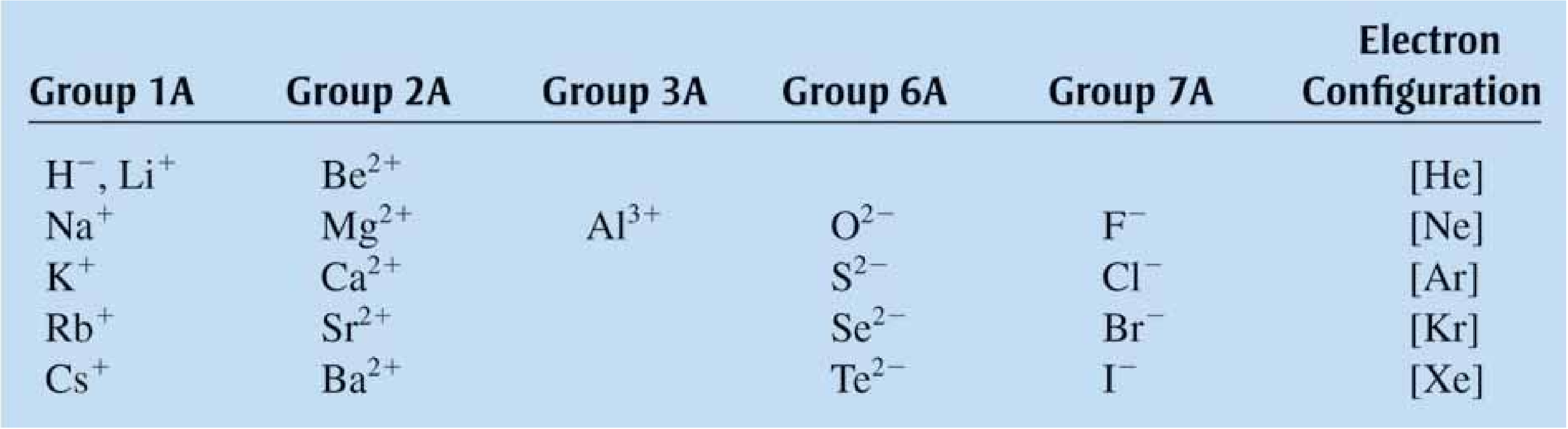
$$\begin{array}{ll} \mathrm{Ca:} & [\mathrm{Ar}]4s^2 \\ \mathrm{O:} & [\mathrm{He}]2s^2 2p^4 \end{array}$$

- Note that oxygen needs two electrons to fill its 2*s* and 2*p* valence orbitals and to achieve the configuration of neon ($1s^2 2s^2 2p^6$).
- And by losing two electrons, calcium can achieve the configuration of argon. Two eletrons are therefore transferred:

$$\begin{tikzcd} \mathrm{Ca} \arrow[rr, bend right, "2e^-"'] & + & \mathrm{O} \arrow[r] & \mathrm{Ca}^{2+} + \mathrm{O}^{2-} \end{tikzcd}$$

- Table 8.3 shows common elements that form ions with noble gas electron configurations in ionic compounds.

TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds



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

Sizes of Ions

- Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biologic effects of ions.
- Most often, ionic radii are determined from the measured distances between ion centers in ionic compounds.
- Various factors influence ionic size. We will first consider the relative sizes of an ion and its parent atom.

- It is also important to know how the sizes of ions vary depending on the positions of the parent elements in the periodic table. Figure 8.8 shows the sizes of the most important ions and their position in the periodic table.
- One trend worth noting involves the relative sizes of a set of isoelectronic ions— *ions containing the same number of electrons*.
- There are two important facts to consider in predicting the relative sizes of ions: the number of electrons and the number of protons.

Figure 8.8

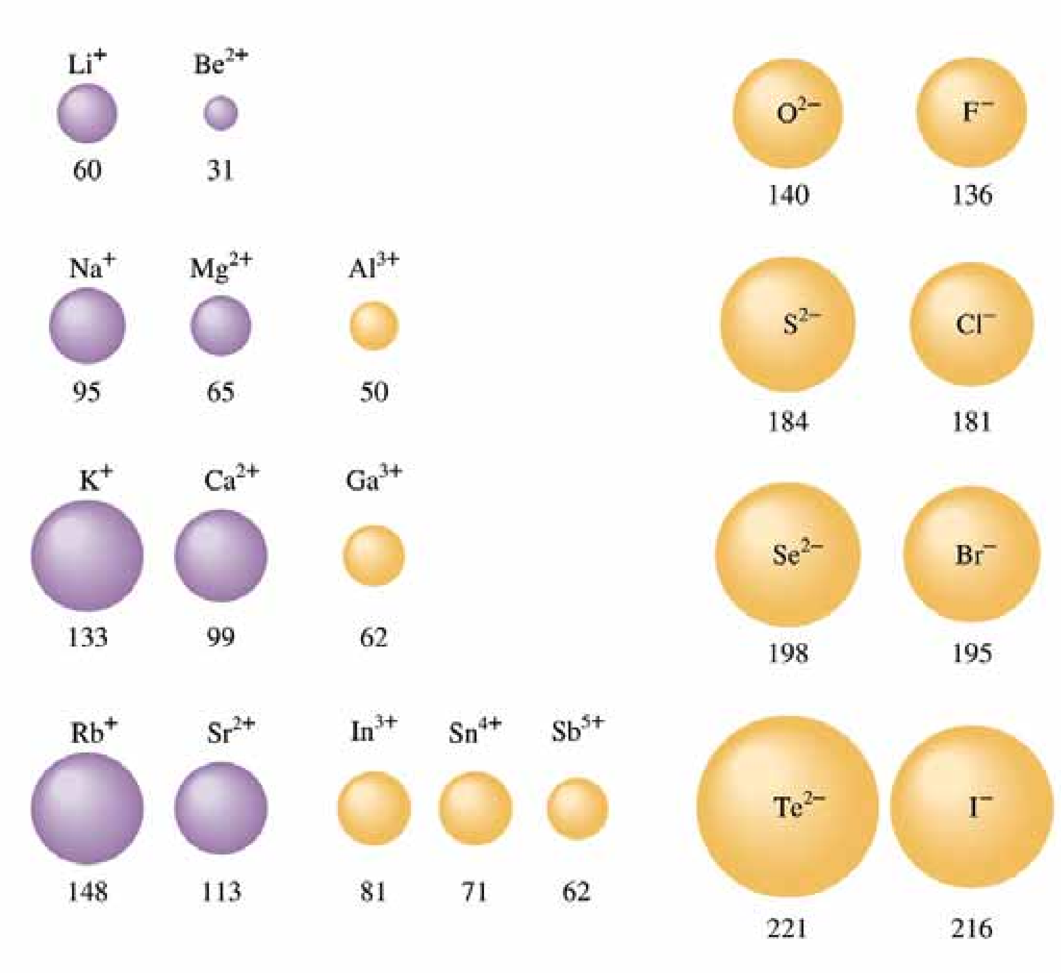

Li⁺
60
Be²⁺
31
O²⁻
140
F⁻
136
Na⁺
95
Mg²⁺
65
Al³⁺
50
S²⁻
184
Cl⁻
181
K⁺
133
Ca²⁺
99
Ga³⁺
62
Se²⁻
198
Br⁻
195
Rb⁺
148
Sr²⁺
113
In³⁺
81
Sn⁴⁺
71
Sb⁵⁺
62
Te²⁻
221
I⁻
216

Figure 8.8

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

Sample Exercise 8.3

Relative Ion Size I

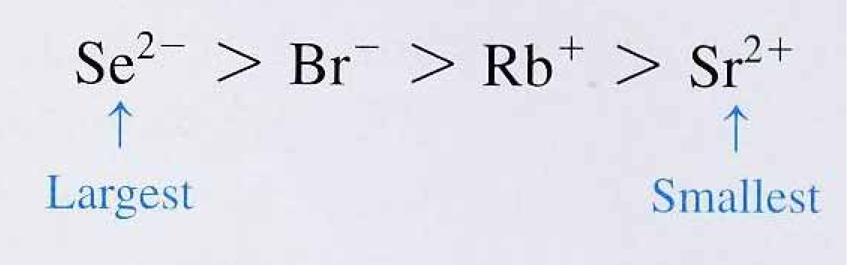
Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{2+} in order of decreasing size.

Solution

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

Sample Exercise 8.3

ion is largest:



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

See Exercises 8.37 and 8.38

Sample Exercise 8.4

Relative Ion Size II

Choose the largest ion in each of the following groups.

a. Li^+, Na^+, K^+, Rb^+, Cs^+

b. Ba^{2+}, $Cs+$, I^-, Te^{2-}

Solution

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

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

Sample Exercise 8.4

smallest nuclear charge is largest:

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

See Exercises 8.39 and 8.40

8.5 Energy Effects in Binary Ionic Compounds

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

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

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

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

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

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

$$\tfrac{1}{2}F_2(g) \longrightarrow F(g)$$

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

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

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

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

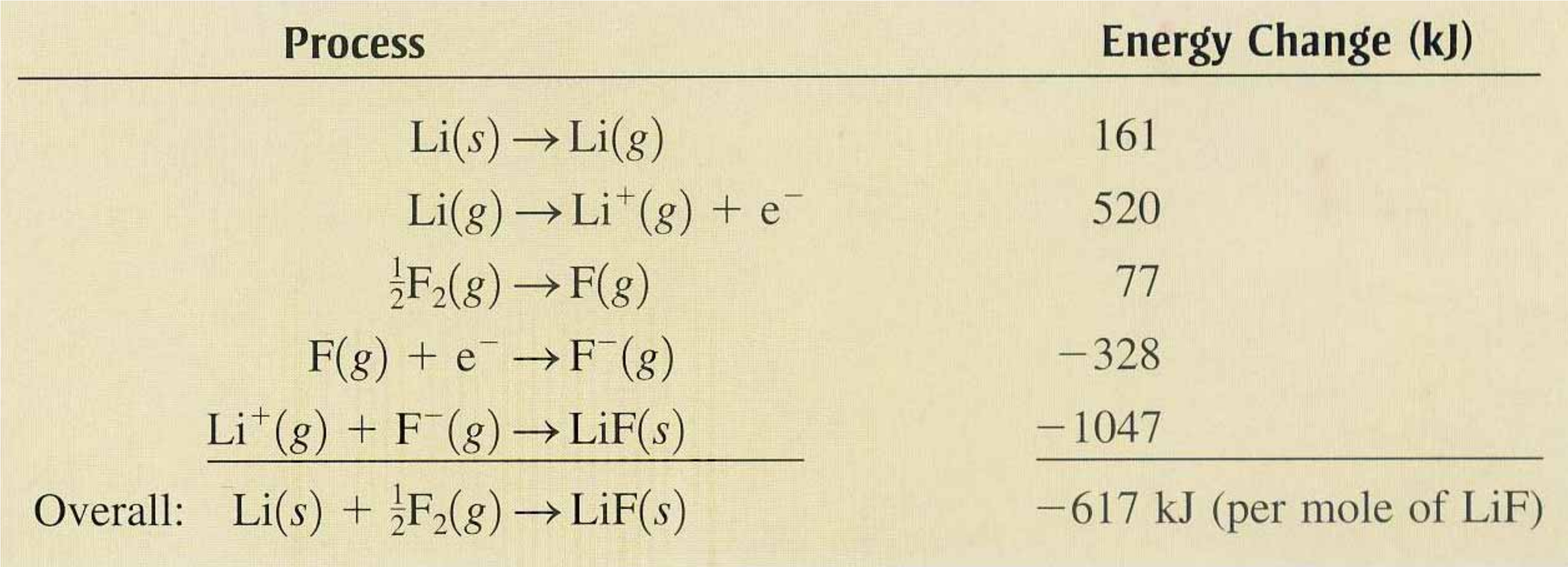
5 Formation of solid lithium fluoride from the gasous Li^+ and F^- ions:

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

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

Lithium fluoride.

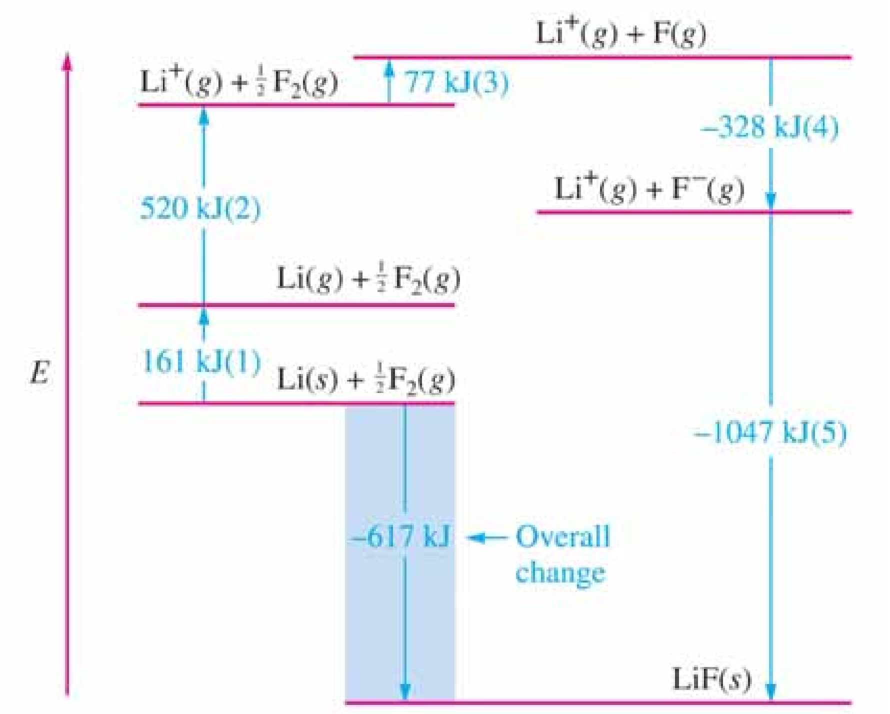
- Since the sum of these five processed yields the desired overall reaction, the sum of the individual energy changes gives the overall energy change:



	Process	Energy Change (kJ)
	$Li(s) \rightarrow Li(g)$	161
	$Li(g) \rightarrow Li^{+}(g) + e^{-}$	520
	$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
	$F(g) + e^{-} \rightarrow F^{-}(g)$	−328
	$Li^{+}(g) + F^{-}(g) \rightarrow LiF(s)$	−1047
Overall:	$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$	−617 kJ (per mole of LiF)

- This process is summarized by the energy diagram in Fig. 8.9. Note that the formation of solid lithium fluoride from its elements is highly exothermic, mainly because of the very large negative lattice energy.

Figure 8.9

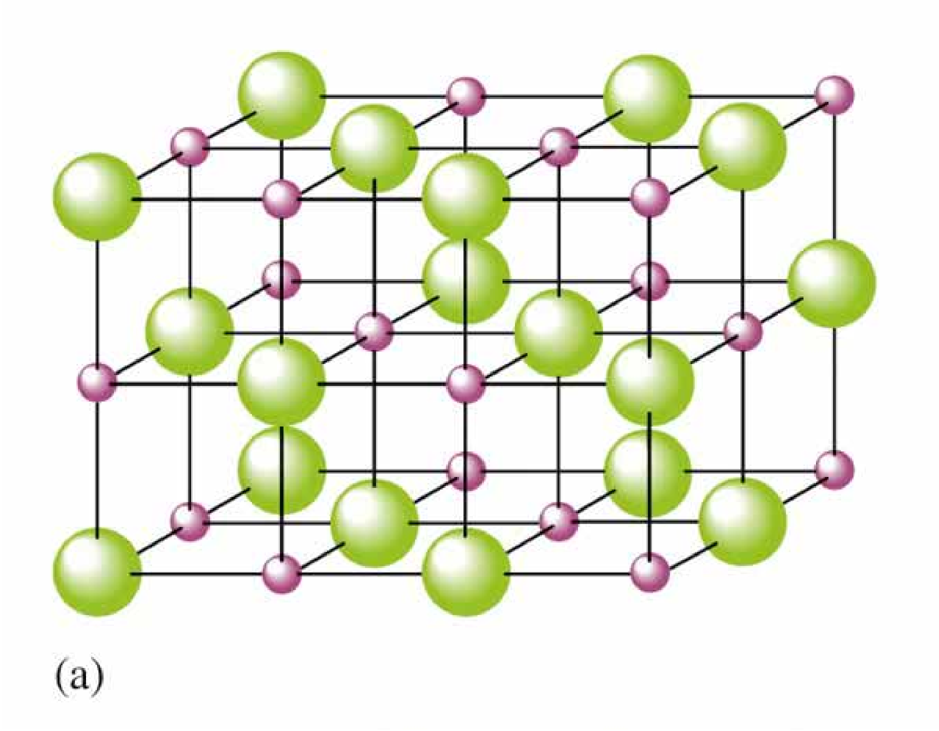


The energy changes involved in the formation of solid lithium fluoride from its elements. The numbers in parentheses refer to the reaction steps discussed in the text.

- The structure of solid lithium fluoride is represented in Fig. 8.10.
- Note the alternating arrangement of the Li^+ and F^- ions.
- Also note that each Li^+ is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions.
- All the binary ionic compounds formed by an alkali metal and a halogen have the structure shown in Fig. 8.10, except for the cesium salts.

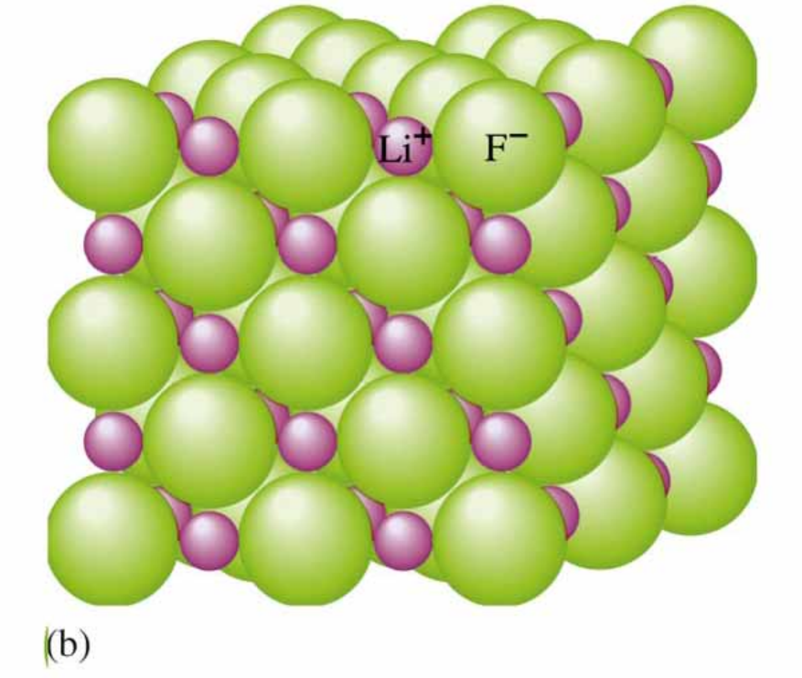
- The arrangement of ions shown in Fig. 8.10 is often called the *sodium chloride structure*, after the most common substance that possesses it.

Figure 8.10



The structure of lithium fluoride. (a) Represented by ball-and-stick model. Note that each Li^+ ion is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions.

Figure 8.10



(b) Represented with the ions shown as spheres. The structure is determined by packing the spherical ions in a way that both maximizes the ionic attractions and minimizes the ionic repulsions.

Lattice Energy Calculations

- Lattice energy can be represented by a modified form of Coulomb’s law:

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

- where k is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions, Q_1 and Q_2 are the charge on the ions, and r is the shortest distance between the centers of the cations and anions.

- Note that the lattice energy has a negative sign when Q_1 and Q_2 have opposite signs.
- The importance of the charge in ionic solids can be illustrated by comparing the energies involved in the fornation of NaF(*s*) and MgO(*s*).

- The energy diagram for the formation of the two solids is given in Fig. 8.11. Note several important features:

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

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

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

Figure 8.11

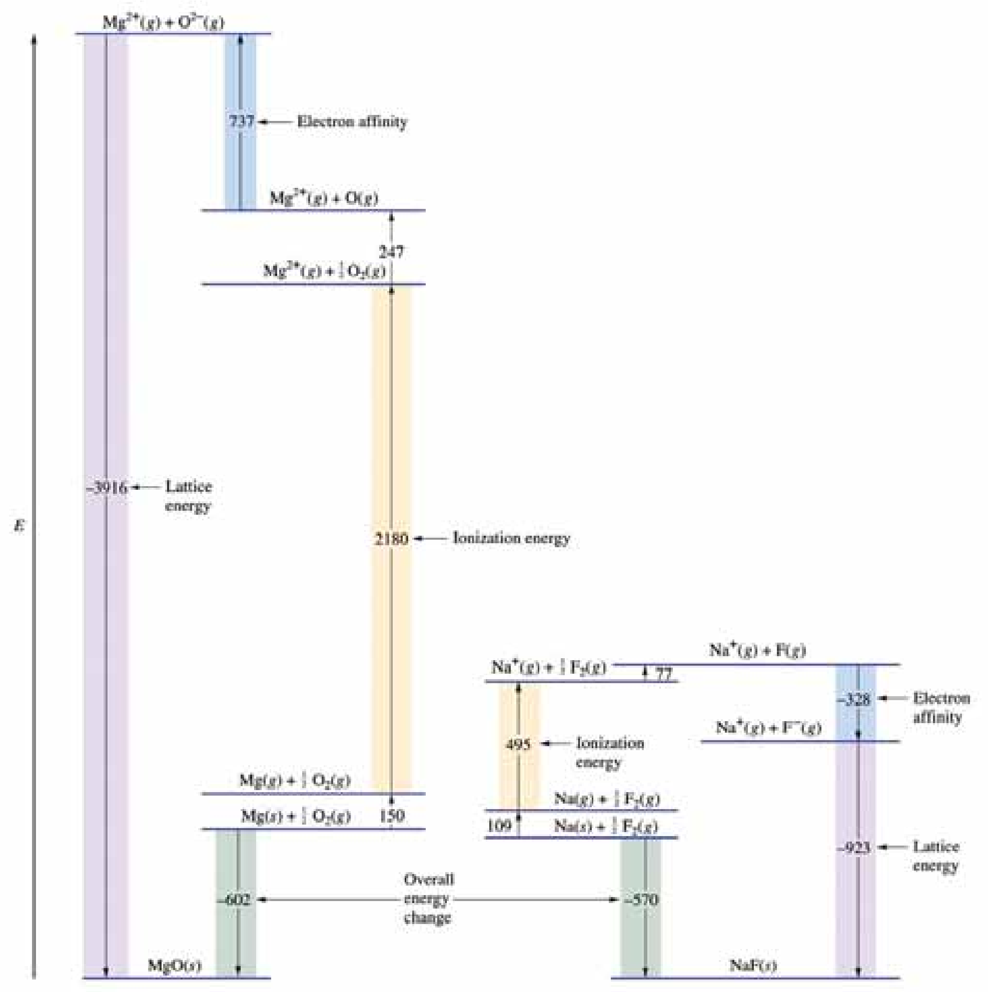

$Mg^{2+}(g) + O^{2-}(g)$
737 ← Electron affinity
$Mg^{2+}(g) + O(g)$
247
$Mg^{2+}(g) + \frac{1}{2}O_2(g)$
–3916 ← Lattice energy
E
2180 ← Ionization energy
$Mg(g) + \frac{1}{2}O_2(g)$
$Mg(s) + \frac{1}{2}O_2(g)$
150
–602
Overall energy change
–570
MgO(s)
$Na^+(g) + F(g)$
$Na^+(g) + \frac{1}{2}F_2(g)$
77
–328 ← Electron affinity
$Na^+(g) + F^-(g)$
495 ← Ionization energy
$Na(g) + \frac{1}{2}F_2(g)$
109
$Na(s) + \frac{1}{2}F_2(g)$
–923 ← Lattice energy
NaF(s)

Figure 8.11

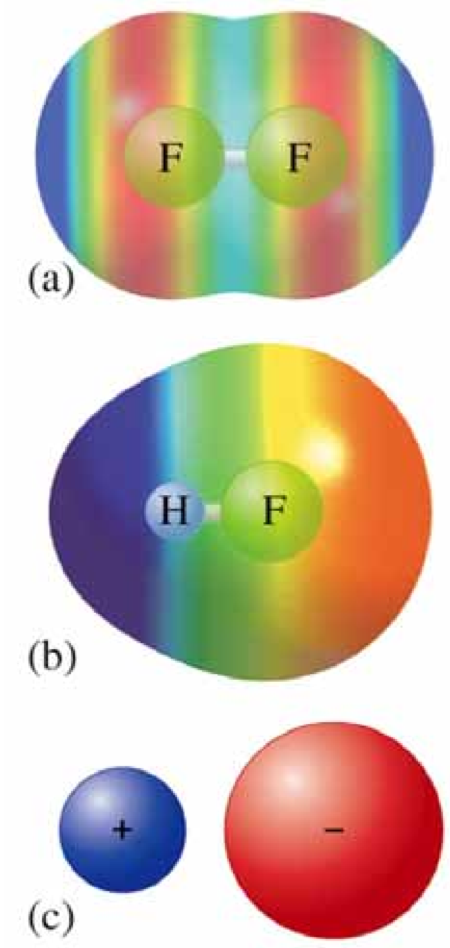
Comparison of the energy changes involved in the formation of solid sodium fluoride and solid magnesium oxide. Note the large lattice energy for magnesium oxide (where doubly charged ions are combining) compared with that for sodium fluoride (where singly charged ions are combining).

8.6 Partial Ionic Character of Covalent Bonds

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

Figure 8.12

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



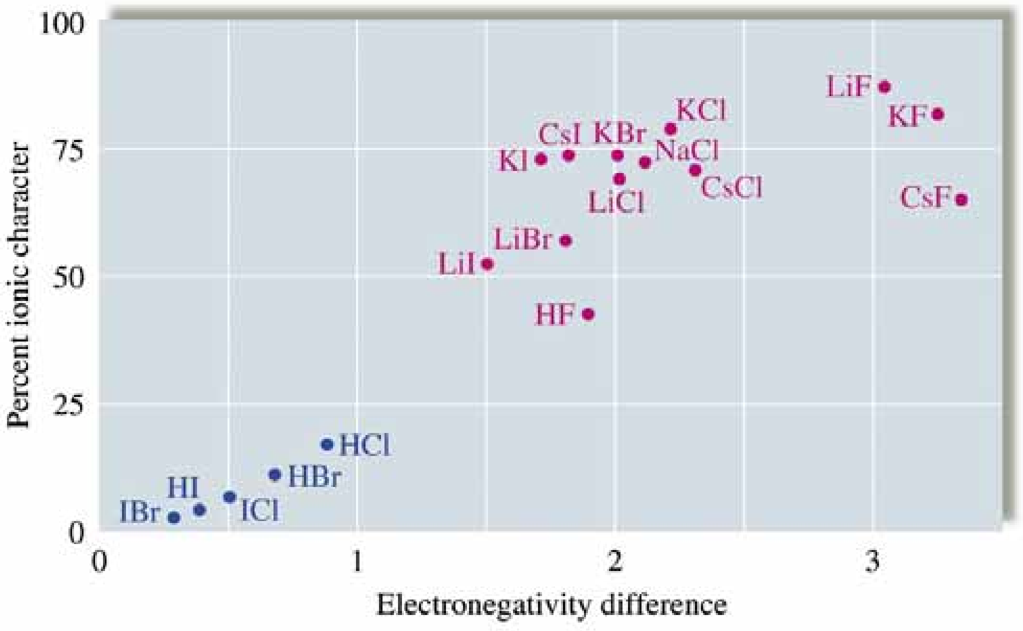
- The percent ionic character of a bond can be defined as

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

- Application of this definition to various compounds (in the gas phase) gives the results shown in Fig. 8.13.
- Note from this plot that ionic character increases with electronrgativity difference.

- Ionic compounds: *Any compound that conducts an electric current when melted will be classified as ionic.*

Figure 8.13

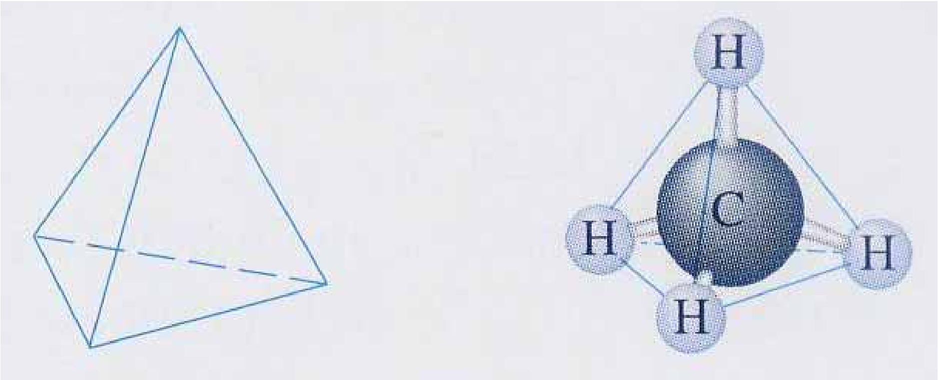


The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms. Note that the compounds with ionic character greater than 50% are normally considered to be ionic compounds.

8.7 The Covalent Chemical Bond: A Model

- Chemical bonds can be viewed as forces that cause a group of atoms to behave as a unit.
- *Bonds result from the tendency of a system to seek its lowest possible energy*.
- From a simplistic point of view, bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms.

- Approximately 1652 kJ of energy is required to break a mole of methane (CH_4) molecules into separate C and H atoms.
- Or, taking the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms.
- Methane is therefore a stable molecule relative to its separated atoms.

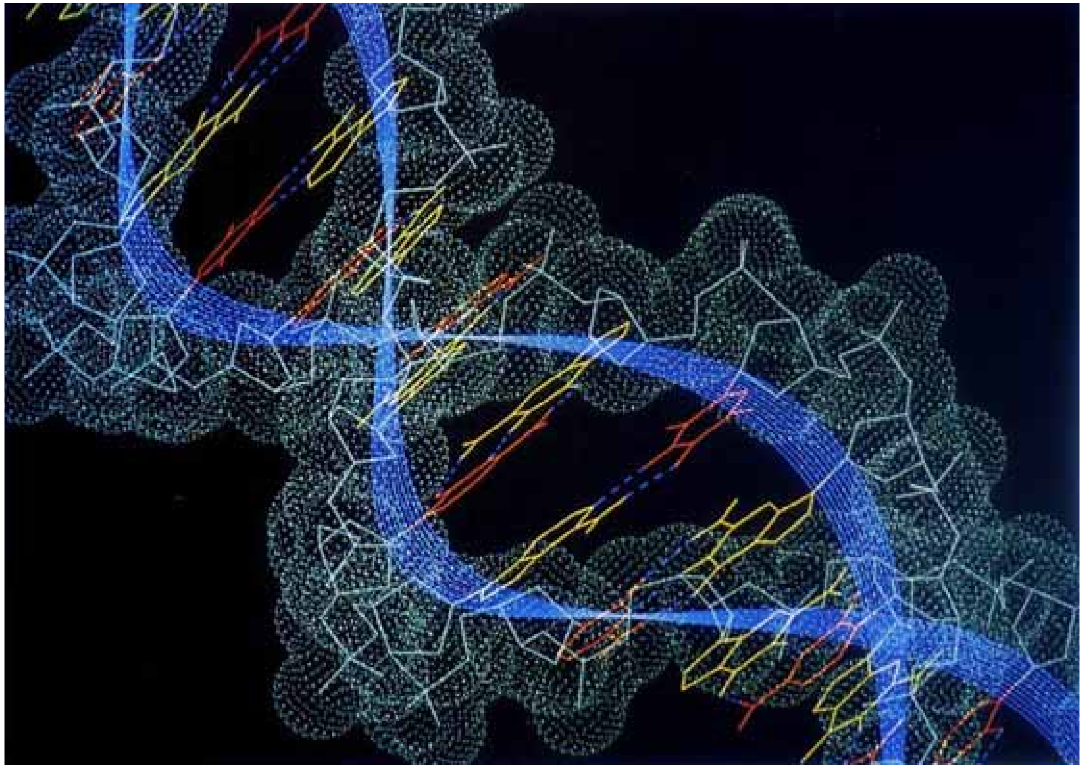


- The energy of stabilization of CH4 is divided equally among the four bonds to give an average C—H bond energy per mole of C—H bonds:

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

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

Models: An Overview



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

Fundamental Properties of Models

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

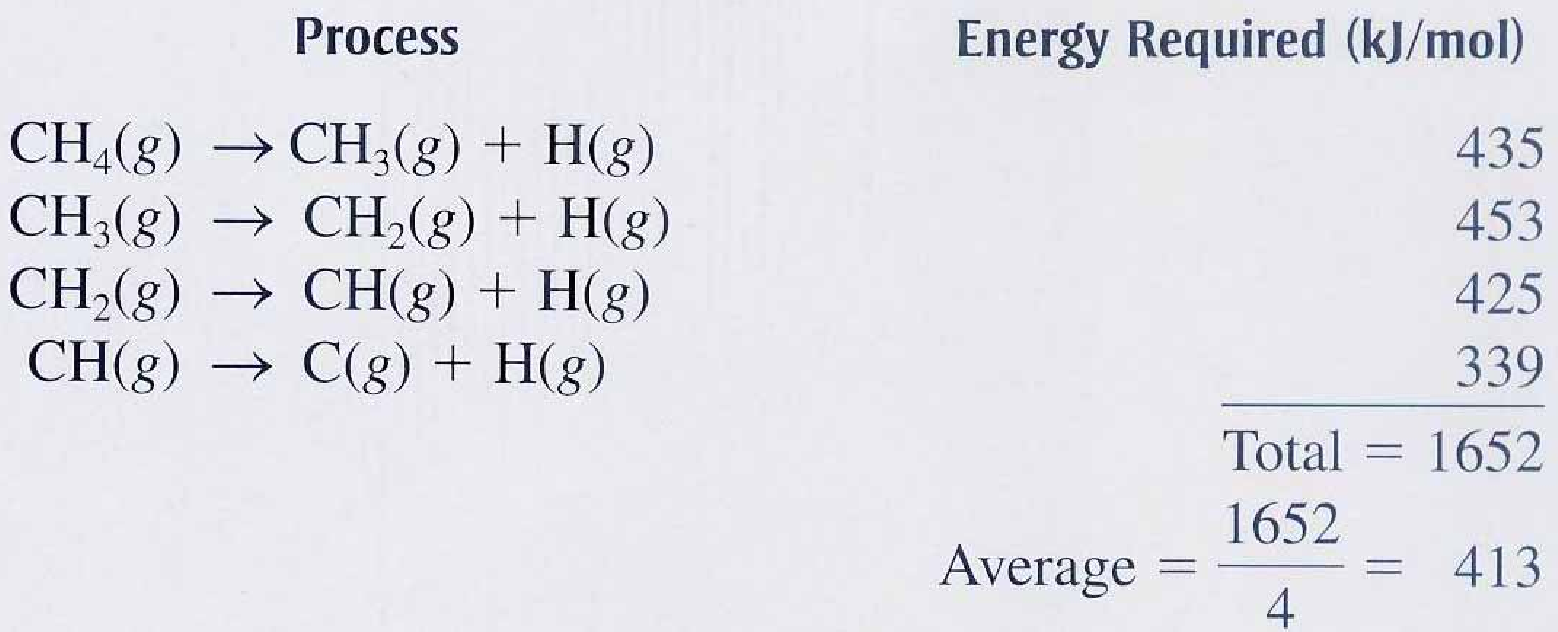
model is like expecting to get an accurate mass for a diamond using a bathroom scale.

For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple aufbau principle used to account for the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper, for example, do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the simple model. However, this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we must apply it with caution and not expect it to be correct in every case.

- When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes. (Try to remember this when you get back your next chemistry test.)

8.8 Covalent Bond Energies and Chemical Reactions

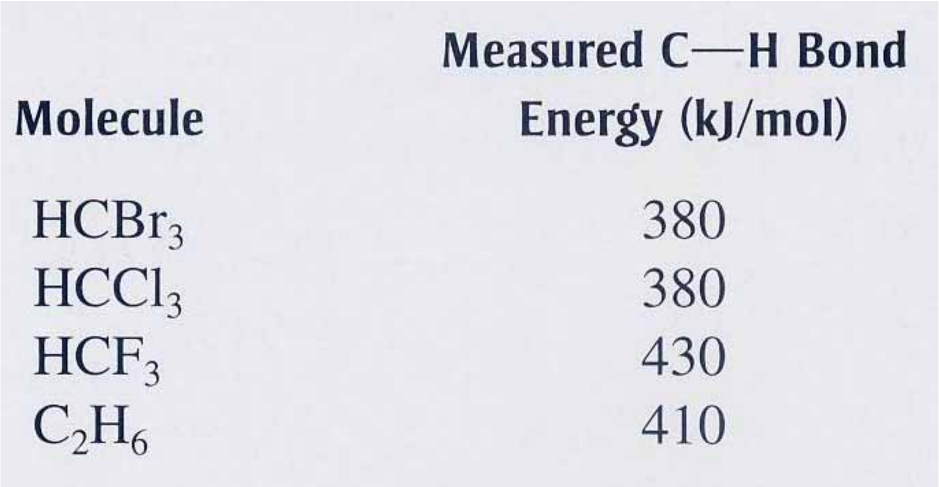
- One important consideration is to establish the sensitivity of a particular type of bond to its molecular environment.



Process	Energy Required (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	453
$CH_2(g) \rightarrow CH(g) + H(g)$	425
$CH(g) \rightarrow C(g) + H(g)$	339
	Total = 1652

$$\text{Average} = \frac{1652}{4} = 413$$

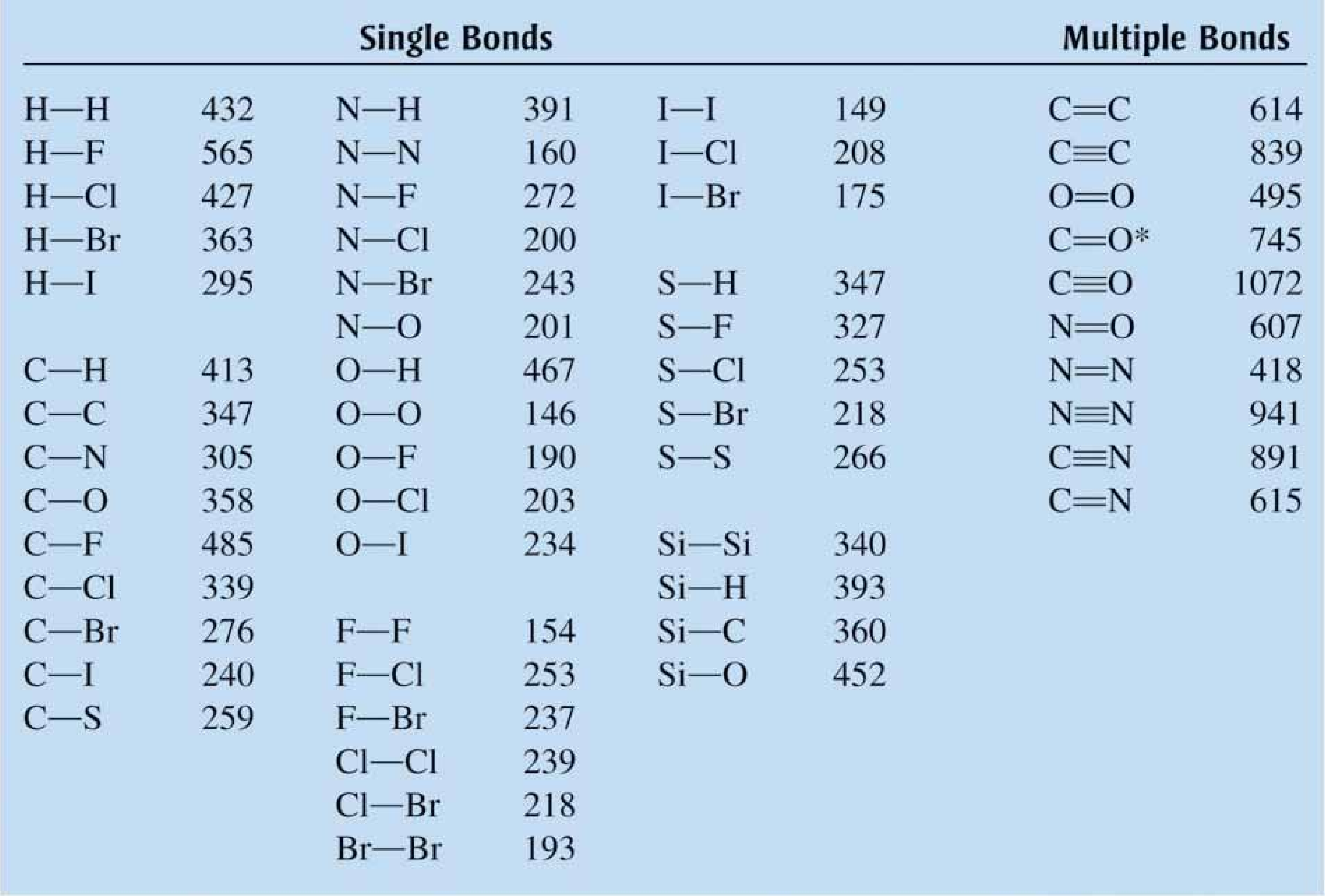
- The degree of sensitivity of a bond to its environment also can be seen from experimental measurements of the energy required to break the C—H bond in the following molecules:



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

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

TABLE 8.4 Average Bond Energies (kj/mol)

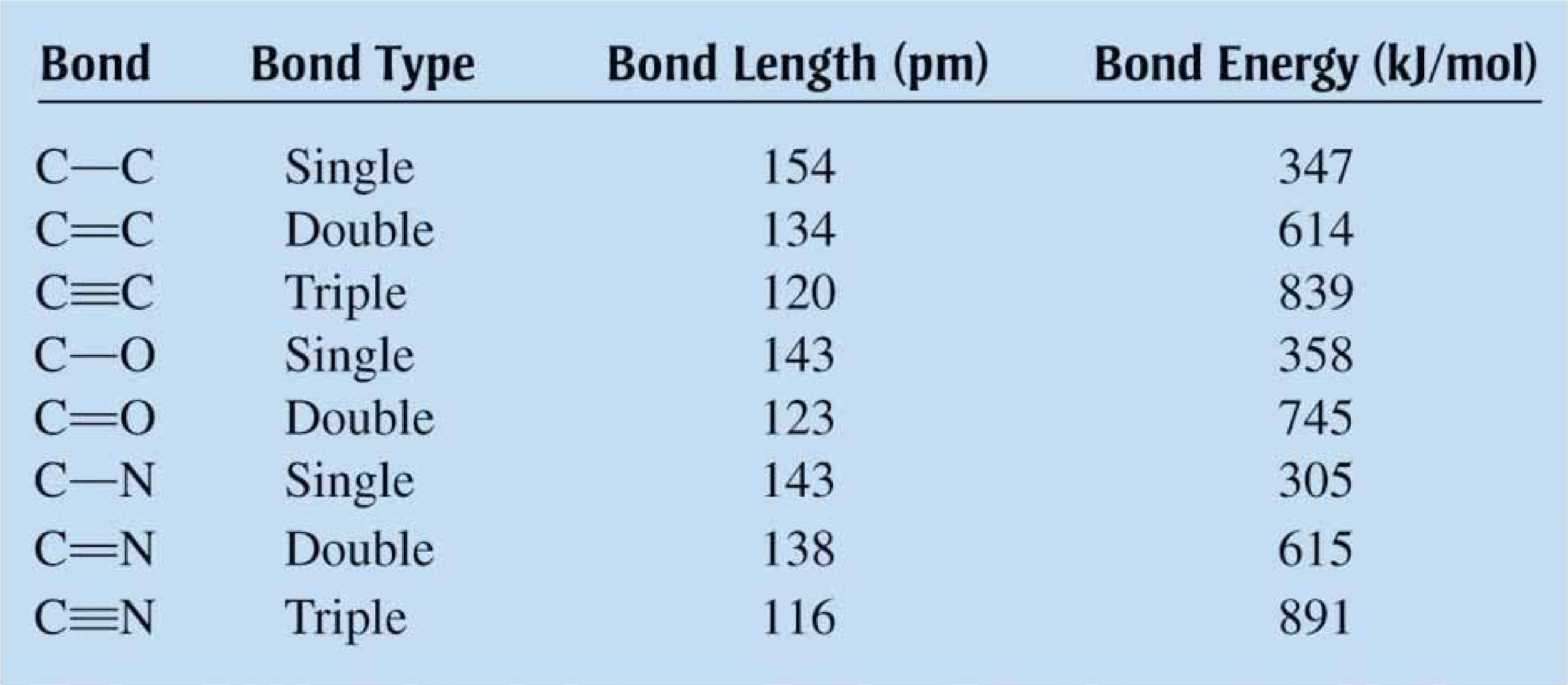


Single Bonds						Multiple Bonds	
H—H	432	N—H	391	I—I	149	C=C	614
H—F	565	N—N	160	I—Cl	208	C≡C	839
H—Cl	427	N—F	272	I—Br	175	O=O	495
H—Br	363	N—Cl	200			C=O*	745
H—I	295	N—Br	243	S—H	347	C≡O	1072
		N—O	201	S—F	327	N=O	607
C—H	413	O—H	467	S—Cl	253	N=N	418
C—C	347	O—O	146	S—Br	218	N≡N	941
C—N	305	O—F	190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

*C=O(CO_2) = 799

- The bond energies for these *multiple bonds* are also given in Table 8.4.
- As the number of shared electrons increases, the bond length shortens. This relationship is shown for selected bonds in Table 8.5.

TABLE 8.5 Bond Lengths for Selected Bonds



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

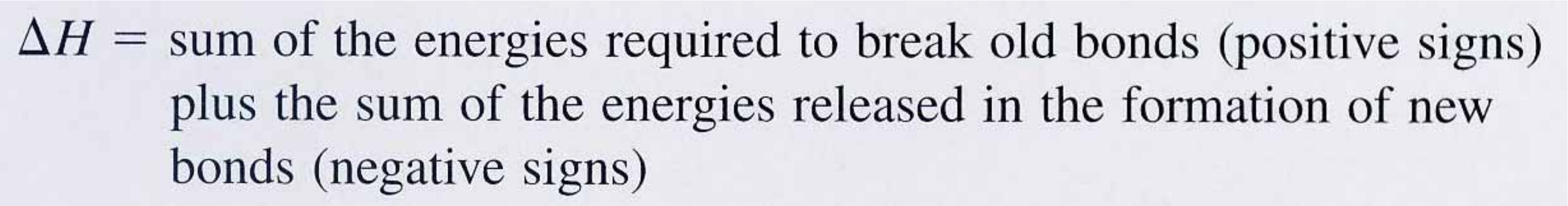
Bond Energy and Enthalpy

- Bond energy values can be used to calculate approximate energies for reactions.

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

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

- The energy terms associated with bond breaking have *positive* signs.
- The formation of a bond releases energy, an exothermic process, so the energy terms associated with bond making carry a *negative* sign.



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

- This leads to the expression

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

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

$$\Delta \text{H} = \text{DH—H} + \text{DF—F} - 2\text{DH—F} = -544\text{kJ}$$

Sample Exercise 8.5

ΔH from Bond Energies

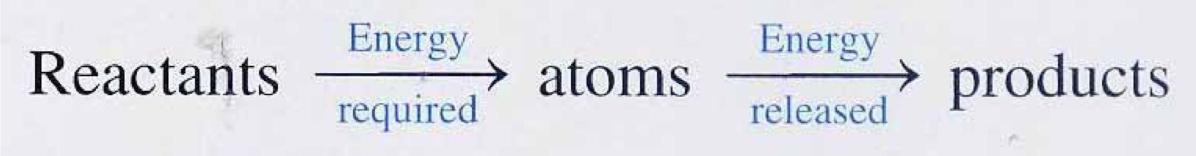
Using the bond energies listend in Table 8.4, calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2).

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

Solution

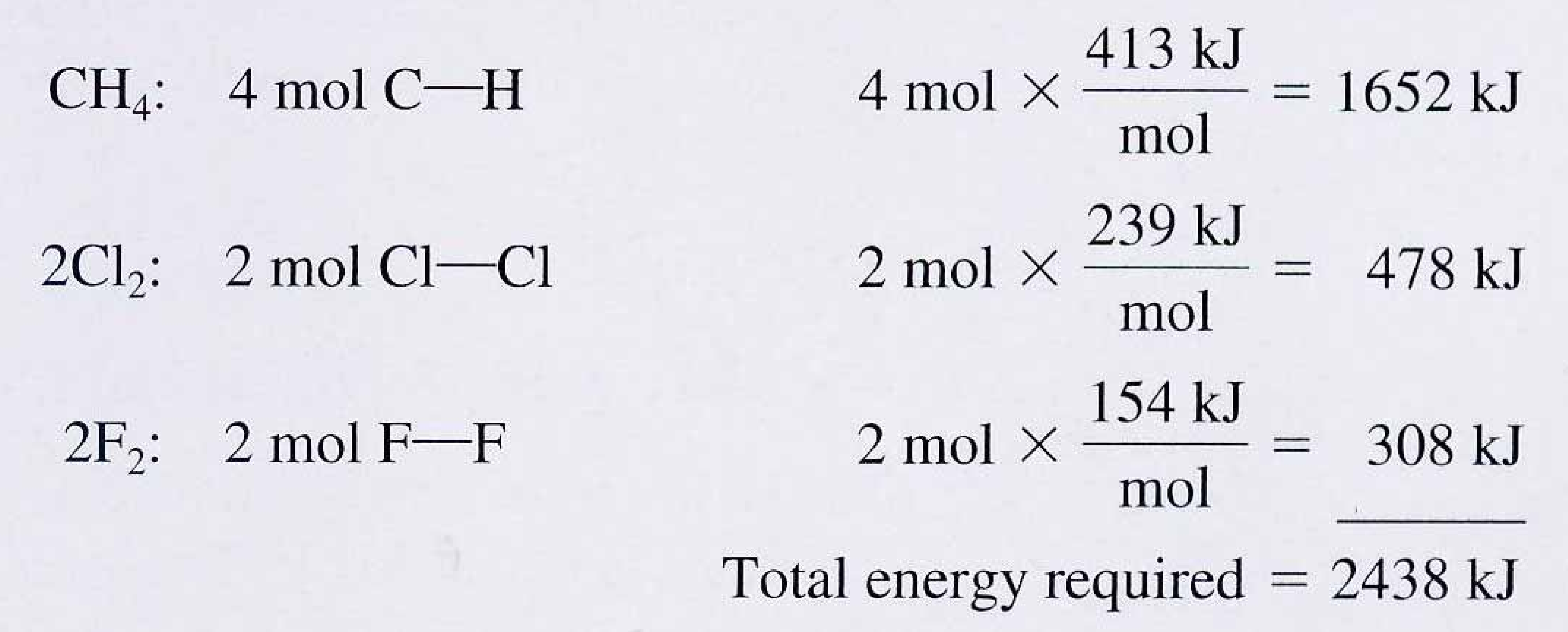
The idea here is to break the bonds in the gaseous reactants to give individual atoms and then assemble these atoms into the gaseous products by forming new bonds:

Sample Exercise 8.5



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

Reactant Bonds Broken:



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

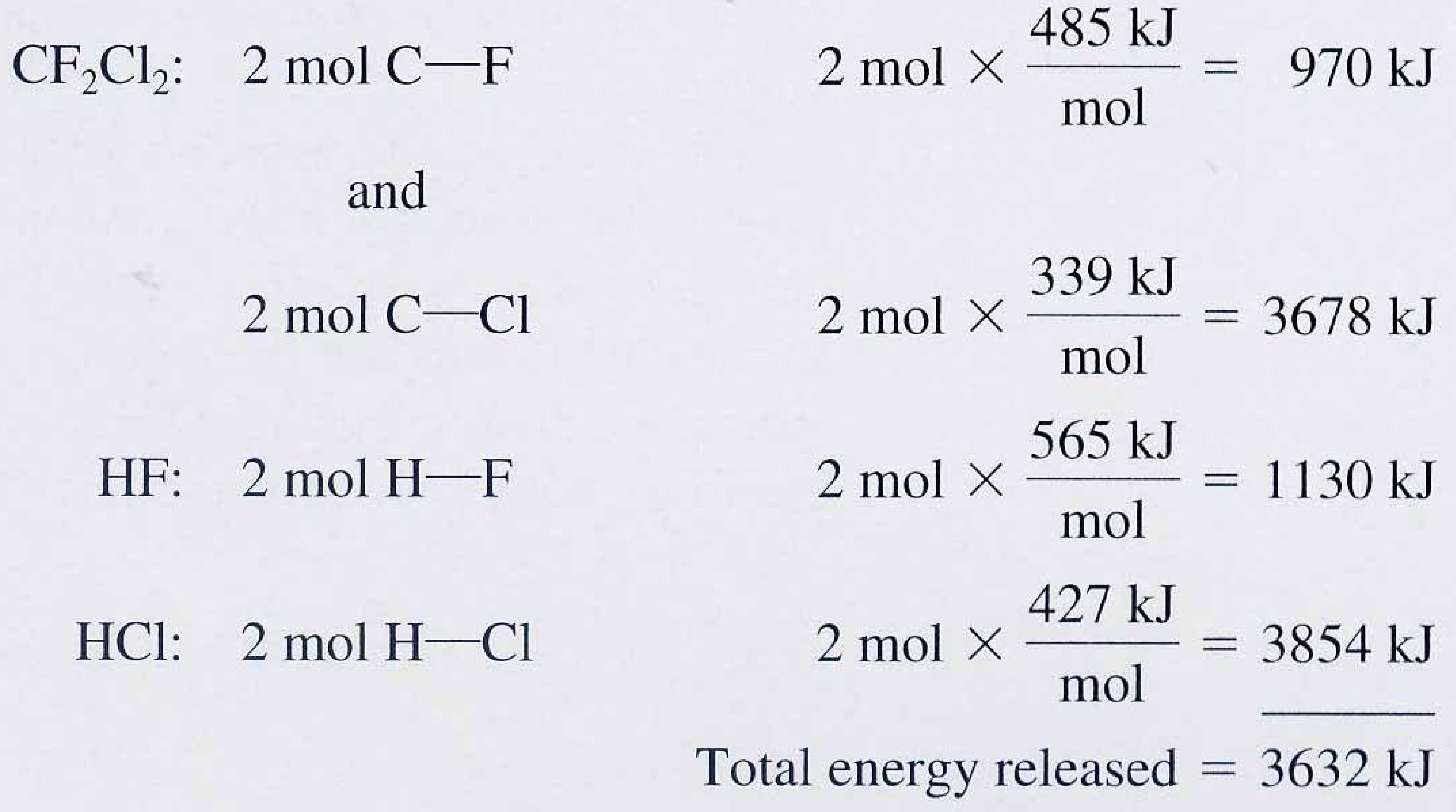
$2Cl_2$: 2 mol Cl—Cl $\quad 2\text{ mol} \times \dfrac{239\text{ kJ}}{\text{mol}} = 478\text{ kJ}$

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

Total energy required = 2438 kJ

Sample Exercise 8.5

Product Bonds Formed:



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

and

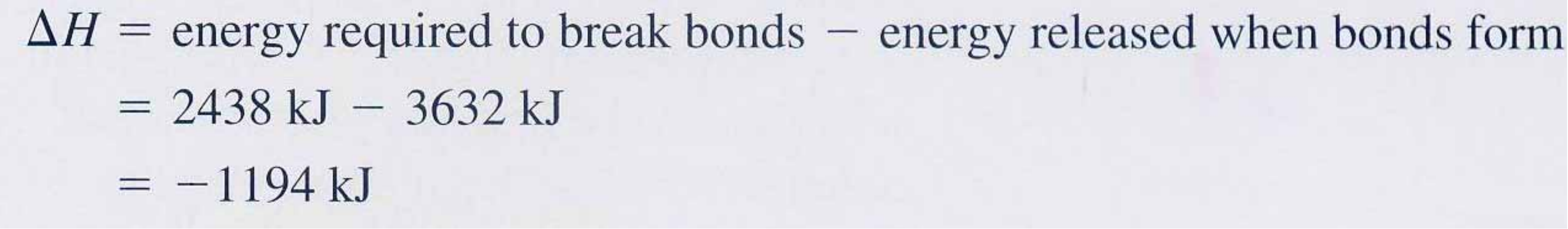
2 mol C—Cl $\quad 2\text{ mol} \times \dfrac{339\text{ kJ}}{\text{mol}} = 3678\text{ kJ}$

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

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

Total energy released = 3632 kJ

Sample Exercise 8.5



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

See Exercises 8.53 through 8.60

8.9 The Localized Electron Bonding Model

- **localized electron (LE) model**: *a molecule is composed of atoms that are bond together by sharing pairs of electrons using the atomic orbitals of the bond atoms.*
- Electron pairs in the molecule are assumed to be localized on an a particular atom or in the space between two atms.

- Those pairs of electrons localized on an atom are called **lone pairs**, and those found in the space between the atoms are called **bonding pairs**.
- LE model has three parts:

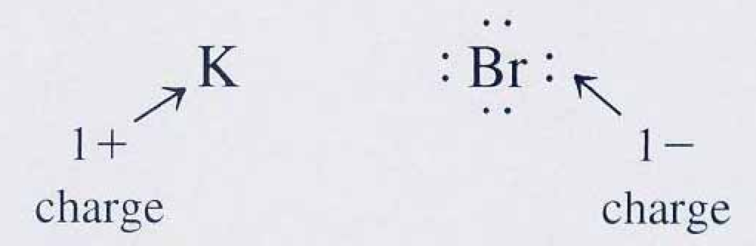
1. Description of the valence electron arrangement in the molecule using Lewis structures (will be discussed in the next section).
2. Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model (will be discussed in Section 8.13).

3. Description of the type of atomic orbitals used by the atoms to share electrons or hold lone pairs (will be discussed in Chapter 9).

8.10 Lewis Structures

- The **Lewis structure** of a molecule shows how the valence electrons are arranged among the atoms in the molecule. These representations are named after G. N. Lewis (Fig. 8.14).
- The *most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configurations*.

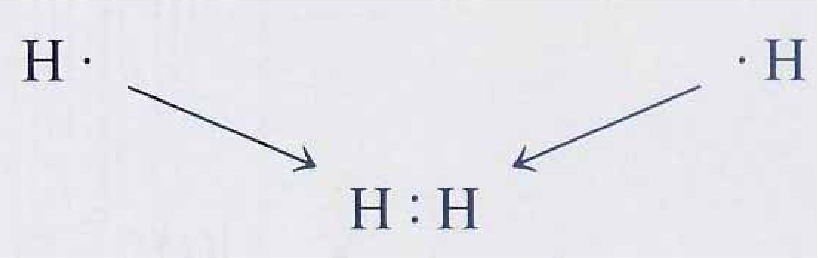
- In writing Lewis structures, the rule is that only the valence electrons are included. Using dots to represent electrons, the Lewis structure for KBr is



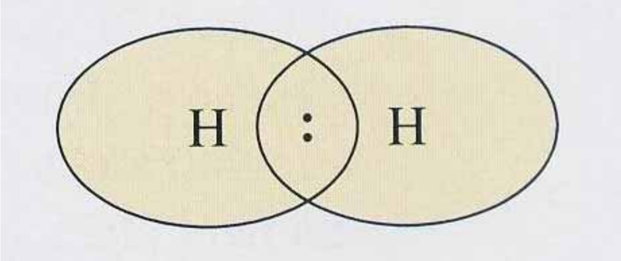
- No dots are shown on the K^+ ion because it has no valence electrons. The Br^- ion is shown with eight electrons because it has a filled valence shell.

The principle of achieving a noble gas electron configuration applies to these electrons as follows:

- Hydrogen forms stable molecules where it shares two electrons. That is, it follows a duet rule.



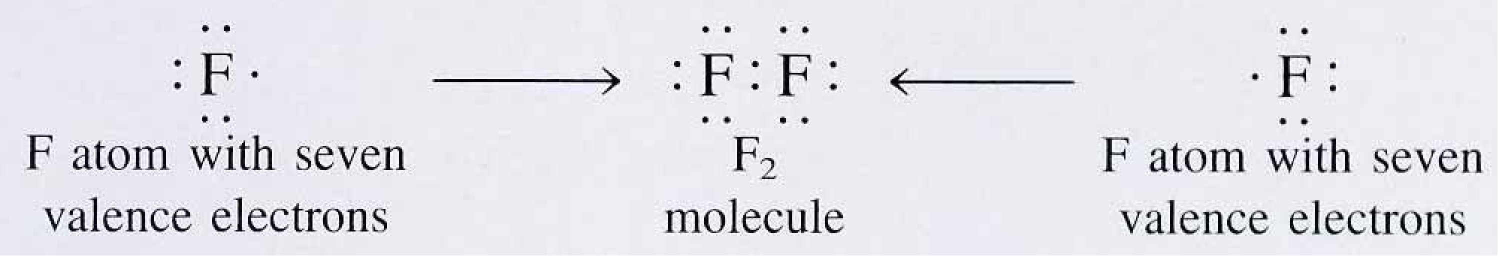
- By sharing electrons, each hydrogen in H_2, in effect, has two electrons; that is, each hydrogen has a filled valence shell.



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

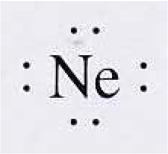
He :

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



Note that each fluorine atom in F2 is, in effect, surrounded by eight electrons, two of which are shared with the other atom. Each fluorine atom also has three pairs of electrons not involved in bonding.

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



Steps for Writing Lewis Structures

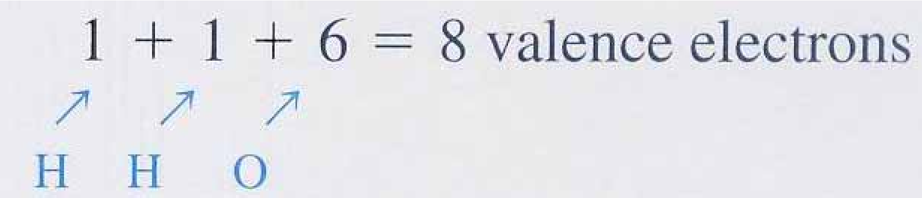
➡ 1 Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the total number of electrons that is important.

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

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

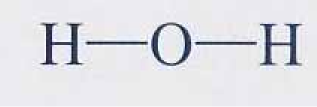
- To see how these steps are applied, we will draw the Lewis structures of a few molecules.

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



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

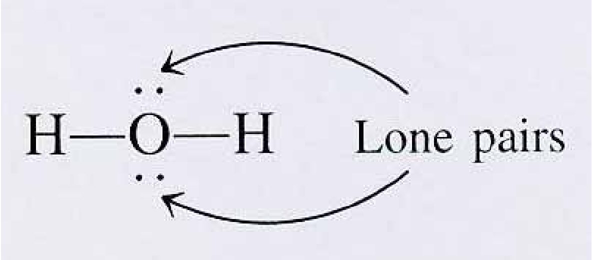
2 **Using a pair of electrons per bond, we draw in the two O—H single bonds:**



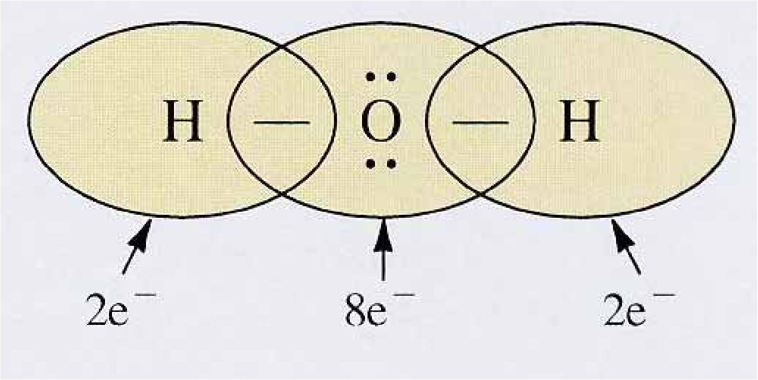
H—O—H

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

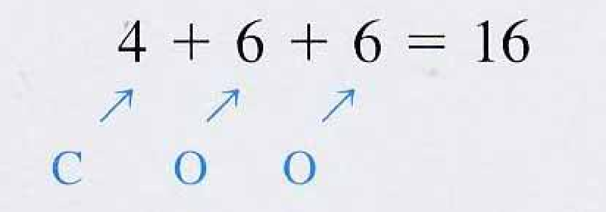
➡ 3 **We distribute the remaining electrons to achieve a noble gas electron configuration for each atom.**



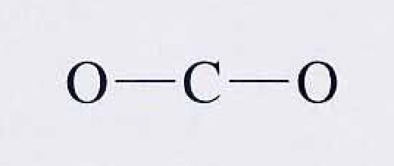
- This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight, as shown below:



- As a second example, let’s write the Lewis structure for carbon dioxide.



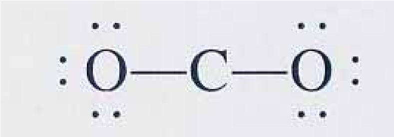
$$\underset{\overset{\nearrow}{\text{C}}}{4} + \underset{\overset{\nearrow}{\text{O}}}{6} + \underset{\overset{\nearrow}{\text{O}}}{6} = 16$$



$$\text{O}-\text{C}-\text{O}$$

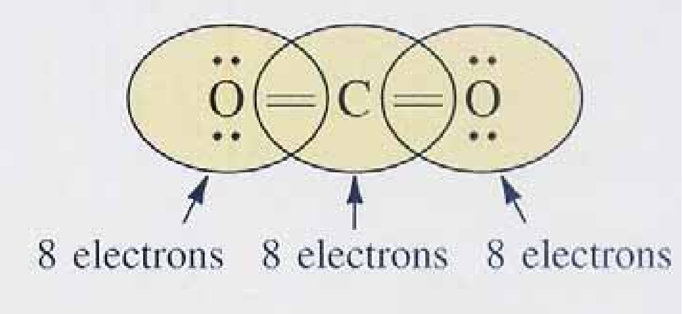
- the remaining electrons are distributed to achieve noble gas configurations on each atom. In this case we have 12 electrons (16 — 4) remaining after the bonds are draw.

- The distribution of these electrons is determined by a trial-and-error process.
- We have 6 pairs of electrons to distribute. Suppose we try 3 pairs on each oxygen to give



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

- Suppose there are 2 shared pairs between the carbon and each oxygen:



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

Sample Exercise 8.6

Writing Lewis Structures

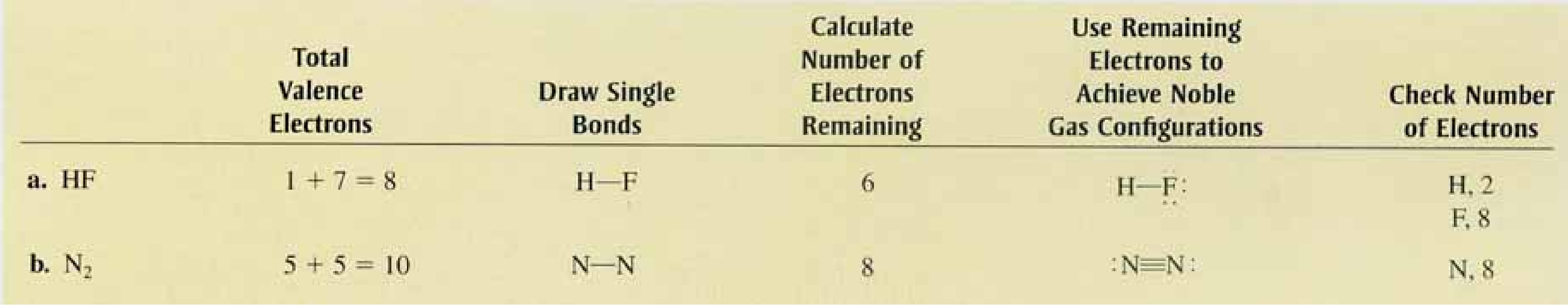
Give the Lewis structure for each of the following.

a. HF **d.** CH_4

b. N_2 **e.** CF_2

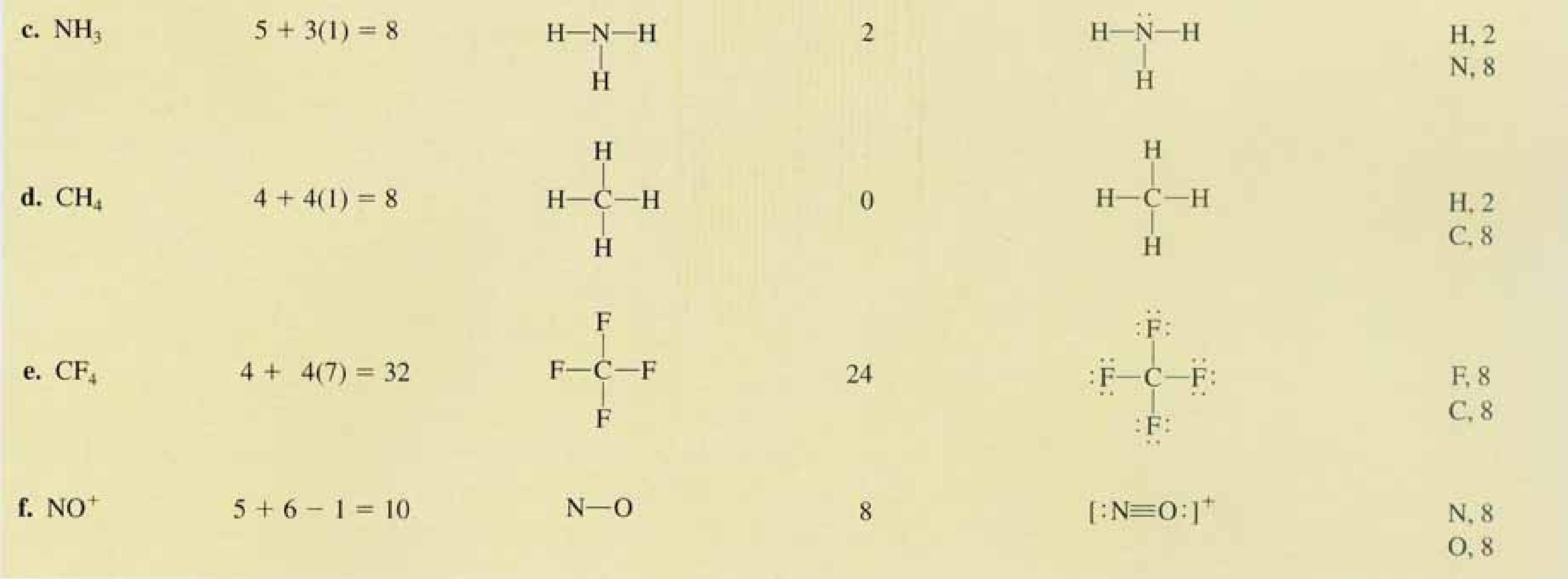
c. NH_3 **f.** NO^+

Solution



	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	1 + 7 = 8	H—F	6	$\mathrm{H{-}\overset{..}{\underset{..}{F}}{:}}$	H, 2 F, 8
b. N_2	5 + 5 = 10	N—N	8	$\mathrm{{:}N{\equiv}N{:}}$	N, 8

Sample Exercise 8.6



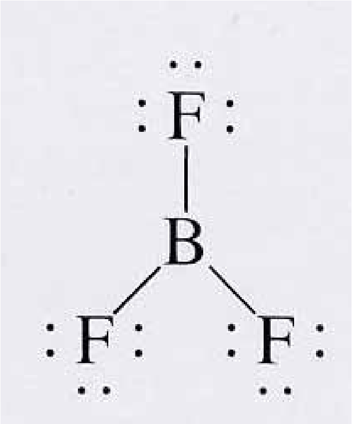
c. NH_3	5 + 3(1) = 8	H—N—H | H	2	H—N̈—H | H	H, 2 N, 8
d. CH_4	4 + 4(1) = 8	H | H—C—H | H	0	H | H—C—H | H	H, 2 C, 8
e. CF_4	4 + 4(7) = 32	F | F—C—F | F	24	:F̈: | :F̤̈—C—F̤̈: | :F̤:	F, 8 C, 8
f. NO^+	5 + 6 − 1 = 10	N—O	8	$[:N \equiv O:]^+$	N, 8 O, 8

See Exercises 8.67 and 8.68

8.11 Exceptions to the Octet Rule

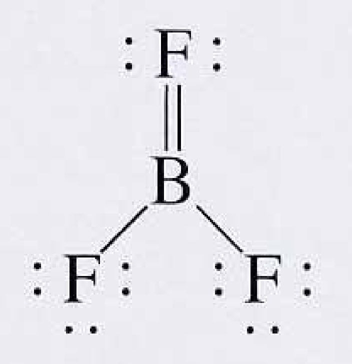
- With such a simple model, some exceptions are inevitable.
- Boron, tends to form compounds in which octet.
- Boron trifluoride (BF_3), a gas at normal temperatures and pressures, reacts very energetically with molecules such as water and ammonia that have available electron pairs (lone pairs).

- The Lewis structure often drawn for BF_3 is



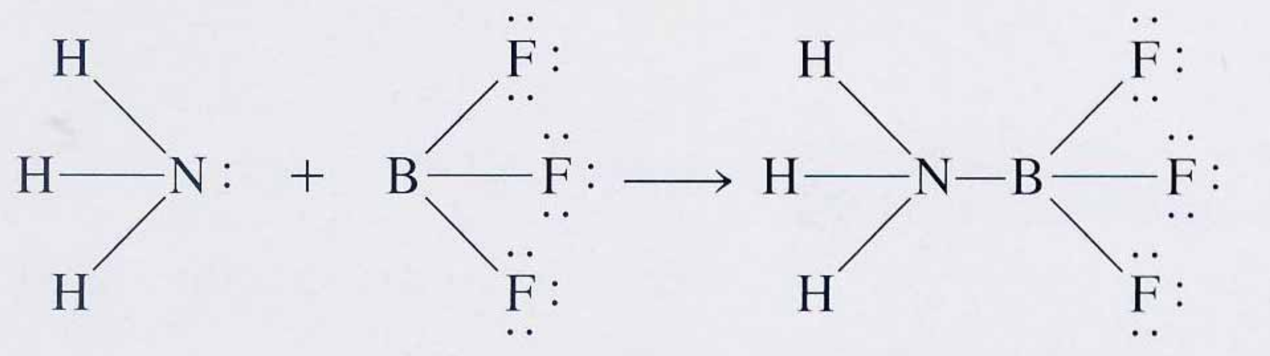
- Note that in this structure boron has only 6 electrons around it.

- The octet rule for boron can be satisfied by drawing a structure with a double bond, such as



- Recent studies indicate that double bonding may be important in BF_3.

- However, the boron atom in BF_3 certainly behaves as if it is electron-deficient, as indicated by the reactivity of BF_3 toward electron-rich molecules, for example, toward NH_3 to form H_3NBF_3:

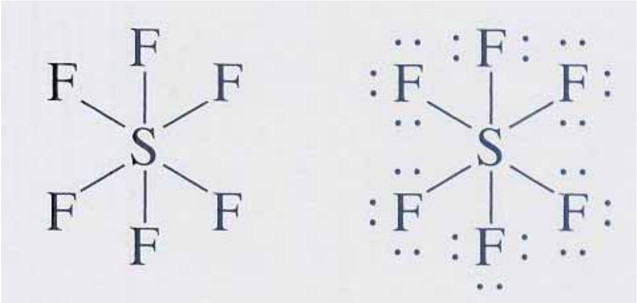


- In this stable compound, boron has an octet of electrons.

- Some atoms exceed the octet rule. This is behavior is observed only for those elements in Period 3 of the periodic table and beyond.
- To see how this arises, we will consider the Lewis structures for sulfur hexafluoride (SF6), a well-known and very stable molecule. The sum of the valence electrons is

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

- We have used 12 electrons to form the S—F bonds, which leaves 36 electrons.



- We have used 12 electrons to form the S—F bonds, which leaves 36 electrons.
- This structure uses all 48 valence electrons for SF_6, but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule.

- The sulfur atom is SF_6 can have 12 electrons around it by using the 3*s* and 3*p* orbitals to hold 8 electrons, with the extra 4 electrons placed in the formerly empty 3*d* orbitals.

Lewis Structures: Comments About the Octet Rule

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

Sample Exercise 8.7

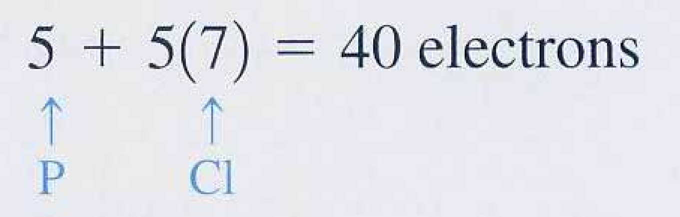
Lewis Structures for Molecule That Violate the Octet Rule I

Write the Lewis structure for PCl_5.

Solution

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

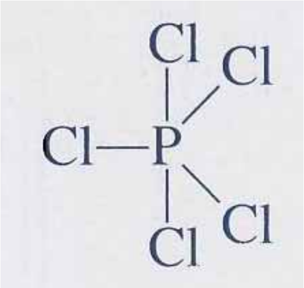
➡ 1 Sum the valence electrons.



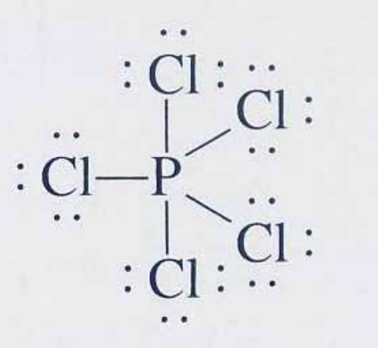
$$\underset{\substack{\uparrow \\ \text{P}}}{5} + \underset{\substack{\uparrow \\ \text{Cl}}}{5}(7) = 40 \text{ electrons}$$

Sample Exercise 8.7

➡ 2 Indicate single bonds between bound atoms.



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



Sample Exercise 8.7

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

See Exercises 8.71 and 8.72

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

Sample Exercise 8.8

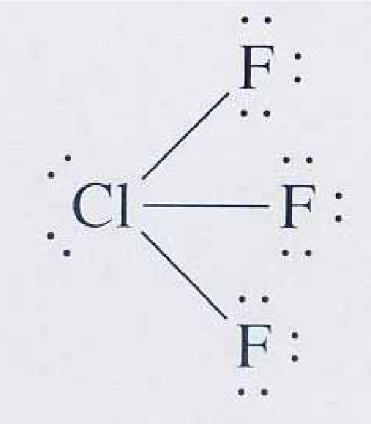
Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structures for each molecule or ion.

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

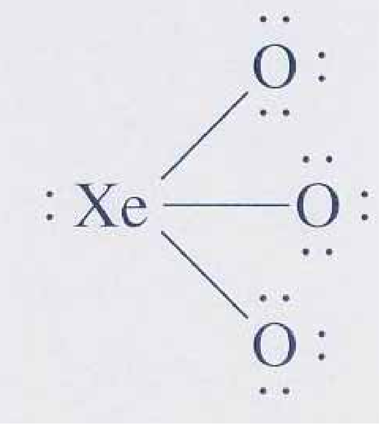
Solution

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

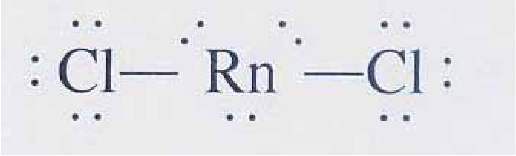


Sample Exercise 8.8

b. All atoms obey the octet rule.

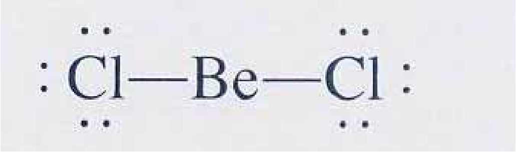


c. Radon, a noble gas in Period 6, accepts the extra electrons.

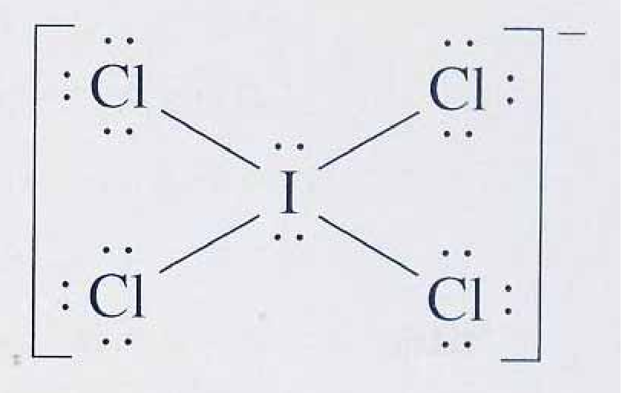


Sample Exercise 8.8

d. Beryllium is electron-deficient.



e. Iodine exceed the octet rule.

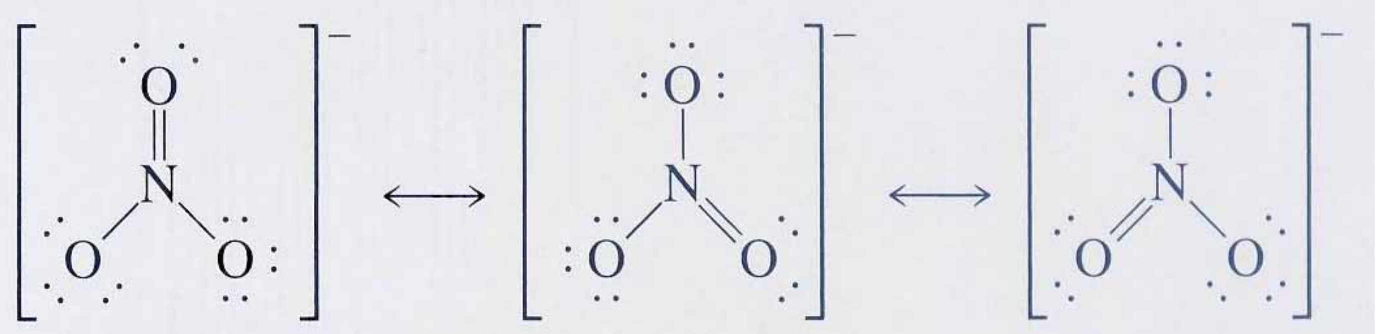


See Exercises 8.71 and 8.72

8.12 Resonance

- The correct description of NO_3^- is *not given by any one* of the three Lewis structures but is given only by the *superposition of all three*.
- The nitrate ion does not exist as any of the three extreme structures but exists as an average of all three.
- **Resonance** *is invoked when more than one valid Lewis structure can be written for a particular molecule*.
- The resulting electron structure of the molecule is given by the average of these **resonance structures**.

- This situation is usually represented by double-headed arrows as follows:



- Note that in all these resonance structures the arrangement of the nuclei is the same.
- Only the placement of the electrons differs.

- The net ionic equation for this reaction is

$$\mathrm{OH^- + HC_2H_3O_2}\,(aq) \longrightarrow \mathrm{H_2O}(l) + \mathrm{C_2H_3O_2^-}(aq)$$

- This reaction illustrates a very important general principle: *The hydroxide ion is such a strong base that for purposes of stoichiometric calculations it can be assumed to react completely with any weak acid that we will encounter.*

Sample Exercise 8.9

Resonance Structures

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

Solution

We will follow the usual procedure for obtaining the Lewis structure for the NO_2^- ion.

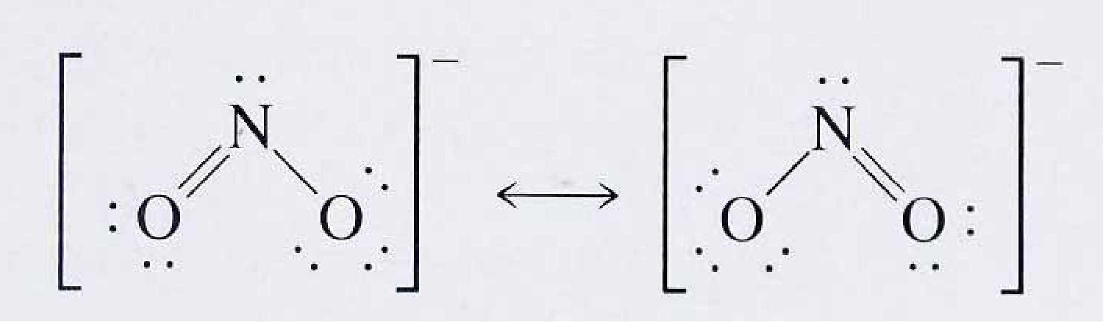
In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons.

Indicating the single bonds gives the structure

$$\mathrm{O{-}N{-}O}$$

Sample Exercise 8.9

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



This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two.*

Sample Exercise 8.9

There are two equivalent N---O bonds, each one intermediate between a single and a double bond.

See Exercises 8.73 through 8.78

Odd-Electron Molecules

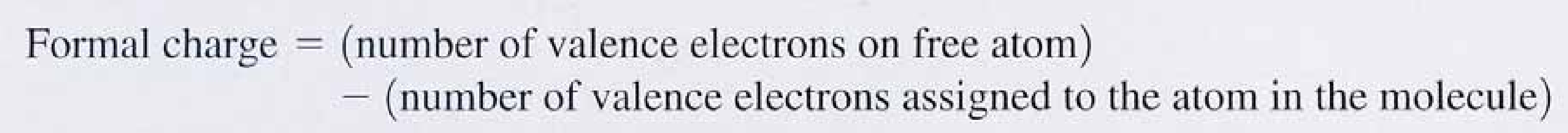
- Relatively few molecules formed from nonmetals contain odd number of electrons.
- One common example is nitric oxide (NO), which is formed when nitrogen and oxygen gases react at the high temperatures in automobile engines.

Formal Charge

- The **formal charge** of an atom in a molecule is *the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.*
- Therefore, to determine the formal charge of a given atom in a molecule, we need to know two things:

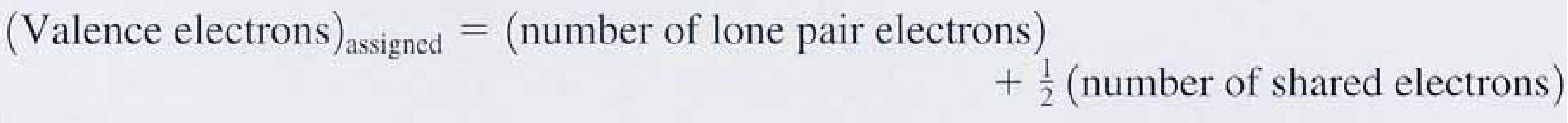
1. The number of valence electrons on the free neutral atom (which has zero net charge because the number of electrons equals the number of protons)

2. The number of valence electrons “beloning” to the atom in a molecule



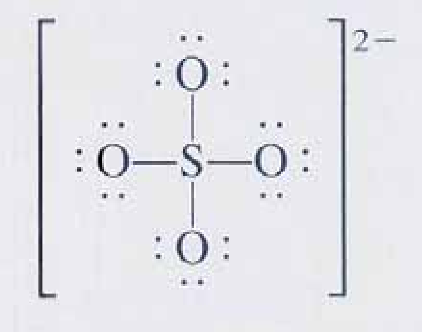
Formal charge = (number of valence electrons on free atom)
− (number of valence electrons assigned to the atom in the molecule)

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

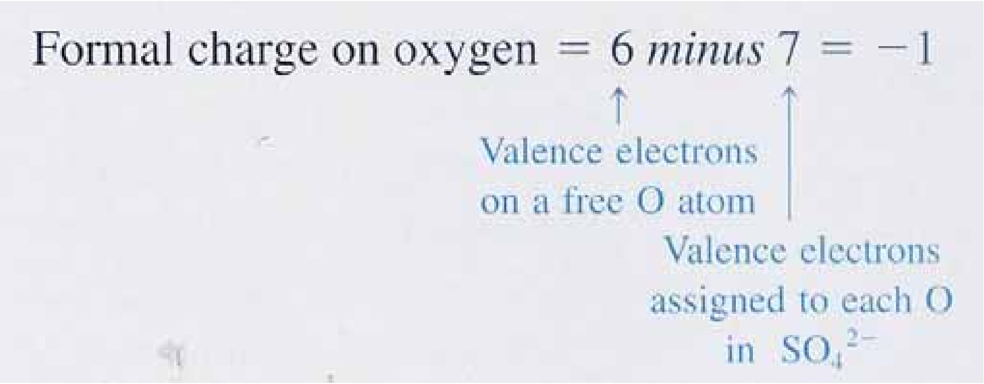


$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \tfrac{1}{2}(\text{number of shared electrons})$$

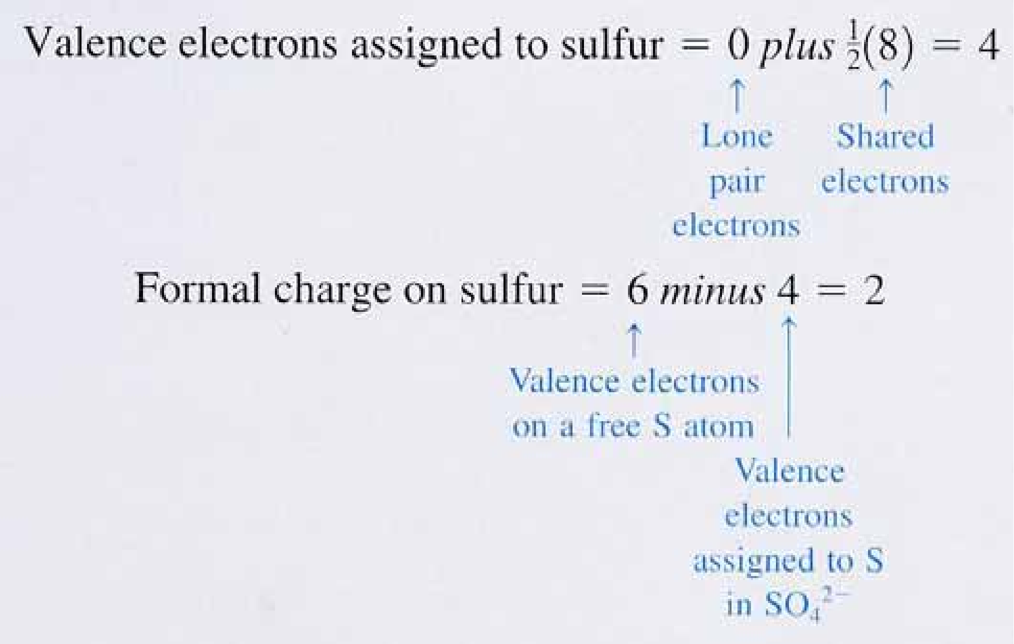
- The possible Lewis structures for the sulfate ion, which has 32 valence electrons.
- For the Lewis structure



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



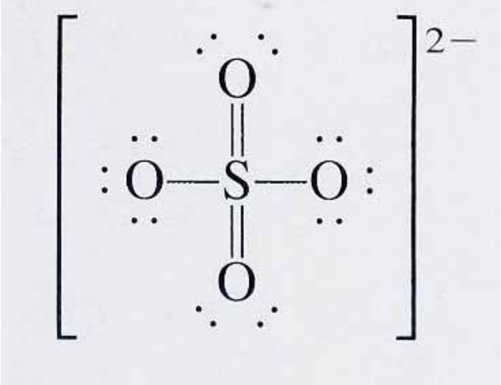
$$\text{Formal charge on oxygen} = \underset{\substack{\uparrow\\ \text{Valence electrons}\\ \text{on a free O atom}}}{6}\ \textit{minus}\ \underset{\substack{\uparrow\\ \text{Valence electrons}\\ \text{assigned to each O}\\ \text{in } SO_4^{2-}}}{7} = -1$$



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

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

- A second possible Lewis structure is

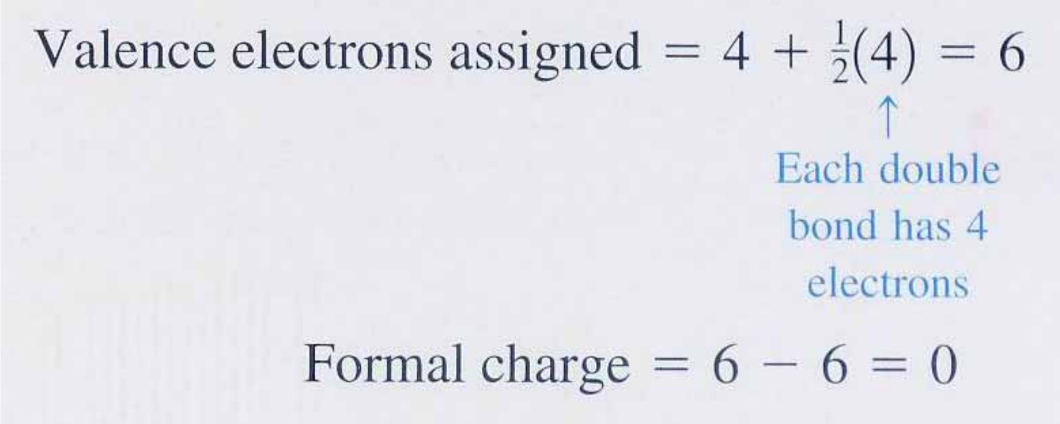


- For oxygen atoms with single bonds:

Valence electrons assigned = 6 + ½(2) = 7

Formal charge = 6 − 7 = −1

- For oxygen atoms with double bonds:



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

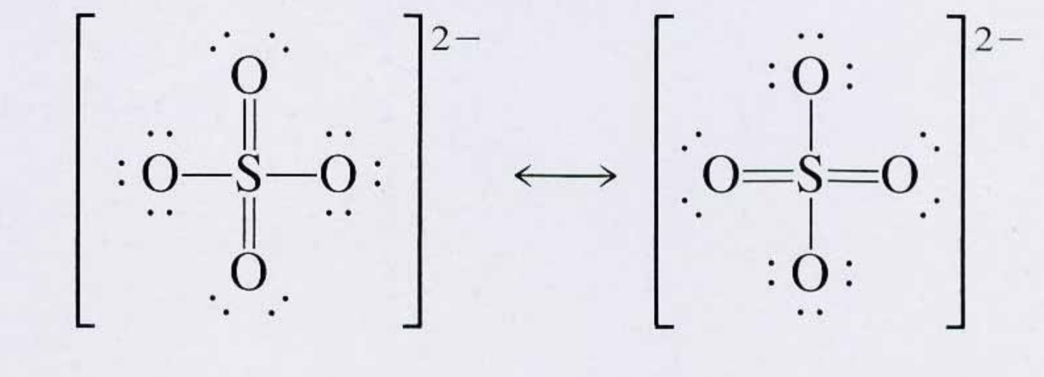
$$\text{Formal charge} = 6 - 6 = 0$$

- For the sulfur atom:

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

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

- Thus, for the sulfate ion, we might expect resonance structures such as



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

Rules Governing Formal Charge

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

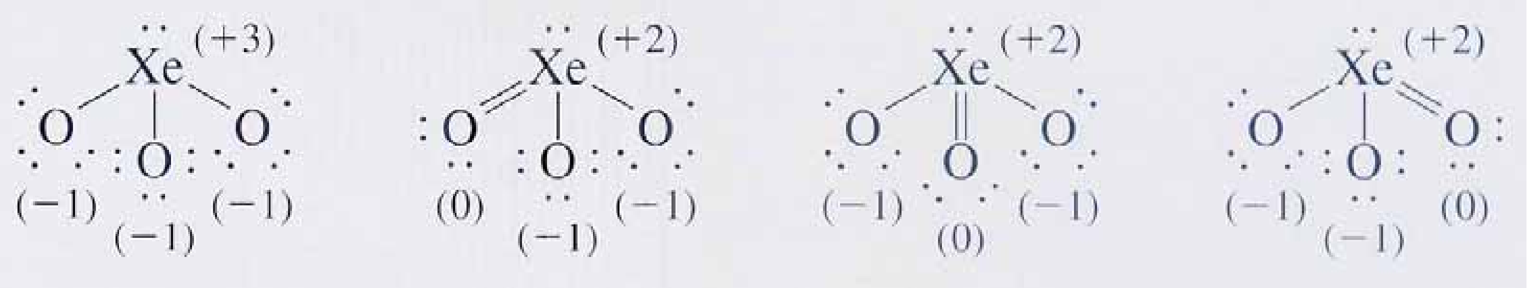
Sample Exercise 8.10

Formal Charges

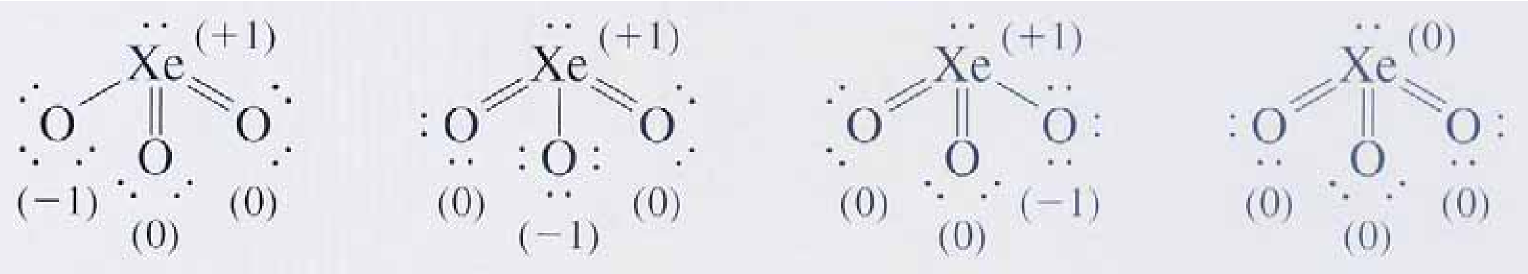
Give possible Lewis structures for XeO_3, an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

Solution

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



Sample Exercise 8.10



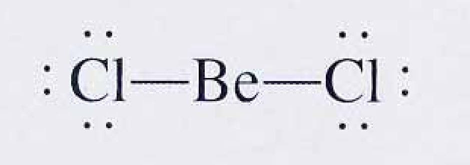
Based on the ideas of formal charge, we would predict that the Lewis structures with the lower values of formal charge would be must appropriate for describing the bonding in XeO_3.

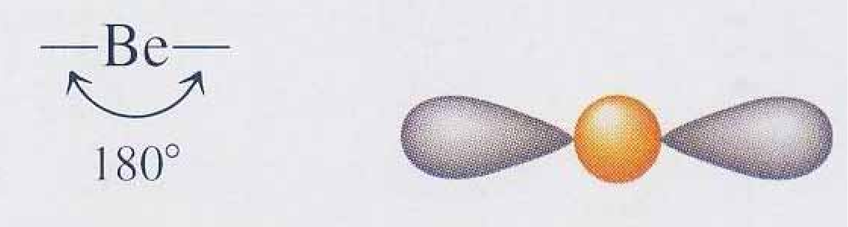
See Exercises 8.81 through 8.86

8.13 Molecule Structure: The VSEPR Model

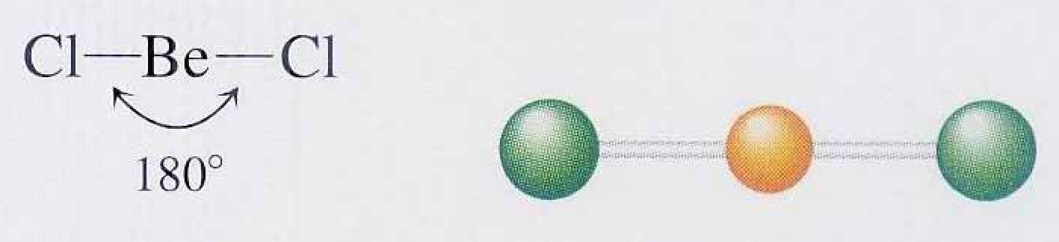
- The structures of molecule play a very important role in determining their chemical properties.
- Many accurate methods now exist for determining **molecular structure**, the threed-imensional arrangement of the atoms in a molecule.
- A model, called the **valence shell electron-pair repulsion (VSEPR) model**, is useful in predicting the geometries of molecules formed from nonmetals.

- The main postulate of this model is that *the structure around a given atom is determined principally by minimizing electron-pair repulsions*.
- The molecule $BeCl_2$,

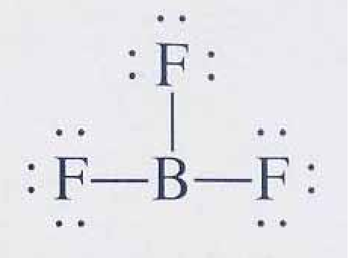


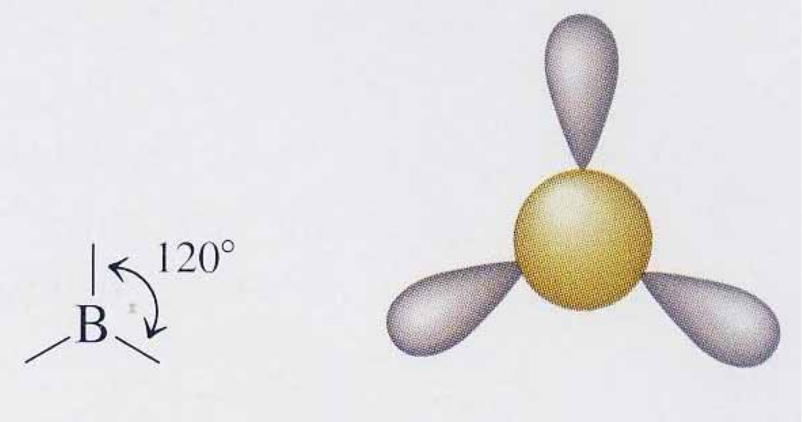


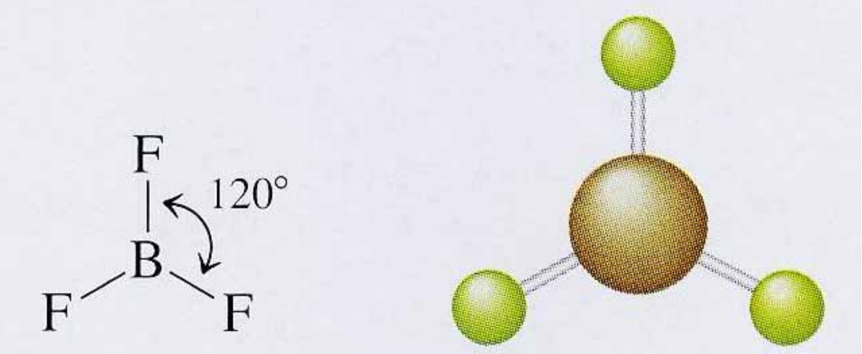
- Since each electron pair in beryllium is shared with a chlorine atom, the molecule has a linear structure with a 180-degree bond angle:



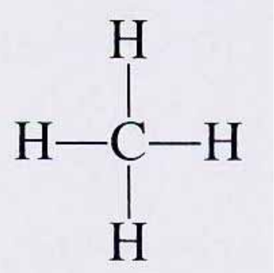
- BF_3,

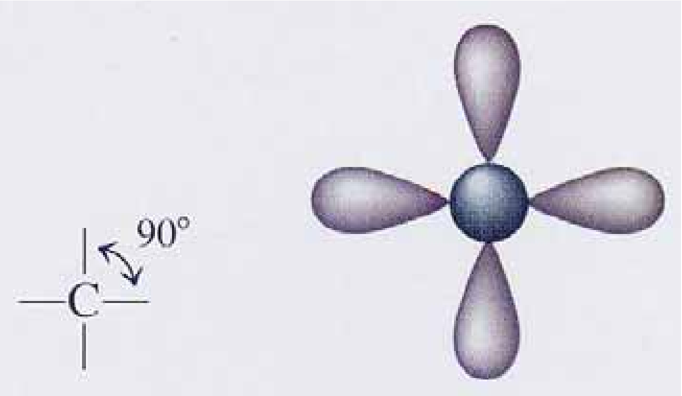



120°
B

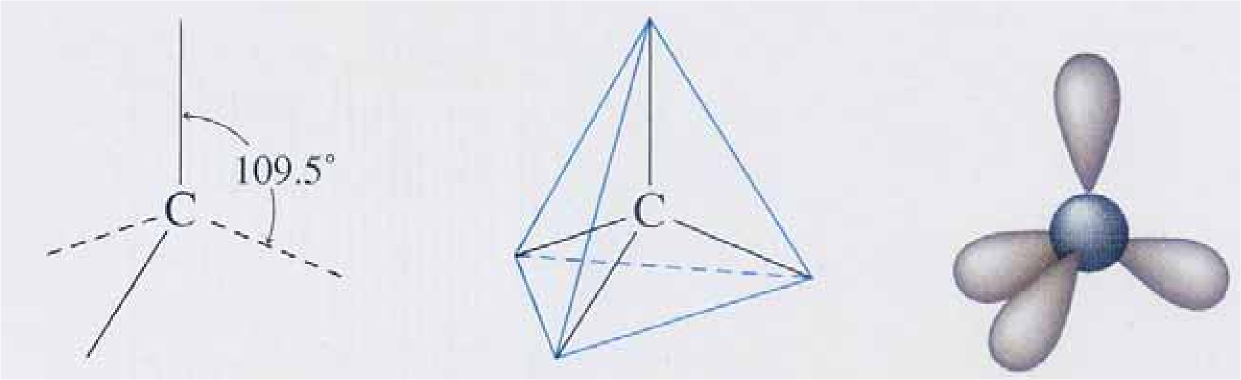

F
120°
B
F
F

- This is a planer (flat) and triangular molecule, which is commonly described as a **trigo-nal planar structure**.
- methane molecule,



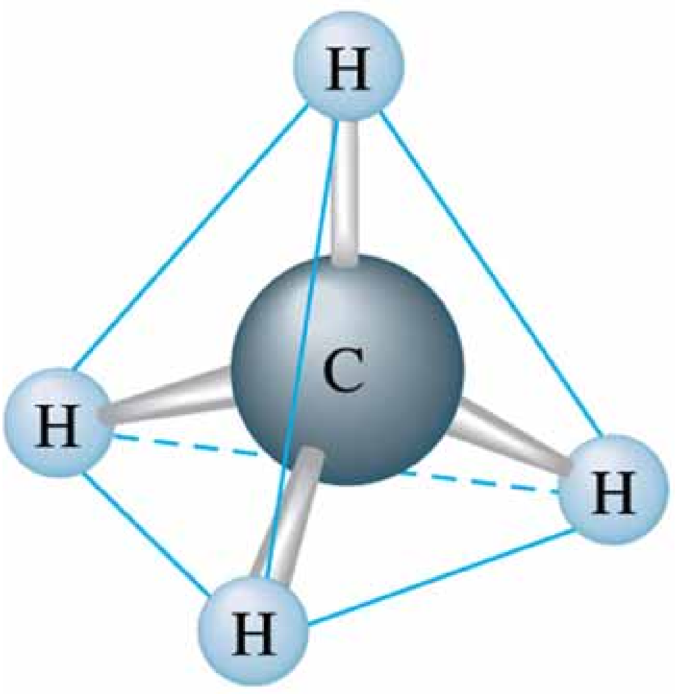


- The tetrahedral structure has angles of 109.5 degrees:



- *whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally.*

Figure 8.15



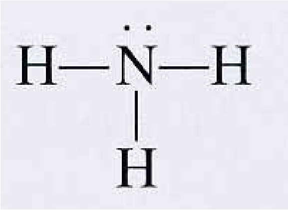
The molecular structure of methane. The tetrahedral arrangement of electron pairs produces a tetrahedral arrangement of hydrogen atoms.

Steps to Apply the VSEPR Model

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

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

1 **Draw the Lewis structure:**



2 **Count the pairs of electrons and arrange them to minimize repulsions.**

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

4 **Name the molecular structure. It is very important to recognize that the name of the molecular structure is always based on the *positions of the atoms*.**

- The molecular structure of ammonia is a **trigonal pyramid** (one side is different from the other three) rather than a tetrahedron, as shown in Fig. 8.16(c).

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

Figure 8.16

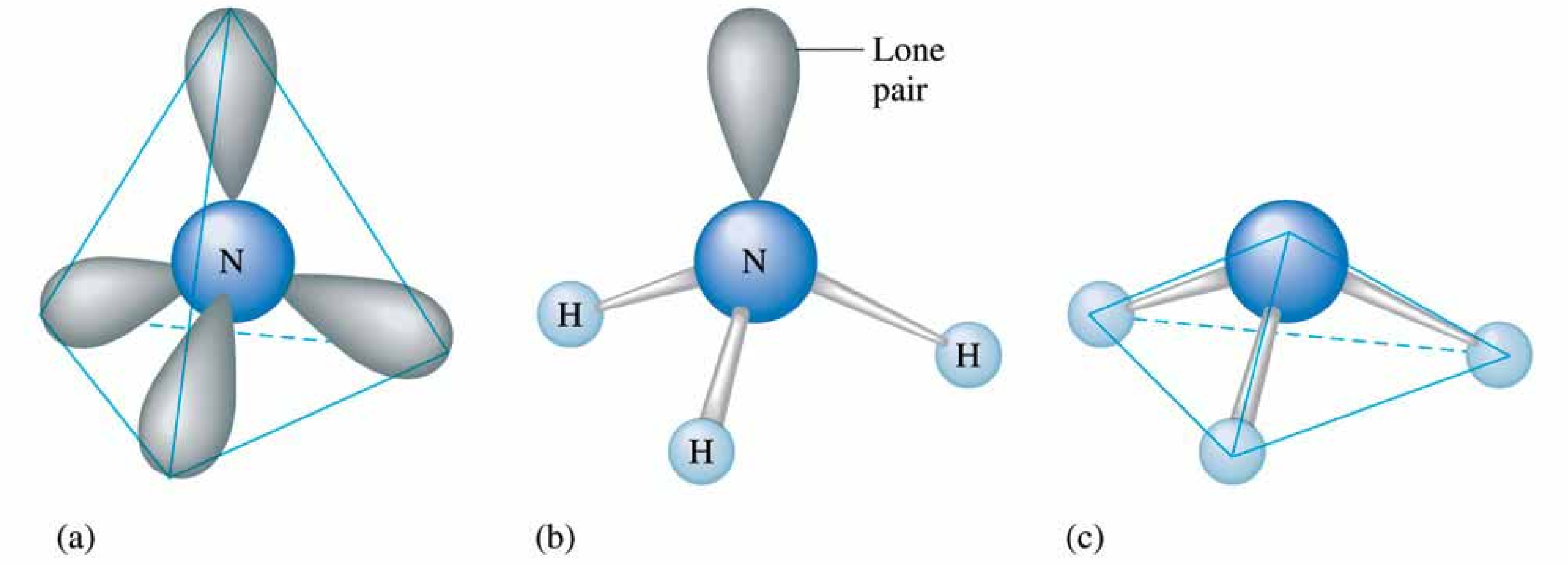


Figure 8.16

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

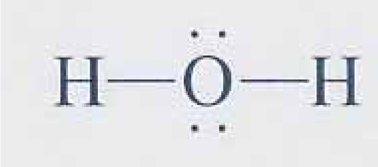
Sample Exercise 8.11

Prediction of Molecular Structure I

Describe the molecular structure of the water molecule.

Solution

The Lewis structure for water is



$$H-\underset{\cdot\cdot}{\ddot{O}}-H$$

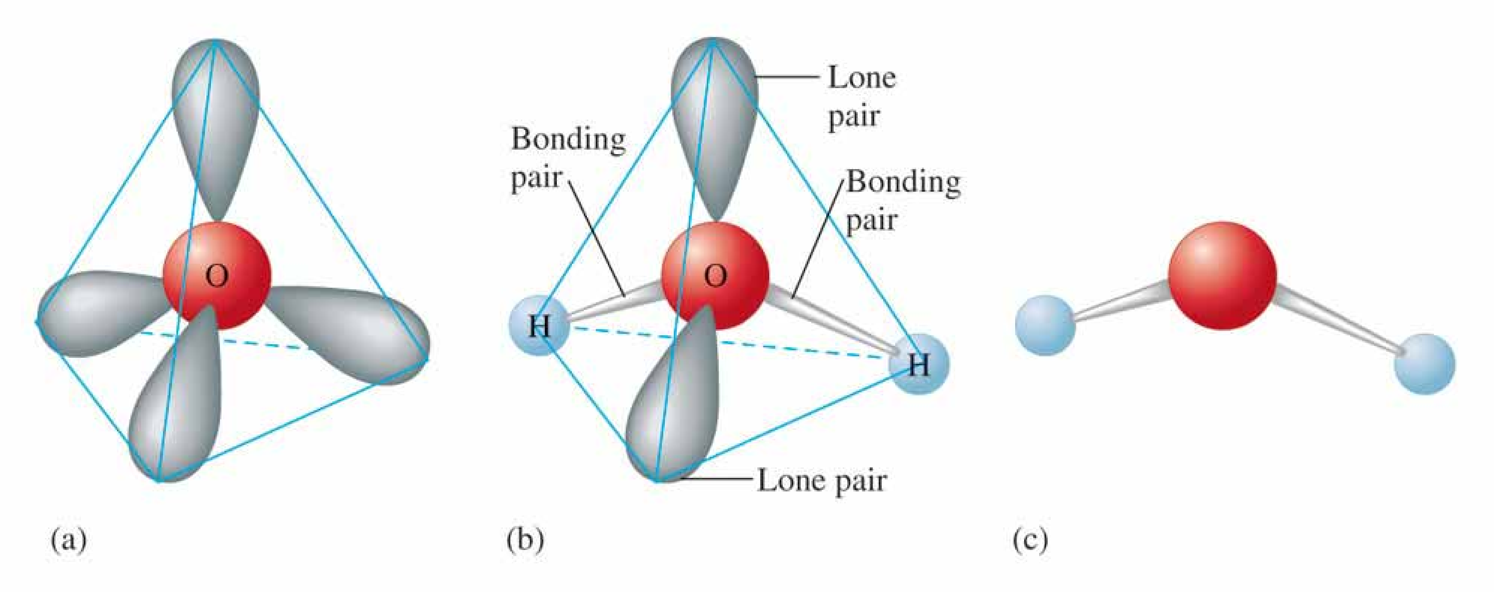
There are four pairs of electrons: two bonding pairs and two nonbonding pairs. To minimize repulsions, these are best arranged in a tetrahedral array, as shown in Fig. 8.17(a).

Sample Exercise 8.11

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

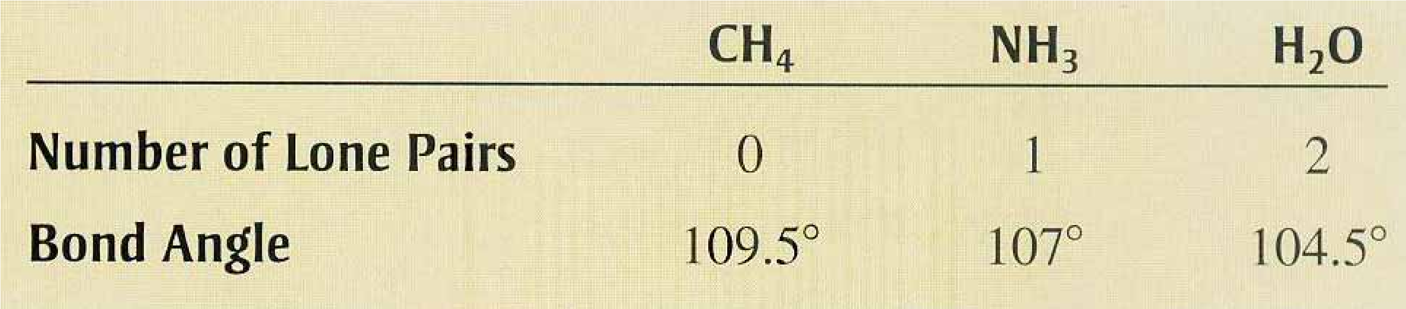
See Exercises 8.91 and 8.92

Figure 8.17



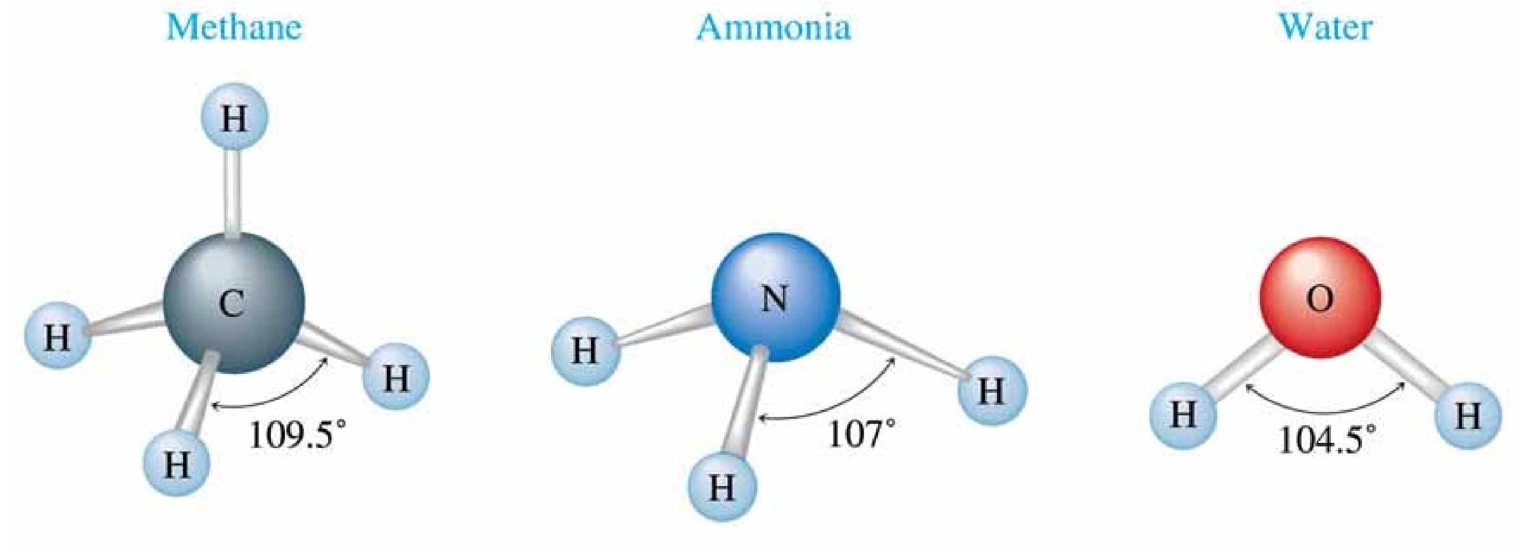
(a) The tetrahedral arrangement of the four electron pairs around oxygen in the water molecule. (b) Two of the electron pairs are shared between oxygen and the hydrogen atoms and two are lone pairs. (c) The V-shaped molecular structure of the water molecule.

- From the previous discussion we would predict that the H—X—H bond angle in CH_4, NH_3, and H_2O should be the tetrahedral angle of 109.5 degrees.
- Experimental studies, show that the actual bond angles are those given in Fig. 8.18.



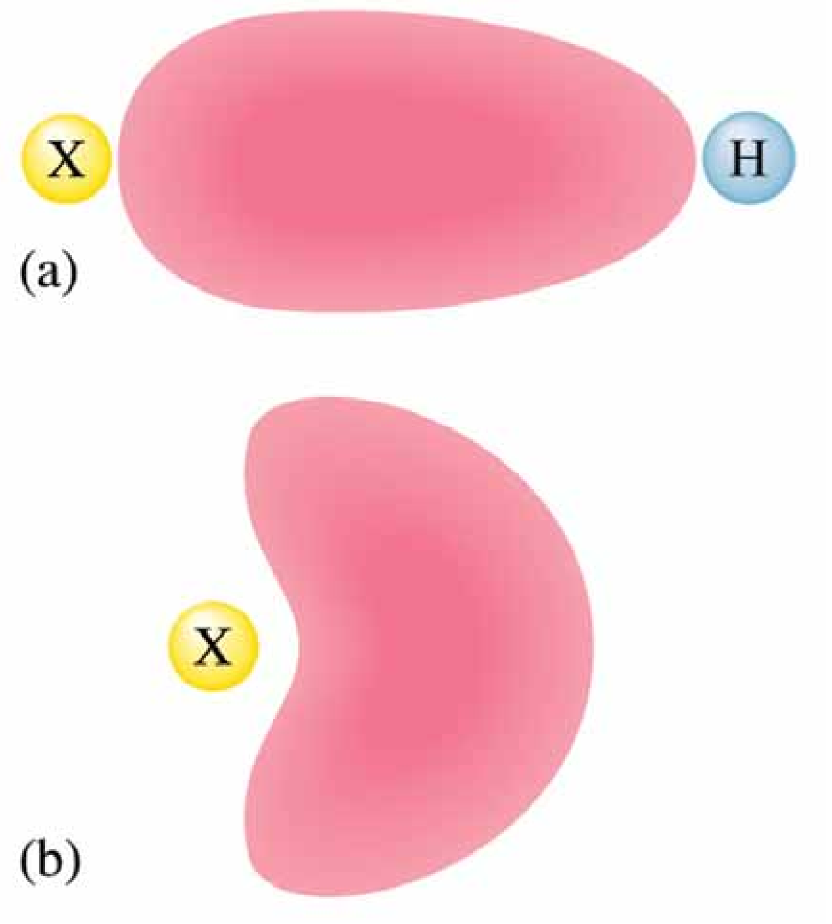
	CH_4	NH_3	H_2O
Number of Lone Pairs	0	1	2
Bond Angle	109.5°	107°	104.5°

Figure 8.18



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

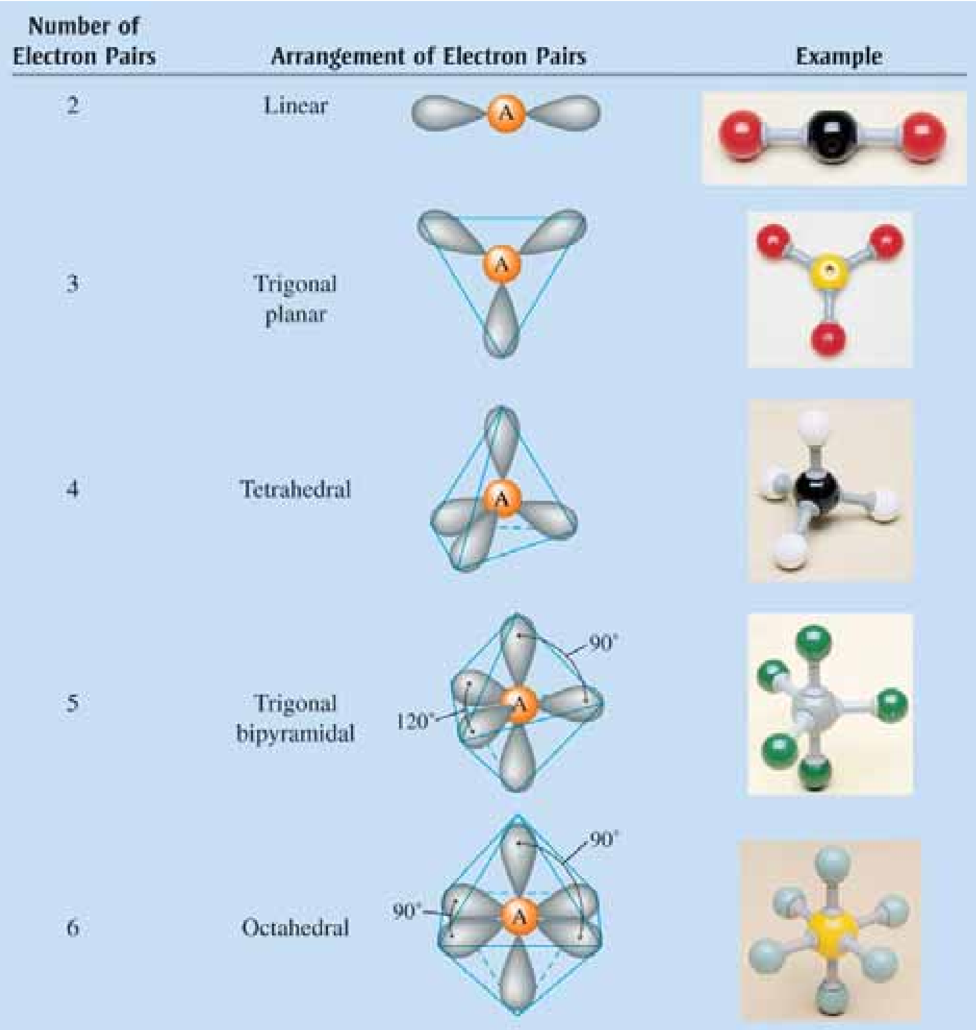
Figure 8.19



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

- As a result of these observations, we make the following addition to the original postulate of the VSEPR model: *Lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs*.
- So far we have considered cases with two, three, and four electron pairs around the central atom. These are summarized in Table 8.6.

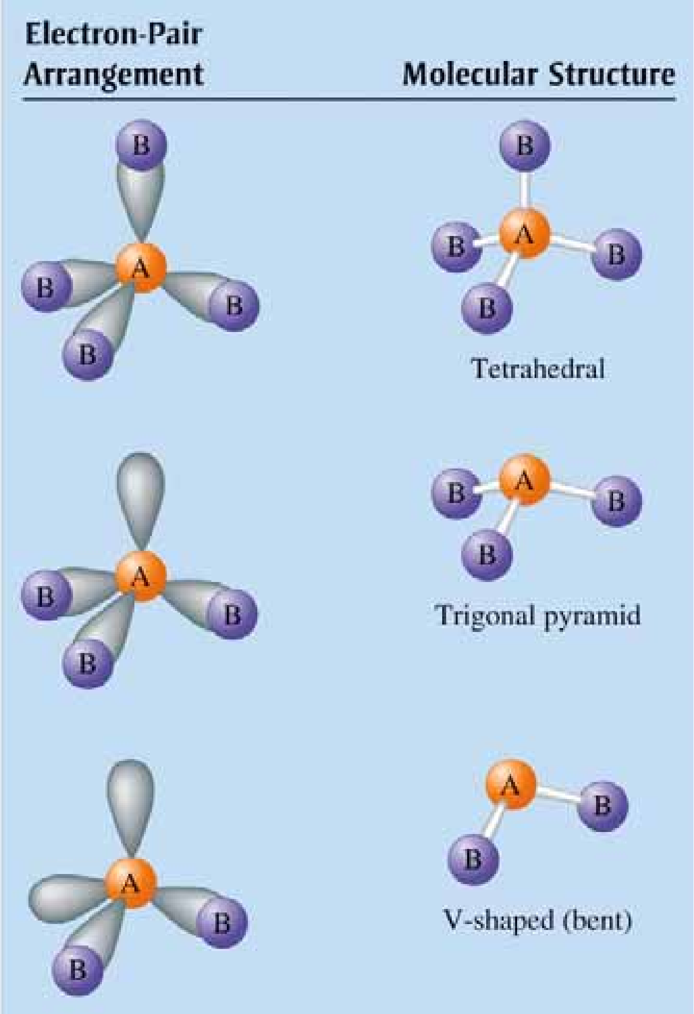
TABLE 8.6 Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion



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

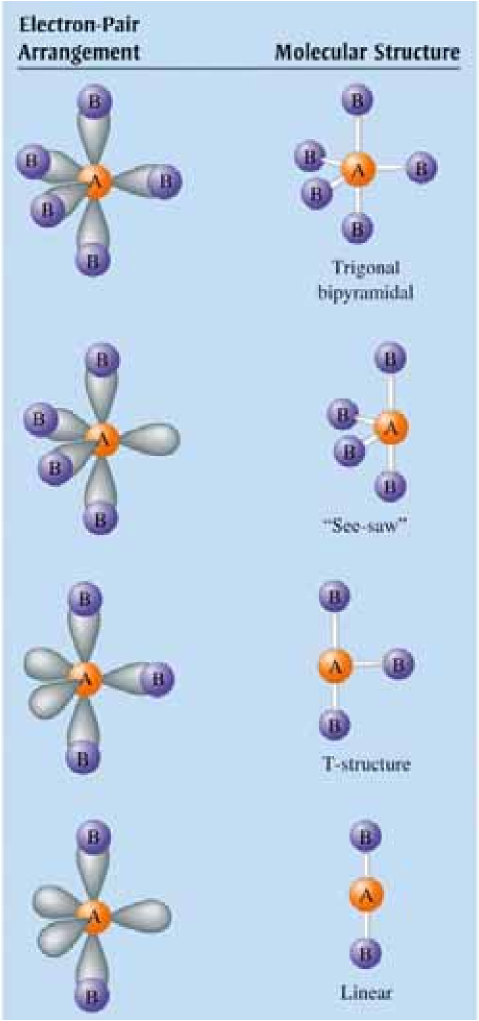
- Table 8.7 summarizes the structures possible for molecules in which there are four electron pairs around the central atom with various numbers of atoms bonded to it.
- Note that molecules with four pairs of electrons around the central atom can be tetrahedral (AB_4), trugonal pyamidal (AB_3), and V-shaped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

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



- For five pairs of electrons, there are several possible choices. The one that produces minimum repulsion is **trigonal bipyramid**.
- Note from Table 8.6 that this arrangement has two different angles, 90 degrees and 120 degrees.
- Table 8.8 summarizes the structures possible for molecules in which there are five electron pairs around the central atom with various numbers of atoms bonded to it.

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



- Note that molecules with five pairs of electrons around the central atom can be trigonal bipyamidal (AB_5), see-saw (AB_4), T-shaped (AB_3), and linear (AB_2).
- Six pairs of electrons can best be arranged around a given atom with 90-degree angles to form an **octahedral structure**, as shown in Table 8.6.

Sample Exercise 8.12

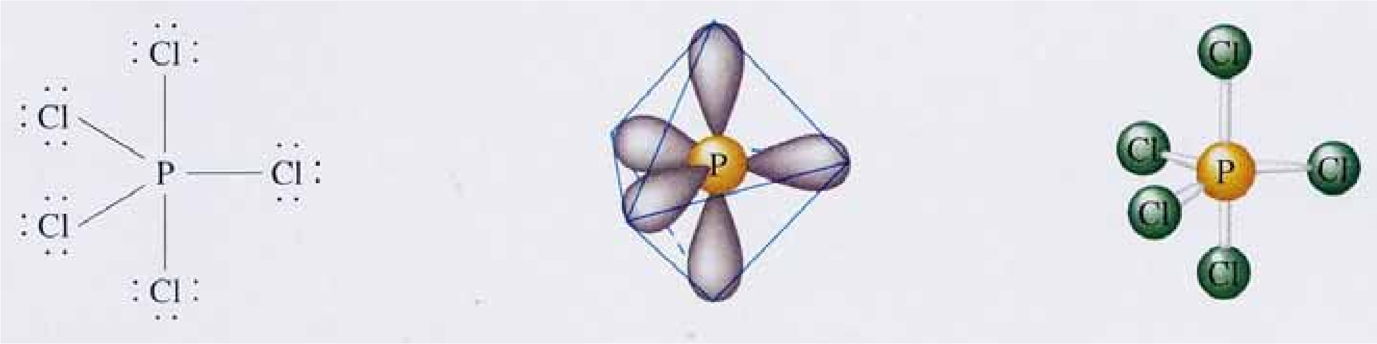
Prediction of Molecular Structure II

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

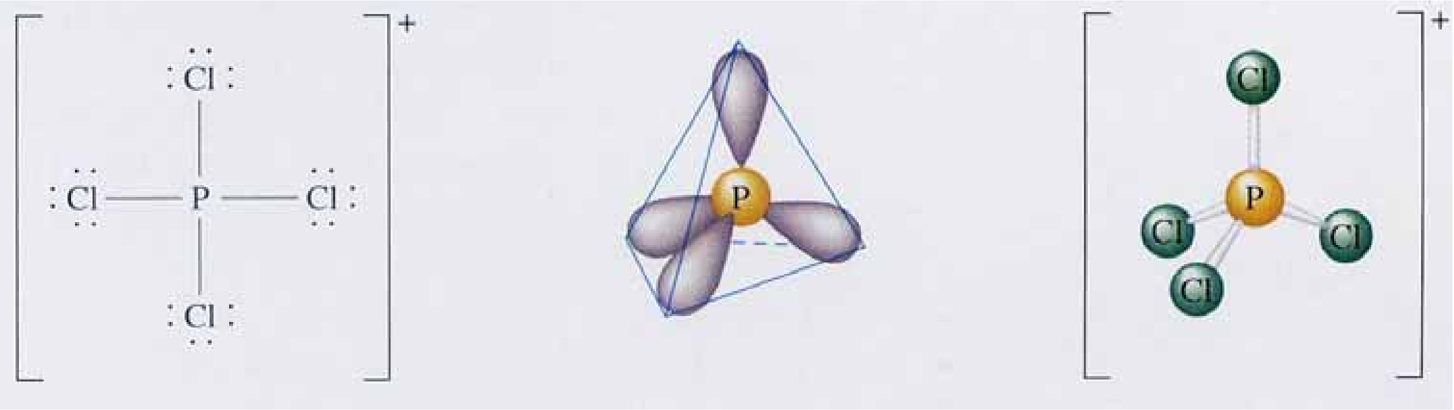
Solution

The Lewis structures for PCl_5 is shown.

Sample Exercise 8.12

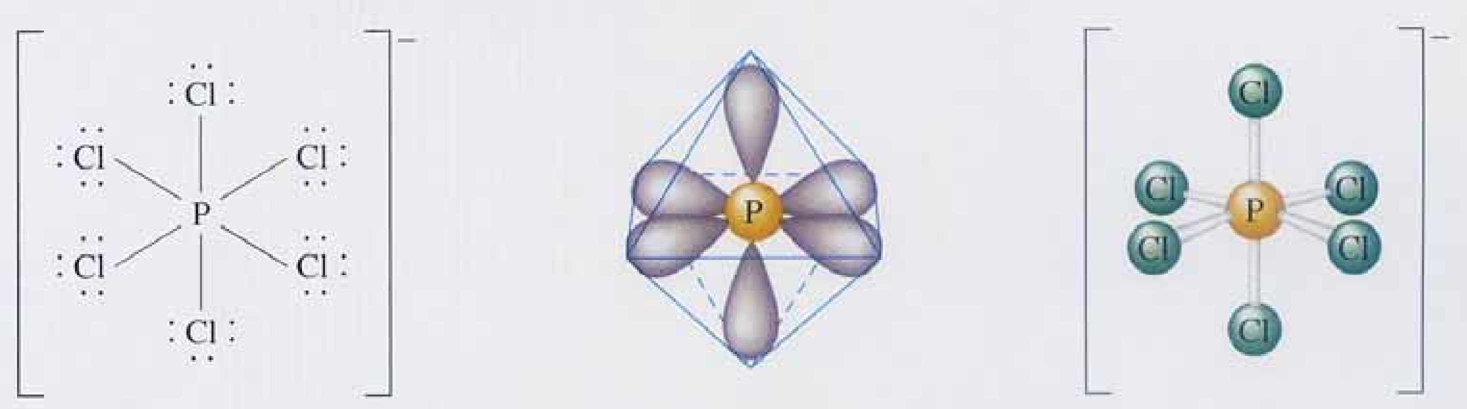


The Lewis structure for the PCl_4^+ ion $(5 + 4(7) - 1 = 32$ valence electrons) is shown below.



Sample Exercise 8.12

The Lewis structure for PCl_6^- $(5 + 6(7) + 1 = 48$ valence electrons) is shown below.



See Exercises 8.89, 8.90, 8.93, and 8.94

Sample Exercise 8.13

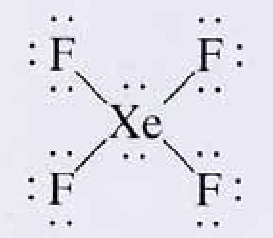
Prediction of Molecular Structure III

Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called inert gases because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4). Predict its structure and whether it has a dipole moment.

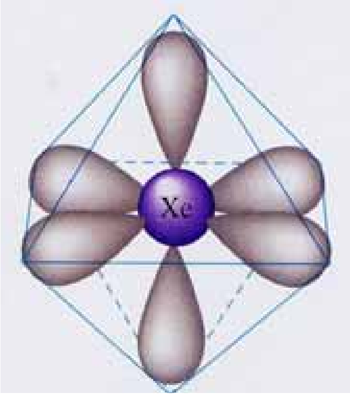
Sample Exercise 8.13

Solution

The Lewis structure for XeF_4 is



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



Sample Exercise 8.13

The structure predicted for this molecule will depend on how the lone pairs and bonding pairs are arranged. Consider the two possibilities shown in Fig. 8.20. The bonding pairs are indicated by the presence of the fluorine atoms. Since the structure predicted differs in the two cases, we must decide which of these arrangements is preferable. The key is to look at the lone pairs. In the structure in part (a), the lone pair-lone pair angle is 90 degrees; in the structure in part (b), the lone pairs are separated by 180 degrees. Since lone pairs require more

Sample Exercise 8.13

room than bonding pairs, a structure with two lone pairs at 90 degrees is unfavorable. Thus the arrangement in Fig. 8.20(b) is preferred, and the molecular structure is predicted to be square planar. Note that this molecule is not described as being octahedral. There is an octahedral arrangement of electron pairs, but the atoms form a **square planar structure**.

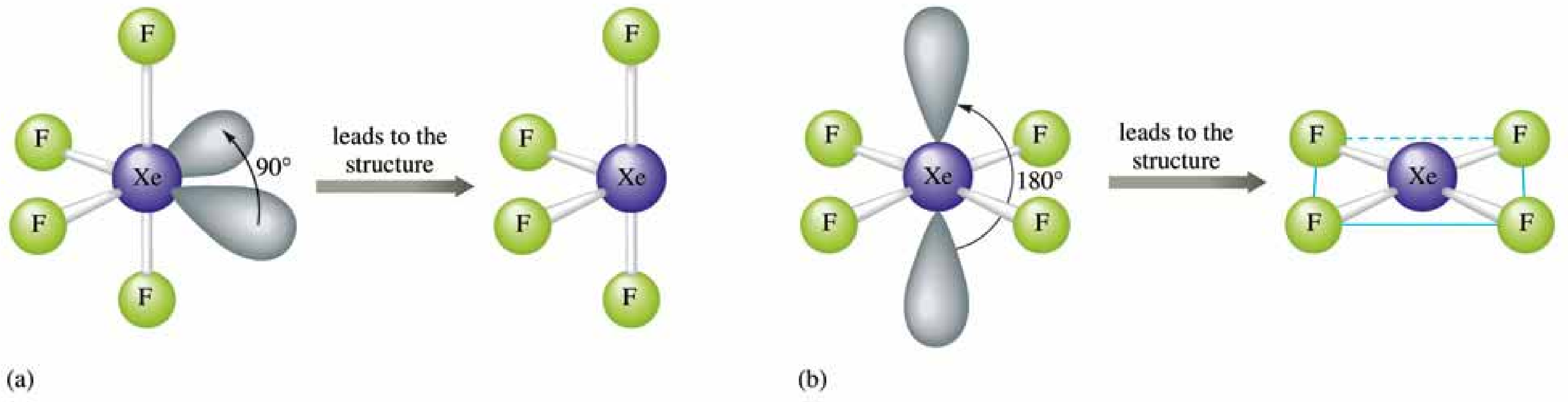
Although each Xe—F bond is polar (fluorine has a greater electronegativity than xenon), the square planar arrangement of these bonds causes the polarities to cancel.

Sample Exercise 8.13

Thus XeF_4 has no dipole moment, as shown in the margin.

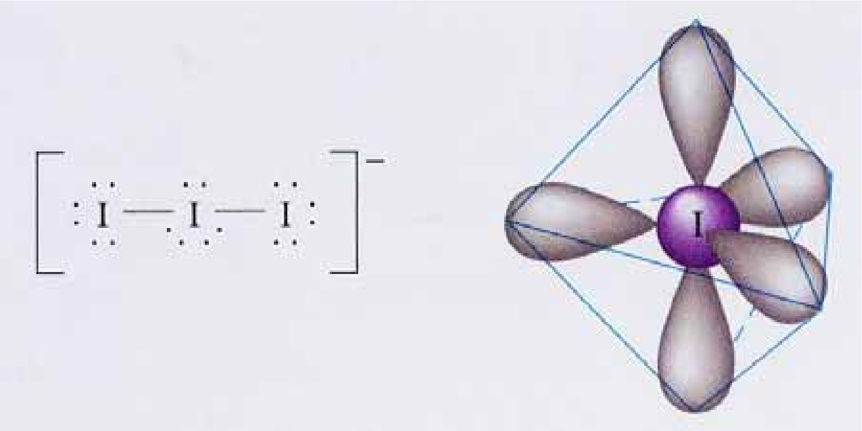
See Exercises 8.95 through 8.98.

Figure 8.20



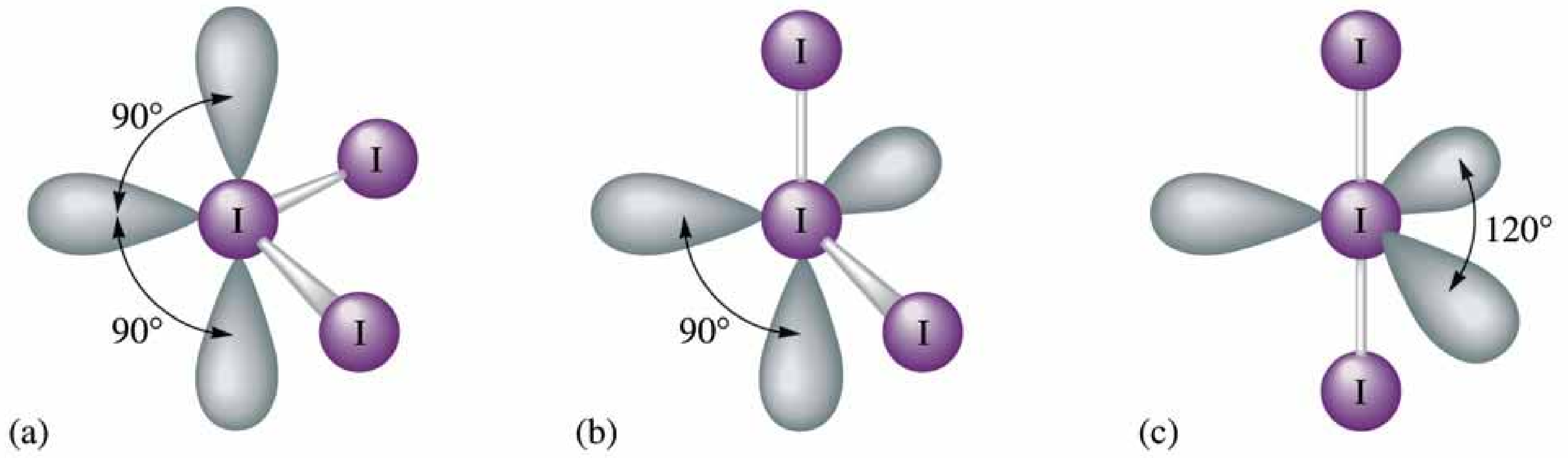
Possible electron-pair arrangements for XeF_4. Since arrangement (a) has lone pairs at 90 degrees from each other, it is less favorable than arrangement (b), where the lone pairs are at 180 degrees.

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



- Several possible arrangements of lone pairs are shown in Fig. 8.21.

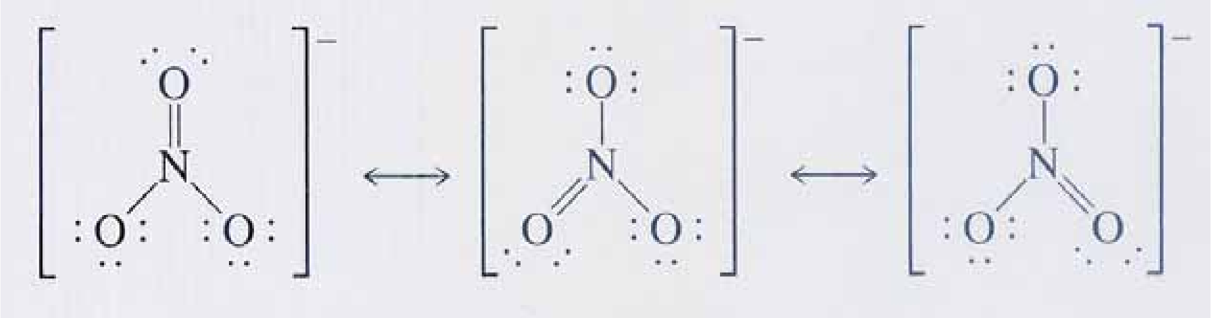
Figure 8.21



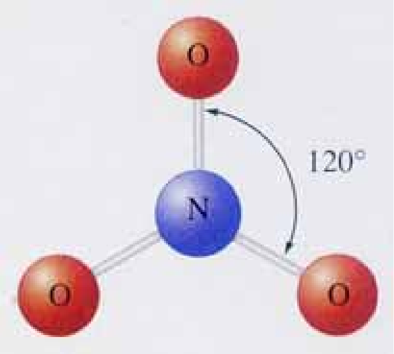
Three possible arrangements of the electron pairs in the I_3^- ion. Arrangement (c) is preferred because there are no 90-degree lone pair-lone pair interactions.

The VSEPR Model and Multiple Bonds

- NO_3^- ion, which requires three resonance structures to describe its electronic structure:



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



- This planar structure is the one expected for three pairs of electrons around a central atom, which means that *a double bond should be counted as one effective pair in using the VSEPR model.*
- *For the VSEPR model, multiple bonds count as one effective electron pair*.

- The molecular structure of nitrate also shows us one more important point: *When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.*

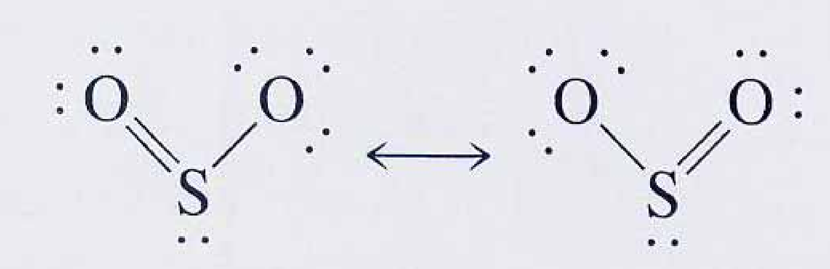
Sample Exercise 8.14

Structures of Molecules with Multiple Bonds

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

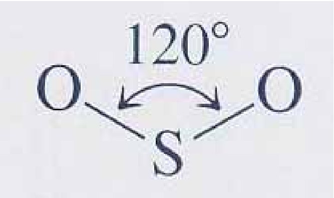
Solution

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



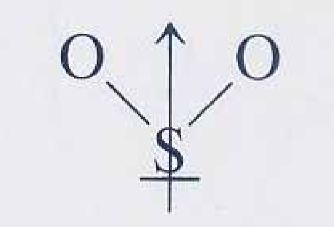
Sample Exercise 8.14

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



Sample Exercise 8.14

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



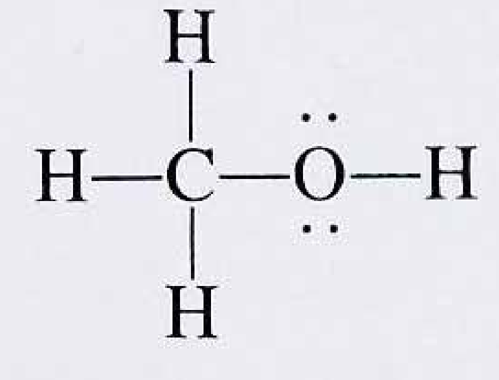
Since the molecule is V-shaped, the polar bonds do not cancel.

See Exercises 8.99 and 8.100

- The angle in the SO_2 molecule is actually quite close to 120 degrees.
- We will follow the general principle that *a 120-degree angle provides lone pairs with enough space so that distortions do not occur*.
- *Angles less than 120 degrees are distorted when lone pairs are present.*

Molecules Containing No Single Central Atom

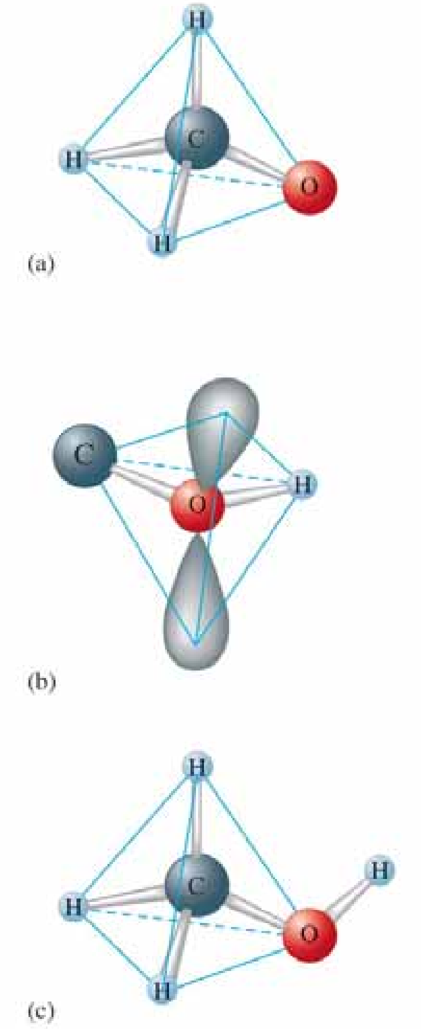
- The VSEPR model can be readily extended to more complicated molecules, such as methanol (CH_3OH).



- Note that there are four pairs of electrons around the carbon, which requires a tetrahedral arrangement, as shown in Fig. 8.22(a).

- The tetrahedron will be slightly distorted by the space requirements of the lone pairs [Fig. 8.22(b)].
- The overall geometric arrangement for the molecule is shown in Fig. 8.22(c).

Figure 8.22



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

Summary of the VSEPR Model

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

- Determine the Lewis structure(*s*) for the molecule.
- For molecules with resonance structures, use any of the structures to predict the molecular structure.
- Sum the electron pairs around the central atom.
- In counting pairs, count each multiple bond as a single effective pair.
- The arrangement of the pairs is determined by minimizing electron-pair repulsions. These arrangements are shown in Table 8.6.

- Lone pairs require more space than bonding pairs do. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120 degrees.