

## 220 Chapter Five Gases

- 35.** An 11.2-L sample of gas is determined to contain 0.50 mol of N<sub>2</sub>. At the same temperature and pressure, how many moles of gas would there be in a 20.-L sample?

- 36.** Consider the following chemical equation.



If 25.0 mL of NO<sub>2</sub> gas is completely converted to N<sub>2</sub>O<sub>4</sub> gas under the same conditions, what volume will the N<sub>2</sub>O<sub>4</sub> occupy?

- 37.** Complete the following table for an ideal gas.

P(atm)	V(L)	n(mol)	T
a. 5.00		2.00	155°C
b. 0.300	2.00		155 K
c. 4.47	25.0	2.01	
d.	2.25	10.5	75°C

- 38.** Complete the following table for an ideal gas.

P	V	n	T
a. $7.74 \times 10^3$ Pa	12.2 mL		25°C
b.	43.0 mL	0.421 mol	223 K
c. 455 torr		$4.4 \times 10^{-2}$ mol	331°C
d. 745 mm Hg	11.2 L	0.401 mol	

- 39.** Suppose two 200.0-L tanks are to be filled separately with the gases helium and hydrogen. What mass of each gas is needed to produce a pressure of 135 atm in its respective tank at 24°C?

- 40.** A flask that can withstand an internal pressure of 2500 torr, but no more, is filled with a gas at 21.0°C and 758 torr and heated. At what temperature will it burst?

- 41.** A 2.50-L container is filled with 175 g argon.

- a. If the pressure is 10.0 atm, what is the temperature?  
b. If the temperature is 225 K, what is the pressure?

- 42.** A person accidentally swallows a drop of liquid oxygen, O<sub>2</sub>(l), which has a density of 1.149 g/mL. Assuming the drop has a volume of 0.050 mL, what volume of gas will be produced in the person's stomach at body temperature (37°C) and a pressure of 1.0 atm?

- 43.** A gas sample containing 1.50 mol at 25°C exerts a pressure of 400. torr. Some gas is *added* to the same container and the temperature is increased to 50.°C. If the pressure increases to 800. torr, how many moles of gas were added to the container? Assume a constant-volume container.

- 44.** A bicycle tire is filled with air to a pressure of 100. psi at a temperature of 19°C. Riding the bike on asphalt on a hot day

increases the temperature of the tire to 58°C. The volume of the tire increases by 4.0%. What is the new pressure in the bicycle tire?

- 45.** Consider two separate gas containers at the following conditions:

Container A	Container B
Contents: SO <sub>2</sub> (g)	Contents: unknown gas
Pressure = P <sub>A</sub>	Pressure = P <sub>B</sub>
Moles of gas = 1.0 mol	Moles of gas = 2.0 mol
Volume = 1.0 L	Volume = 2.0 L
Temperature = 7°C	Temperature = 287°C

How is the pressure in container B related to the pressure in container A?

- 46.** A container is filled with an ideal gas to a pressure of 40.0 atm at 0°C.

- a. What will be the pressure in the container if it is heated to 45°C?  
b. At what temperature would the pressure be  $1.50 \times 10^2$  atm?  
c. At what temperature would the pressure be 25.0 atm?

- 47.** An ideal gas is contained in a cylinder with a volume of  $5.0 \times 10^2$  mL at a temperature of 30.°C and a pressure of 710. torr. The gas is then compressed to a volume of 25 mL, and the temperature is raised to 820.°C. What is the new pressure of the gas?

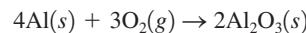
- 48.** A compressed gas cylinder contains  $1.00 \times 10^3$  g of argon gas. The pressure inside the cylinder is 2050. psi (pounds per square inch) at a temperature of 18°C. How much gas remains in the cylinder if the pressure is decreased to 650. psi at a temperature of 26°C?

- 49.** A sealed balloon is filled with 1.00 L of helium at 23°C and 1.00 atm. The balloon rises to a point in the atmosphere where the pressure is 220. torr and the temperature is –31°C. What is the change in volume of the balloon as it ascends from 1.00 atm to a pressure of 220. torr?

- 50.** A hot-air balloon is filled with air to a volume of  $4.00 \times 10^3$  m<sup>3</sup> at 745 torr and 21°C. The air in the balloon is then heated to 62°C, causing the balloon to expand to a volume of  $4.20 \times 10^3$  m<sup>3</sup>. What is the ratio of the number of moles of air in the heated balloon to the original number of moles of air in the balloon? (*Hint:* Openings in the balloon allow air to flow in and out. Thus the pressure in the balloon is always the same as that of the atmosphere.)

### Gas Density, Molar Mass, and Reaction Stoichiometry

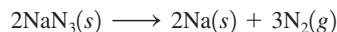
- 51.** Consider the following reaction:



It takes 2.00 L of pure oxygen gas at STP to react completely with a certain sample of aluminum. What is the mass of aluminum reacted?

**52.** A student adds 4.00 g of dry ice (solid CO<sub>2</sub>) to an empty balloon. What will be the volume of the balloon at STP after all the dry ice sublimes (converts to gaseous CO<sub>2</sub>)?

**53.** Air bags are activated when a severe impact causes a steel ball to compress a spring and electrically ignites a detonator cap. This causes sodium azide (NaN<sub>3</sub>) to decompose explosively according to the following reaction:



What mass of NaN<sub>3</sub>(s) must be reacted to inflate an air bag to 70.0 L at STP?

**54.** Concentrated hydrogen peroxide solutions are explosively decomposed by traces of transition metal ions (such as Mn or Fe):



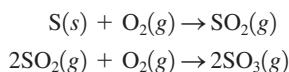
What volume of pure O<sub>2</sub>(g), collected at 27°C and 746 torr, would be generated by decomposition of 125 g of a 50.0% by mass hydrogen peroxide solution? Ignore any water vapor that may be present.

**55.** In 1897 the Swedish explorer Andree tried to reach the North Pole in a balloon. The balloon was filled with hydrogen gas. The hydrogen gas was prepared from iron splints and diluted sulfuric acid. The reaction is



The volume of the balloon was 4800 m<sup>3</sup> and the loss of hydrogen gas during filling was estimated at 20%. What mass of iron splints and 98% (by mass) H<sub>2</sub>SO<sub>4</sub> were needed to ensure the complete filling of the balloon? Assume a temperature of 0°C, a pressure of 1.0 atm during filling, and 100% yield.

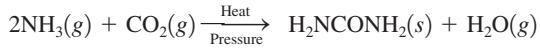
**56.** Sulfur trioxide, SO<sub>3</sub>, is produced in enormous quantities each year for use in the synthesis of sulfuric acid.



What volume of O<sub>2</sub>(g) at 350°C and a pressure of 5.25 atm is needed to completely convert 5.00 g of sulfur to sulfur trioxide?

**57.** Consider the reaction between 50.0 mL of liquid methyl alcohol, CH<sub>3</sub>OH (density = 0.850 g/mL), and 22.8 L of O<sub>2</sub> at 27°C and a pressure of 2.00 atm. The products of the reaction are CO<sub>2</sub>(g) and H<sub>2</sub>O(g). Calculate the number of moles of H<sub>2</sub>O formed if the reaction goes to completion.

**58.** Urea (H<sub>2</sub>NCONH<sub>2</sub>) is used extensively as a nitrogen source in fertilizers. It is produced commercially from the reaction of ammonia and carbon dioxide:

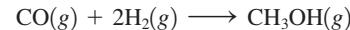


Ammonia gas at 223°C and 90. atm flows into a reactor at a rate of 500. L/min. Carbon dioxide at 223°C and 45 atm flows into the reactor at a rate of 600. L/min. What mass of urea is produced per minute by this reaction assuming 100% yield?

**59.** Hydrogen cyanide is prepared commercially by the reaction of methane, CH<sub>4</sub>(g), ammonia, NH<sub>3</sub>(g), and oxygen, O<sub>2</sub>(g), at high temperature. The other product is gaseous water.

- Write a chemical equation for the reaction.
- What volume of HCN(g) can be obtained from 20.0 L CH<sub>4</sub>(g), 20.0 L NH<sub>3</sub>(g), and 20.0 L O<sub>2</sub>(g)? The volumes of all gases are measured at the same temperature and pressure.

**60.** Methanol, CH<sub>3</sub>OH, can be produced by the following reaction:



Hydrogen at STP flows into a reactor at a rate of 16.0 L/min. Carbon monoxide at STP flows into the reactor at a rate of 25.0 L/min. If 5.30 g of methanol is produced per minute, what is the percent yield of the reaction?

**61.** An unknown diatomic gas has a density of 3.164 g/L at STP. What is the identity of the gas?

**62.** A compound has the empirical formula CHCl. A 256-mL flask, at 373 K and 750. torr, contains 0.800 g of the gaseous compound. Give the molecular formula.

**63.** Uranium hexafluoride is a solid at room temperature, but it boils at 56°C. Determine the density of uranium hexafluoride at 60.°C and 745 torr.

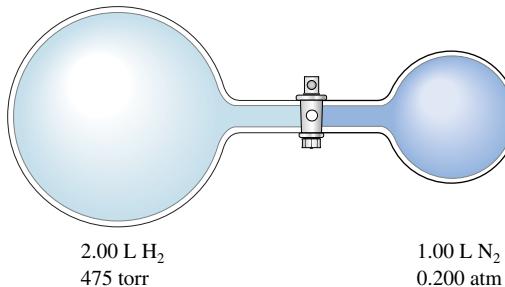
**64.** Given that a sample of air is made up of nitrogen, oxygen, and argon in the mole fractions 78% N<sub>2</sub>, 21% O<sub>2</sub>, and 1.0% Ar, what is the density of air at standard temperature and pressure?

### Partial Pressure

**65.** A piece of solid carbon dioxide, with a mass of 7.8 g, is placed in a 4.0-L otherwise empty container at 27°C. What is the pressure in the container after all the carbon dioxide vaporizes? If 7.8 g solid carbon dioxide were placed in the same container but it already contained air at 740 torr, what would be the partial pressure of carbon dioxide and the total pressure in the container after the carbon dioxide vaporizes?

**66.** A mixture of 1.00 g H<sub>2</sub> and 1.00 g He is placed in a 1.00-L container at 27°C. Calculate the partial pressure of each gas and the total pressure.

**67.** Consider the flasks in the following diagram. What are the final partial pressures of H<sub>2</sub> and N<sub>2</sub> after the stopcock between the two flasks is opened? (Assume the final volume is 3.00 L.) What is the total pressure (in torr)?



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**68.** Consider the flask apparatus in Exercise 67, which now contains 2.00 L of H<sub>2</sub> at a pressure of 360. torr and 1.00 L of N<sub>2</sub> at an unknown pressure. If the total pressure in the flasks is 320. torr after the stopcock is opened, determine the initial pressure of N<sub>2</sub> in the 1.00-L flask.

**69.** The partial pressure of CH<sub>4</sub>(g) is 0.175 atm and that of O<sub>2</sub>(g) is 0.250 atm in a mixture of the two gases.

- What is the mole fraction of each gas in the mixture?
- If the mixture occupies a volume of 10.5 L at 65°C, calculate the total number of moles of gas in the mixture.
- Calculate the number of grams of each gas in the mixture.

**70.** A 1.00-L gas sample at 100.°C and 600. torr contains 50.0% helium and 50.0% xenon by mass. What are the partial pressures of the individual gases?

**71.** Small quantities of hydrogen gas can be prepared in the laboratory by the addition of aqueous hydrochloric acid to metallic zinc.



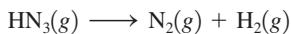
Typically, the hydrogen gas is bubbled through water for collection and becomes saturated with water vapor. Suppose 240. mL of hydrogen gas is collected at 30.°C and has a total pressure of 1.032 atm by this process. What is the partial pressure of hydrogen gas in the sample? How many grams of zinc must have reacted to produce this quantity of hydrogen? (The vapor pressure of water is 32 torr at 30°C.)

**72.** Helium is collected over water at 25°C and 1.00 atm total pressure. What total volume of gas must be collected to obtain 0.586 g of helium? (At 25°C the vapor pressure of water is 23.8 torr.)

**73.** At elevated temperatures, sodium chlorate decomposes to produce sodium chloride and oxygen gas. A 0.8765-g sample of impure sodium chlorate was heated until the production of oxygen gas ceased. The oxygen gas collected over water occupied 57.2 mL at a temperature of 22°C and a pressure of 734 torr. Calculate the mass percent of NaClO<sub>3</sub> in the original sample. (At 22°C the vapor pressure of water is 19.8 torr.)

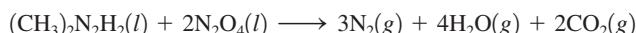
**74.** Xenon and fluorine will react to form binary compounds when a mixture of these two gases is heated to 400°C in a nickel reaction vessel. A 100.0-mL nickel container is filled with xenon and fluorine, giving partial pressures of 1.24 atm and 10.10 atm, respectively, at a temperature of 25°C. The reaction vessel is heated to 400°C to cause a reaction to occur and then cooled to a temperature at which F<sub>2</sub> is a gas and the xenon fluoride compound produced is a nonvolatile solid. The remaining F<sub>2</sub> gas is transferred to another 100.0-mL nickel container, where the pressure of F<sub>2</sub> at 25°C is 7.62 atm. Assuming all of the xenon has reacted, what is the formula of the product?

**75.** Hydrogen azide, HN<sub>3</sub>, decomposes on heating by the following unbalanced reaction:



If 3.0 atm of pure HN<sub>3</sub>(g) is decomposed initially, what is the final total pressure in the reaction container? What are the partial pressures of nitrogen and hydrogen gas? Assume the volume and temperature of the reaction container are constant.

**76.** Some very effective rocket fuels are composed of lightweight liquids. The fuel composed of dimethylhydrazine [(CH<sub>3</sub>)<sub>2</sub>N<sub>2</sub>H<sub>2</sub>] mixed with dinitrogen tetroxide was used to power the Lunar Lander in its missions to the moon. The two components react according to the following equation:



If 150 g of dimethylhydrazine reacts with excess dinitrogen tetroxide and the product gases are collected at 27°C in an evacuated 250-L tank, what is the partial pressure of nitrogen gas produced and what is the total pressure in the tank assuming the reaction has 100% yield?

### Kinetic Molecular Theory and Real Gases

**77.** Calculate the average kinetic energies of CH<sub>4</sub> and N<sub>2</sub> molecules at 273 K and 546 K.

**78.** A 100.-L flask contains a mixture of methane, CH<sub>4</sub>, and argon at 25°C. The mass of argon present is 228 g and the mole fraction of methane in the mixture is 0.650. Calculate the total kinetic energy of the gaseous mixture.

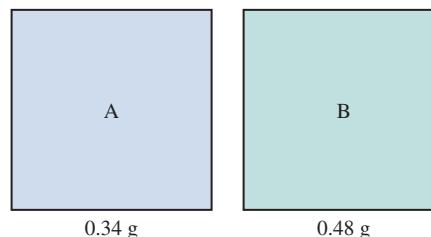
**79.** Calculate the root mean square velocities of CH<sub>4</sub> and N<sub>2</sub> molecules at 273 K and 546 K.

**80.** Consider separate 1.0-L samples of He(g) and UF<sub>6</sub>(g), both at 1.00 atm and containing the same number of moles. What ratio of temperatures for the two samples would produce the same root mean square velocity?

**81.** Consider a 1.0-L container of neon gas at STP. Will the average kinetic energy, average velocity, and frequency of collisions of gas molecules with the walls of the container increase, decrease, or remain the same under each of the following conditions?

- The temperature is increased to 100°C.
- The temperature is decreased to -50°C.
- The volume is decreased to 0.5 L.
- The number of moles of neon is doubled.

**82.** Consider two gases, A and B, each in a 1.0-L container with both gases at the same temperature and pressure. The mass of gas A in the container is 0.34 g and the mass of gas B in the container is 0.48 g.



- Which gas sample has the most molecules present? Explain.
- Which gas sample has the largest average kinetic energy? Explain.

- c. Which gas sample has the fastest average velocity? Explain.  
 d. How can the pressure in the two containers be equal to each other since the larger gas B molecules collide with the container walls more forcefully?

**83.** Consider three identical flasks filled with different gases.

Flask A: CO at 760 torr and 0°C  
 Flask B: N<sub>2</sub> at 250 torr and 0°C  
 Flask C: H<sub>2</sub> at 100 torr and 0°C

- a. In which flask will the molecules have the greatest average kinetic energy?  
 b. In which flask will the molecules have the greatest average velocity?

**84.** Consider separate 1.0-L gaseous samples of H<sub>2</sub>, Xe, Cl<sub>2</sub>, and O<sub>2</sub> all at STP.

- a. Rank the gases in order of increasing average kinetic energy.  
 b. Rank the gases in order of increasing average velocity.  
 c. How can separate 1.0-L samples of O<sub>2</sub> and H<sub>2</sub> each have the same average velocity?

**85.** Freon-12 is used as a refrigerant in central home air conditioners. The rate of effusion of Freon-12 to Freon-11 (molar mass = 137.4 g/mol) is 1.07:1. The formula of Freon-12 is one of the following: CF<sub>4</sub>, CF<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, CFCl<sub>3</sub>, or CCl<sub>4</sub>. Which formula is correct for Freon-12?

**86.** The rate of effusion of a particular gas was measured and found to be 24.0 mL/min. Under the same conditions, the rate of effusion of pure methane (CH<sub>4</sub>) gas is 47.8 mL/min. What is the molar mass of the unknown gas?

**87.** One way of separating oxygen isotopes is by gaseous diffusion of carbon monoxide. The gaseous diffusion process behaves like an effusion process. Calculate the relative rates of effusion of <sup>12</sup>C<sup>16</sup>O, <sup>12</sup>C<sup>17</sup>O, and <sup>12</sup>C<sup>18</sup>O. Name some advantages and disadvantages of separating oxygen isotopes by gaseous diffusion of carbon dioxide instead of carbon monoxide.

**88.** It took 4.5 minutes for 1.0 L helium to effuse through a porous barrier. How long will it take for 1.0 L Cl<sub>2</sub> gas to effuse under identical conditions?

**89.** Calculate the pressure exerted by 0.5000 mol N<sub>2</sub> in a 1.0000-L container at 25.0°C

- a. using the ideal gas law.  
 b. using the van der Waals equation.  
 c. Compare the results.

**90.** Calculate the pressure exerted by 0.5000 mol N<sub>2</sub> in a 10.000-L container at 25.0°C

- a. using the ideal gas law.  
 b. using the van der Waals equation.  
 c. Compare the results.  
 d. Compare the results with those in Exercise 89.

## Atmosphere Chemistry

**91.** Use the data in Table 5.4 to calculate the partial pressure of He in dry air assuming that the total pressure is 1.0 atm. Assuming a temperature of 25°C, calculate the number of He atoms per cubic centimeter.

**92.** A 1.0-L sample of air is collected at 25°C at sea level (1.00 atm). Estimate the volume this sample of air would have at an altitude of 15 km (see Fig. 5.30).

**93.** Write reactions to show how nitric and sulfuric acids are produced in the atmosphere.

**94.** Write reactions to show how the nitric and sulfuric acids in acid rain react with marble and limestone. (Both marble and limestone are primarily calcium carbonate.)

## Additional Exercises

**95.** Draw a qualitative graph to show how the first property varies with the second in each of the following (assume 1 mol of an ideal gas and *T* in kelvins).

- a. *PV* versus *V* with constant *T*  
 b. *P* versus *T* with constant *V*  
 c. *T* versus *V* with constant *P*  
 d. *P* versus *V* with constant *T*  
 e. *P* versus *1/V* with constant *T*  
 f. *PV/T* versus *P*

**96.** At STP, 1.0 L Br<sub>2</sub> reacts completely with 3.0 L F<sub>2</sub>, producing 2.0 L of a product. What is the formula of the product? (All substances are gases.)

**97.** A form of Boyle's law is *PV* = *k* (at constant *T* and *n*). Table 5.1 contains actual data from pressure–volume experiments conducted by Robert Boyle. The value of *k* in most experiments is  $14.1 \times 10^2$  in Hg · in<sup>3</sup>. Express *k* in units of atm · L. In Sample Exercise 5.3, *k* was determined for NH<sub>3</sub> at various pressures and volumes. Give some reasons why the *k* values differ so dramatically between Sample Exercise 5.3 and Table 5.1.

**98.** An ideal gas at 7°C is in a spherical flexible container having a radius of 1.00 cm. The gas is heated at constant pressure to 88°C. Determine the radius of the spherical container after the gas is heated. (Volume of a sphere =  $4/3\pi r^3$ .)

**99.** A 2.747-g sample of manganese metal is reacted with excess HCl gas to produce 3.22 L of H<sub>2</sub>(g) at 373 K and 0.951 atm and a manganese chloride compound (MnCl<sub>x</sub>). What is the formula of the manganese chloride compound produced in the reaction?

**100.** Equal moles of hydrogen gas and oxygen gas are mixed in a flexible reaction vessel and then sparked to initiate the formation of gaseous water. Assuming that the reaction goes to completion, what is the ratio of the final volume of the gas mixture to the initial volume of the gas mixture if both volumes are measured at the same temperature and pressure?

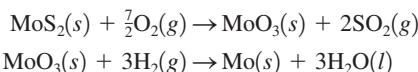
**101.** A 15.0-L tank is filled with H<sub>2</sub> to a pressure of  $2.00 \times 10^2$  atm. How many balloons (each 2.00 L) can be inflated to a pressure of 1.00 atm from the tank? Assume that there is no temperature change and that the tank cannot be emptied below 1.00 atm pressure.

**102.** A spherical glass container of unknown volume contains helium gas at 25°C and 1.960 atm. When a portion of the helium is withdrawn and adjusted to 1.00 atm at 25°C, it is found to have a

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volume of  $1.75 \text{ cm}^3$ . The gas remaining in the first container shows a pressure of  $1.710 \text{ atm}$ . Calculate the volume of the spherical container.

- 103.** A  $2.00\text{-L}$  sample of  $\text{O}_2(g)$  was collected over water at a total pressure of  $785 \text{ torr}$  and  $25^\circ\text{C}$ . When the  $\text{O}_2(g)$  was dried (water vapor removed), the gas had a volume of  $1.94 \text{ L}$  at  $25^\circ\text{C}$  and  $785 \text{ torr}$ . Calculate the vapor pressure of water at  $25^\circ\text{C}$ .
- 104.** A  $20.0\text{-L}$  stainless steel container was charged with  $2.00 \text{ atm}$  of hydrogen gas and  $3.00 \text{ atm}$  of oxygen gas. A spark ignited the mixture, producing water. What is the pressure in the tank at  $25^\circ\text{C}$ ? at  $125^\circ\text{C}$ ?
- 105.** Metallic molybdenum can be produced from the mineral molybdenite,  $\text{MoS}_2$ . The mineral is first oxidized in air to molybdenum trioxide and sulfur dioxide. Molybdenum trioxide is then reduced to metallic molybdenum using hydrogen gas. The balanced equations are

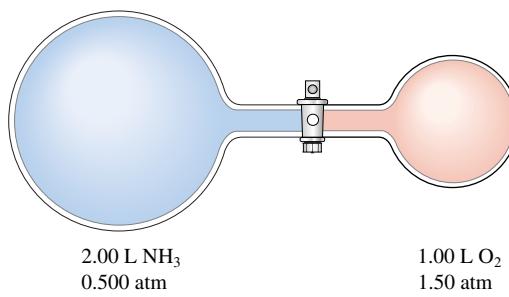


Calculate the volumes of air and hydrogen gas at  $17^\circ\text{C}$  and  $1.00 \text{ atm}$  that are necessary to produce  $1.00 \times 10^3 \text{ kg}$  of pure molybdenum from  $\text{MoS}_2$ . Assume air contains  $21\%$  oxygen by volume and assume  $100\%$  yield for each reaction.

- 106.** Nitric acid is produced commercially by the Ostwald process. In the first step ammonia is oxidized to nitric oxide:



Assume this reaction is carried out in the apparatus diagrammed below.



The stopcock between the two reaction containers is opened, and the reaction proceeds using proper catalysts. Calculate the partial pressure of NO after the reaction is complete. Assume  $100\%$  yield for the reaction, assume the final container volume is  $3.00 \text{ L}$ , and assume the temperature is constant.

- 107.** In the “Méthode Champenoise,” grape juice is fermented in a wine bottle to produce sparkling wine. The reaction is



Fermentation of  $750. \text{ mL}$  grape juice (density =  $1.0 \text{ g/cm}^3$ ) is allowed to take place in a bottle with a total volume of  $825 \text{ mL}$  until  $12\%$  by volume is ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ). Assuming that the  $\text{CO}_2$  is insoluble in  $\text{H}_2\text{O}$  (actually, a wrong assumption), what

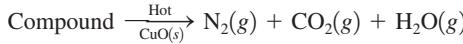
would be the pressure of  $\text{CO}_2$  inside the wine bottle at  $25^\circ\text{C}$ ? (The density of ethanol is  $0.79 \text{ g/cm}^3$ .)

- 108.** One of the chemical controversies of the nineteenth century concerned the element beryllium (Be). Berzelius originally claimed that beryllium was a trivalent element (forming  $\text{Be}^{3+}$  ions) and that it gave an oxide with the formula  $\text{Be}_2\text{O}_3$ . This resulted in a calculated atomic mass of  $13.5$  for beryllium. In formulating his periodic table, Mendeleev proposed that beryllium was divalent (forming  $\text{Be}^{2+}$  ions) and that it gave an oxide with the formula  $\text{BeO}$ . This assumption gives an atomic mass of  $9.0$ . In 1894, A. Combes (*Comptes Rendus* 1894, p. 1221) reacted beryllium with the anion  $\text{C}_5\text{H}_7\text{O}_2^-$  and measured the density of the gaseous product. Combes's data for two different experiments are as follows:

	I	II
Mass	0.2022 g	0.2224 g
Volume	$22.6 \text{ cm}^3$	$26.0 \text{ cm}^3$
Temperature	$13^\circ\text{C}$	$17^\circ\text{C}$
Pressure	$765.2 \text{ mm Hg}$	$764.6 \text{ mm}$

If beryllium is a divalent metal, the molecular formula of the product will be  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ ; if it is trivalent, the formula will be  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_3$ . Show how Combes's data help to confirm that beryllium is a divalent metal.

- 109.** The nitrogen content of organic compounds can be determined by the Dumas method. The compound in question is first reacted by passage over hot  $\text{CuO}(s)$ :



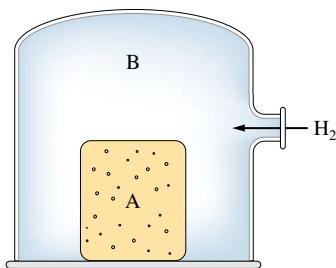
The product gas is then passed through a concentrated solution of KOH to remove the  $\text{CO}_2$ . After passage through the KOH solution, the gas contains  $\text{N}_2$  and is saturated with water vapor. In a given experiment a  $0.253\text{-g}$  sample of a compound produced  $31.8 \text{ mL}$   $\text{N}_2$  saturated with water vapor at  $25^\circ\text{C}$  and  $726 \text{ torr}$ . What is the mass percent of nitrogen in the compound? (The vapor pressure of water at  $25^\circ\text{C}$  is  $23.8 \text{ torr}$ .)

- 110.** A compound containing only C, H, and N yields the following data.
- Complete combustion of  $35.0 \text{ mg}$  of the compound produced  $33.5 \text{ mg}$  of  $\text{CO}_2$  and  $41.1 \text{ mg}$  of  $\text{H}_2\text{O}$ .
  - A  $65.2\text{-mg}$  sample of the compound was analyzed for nitrogen by the Dumas method (see Exercise 109), giving  $35.6 \text{ mL}$  of  $\text{N}_2$  at  $740. \text{ torr}$  and  $25^\circ\text{C}$ .
  - The effusion rate of the compound as a gas was measured and found to be  $24.6 \text{ mL/min}$ . The effusion rate of argon gas, under identical conditions, is  $26.4 \text{ mL/min}$ . What is the molecular formula of the compound?

- 111.** An organic compound contains C, H, N, and O. Combustion of  $0.1023 \text{ g}$  of the compound in excess oxygen yielded  $0.2766 \text{ g}$  of  $\text{CO}_2$  and  $0.0991 \text{ g}$  of  $\text{H}_2\text{O}$ . A sample of  $0.4831 \text{ g}$  of the compound was analyzed for nitrogen by the Dumas method (see Exercise 109). At STP,  $27.6 \text{ mL}$  of dry  $\text{N}_2$  was obtained. In a third experiment, the density of the compound as a gas was found to

be 4.02 g/L at 127°C and 256 torr. What are the empirical and molecular formulas of the compound?

112. Consider the following diagram:

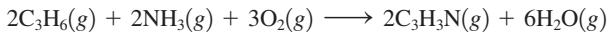


Container A (with porous walls) is filled with air at STP. It is then inserted into a large enclosed container (B), which is then flushed with  $\text{H}_2(g)$ . What will happen to the pressure inside container A? Explain your answer.

113. Without looking at tables of values, which of the following gases would you expect to have the largest value of the van der Waals constant  $b$ :  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , or  $\text{C}_3\text{H}_8$ ? From the values in Table 5.3 for the van der Waals constant  $a$  for the gases  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ , predict which of these gas molecules show the strongest intermolecular attractions.

## Challenge Problems

114. An important process for the production of acrylonitrile ( $\text{C}_3\text{H}_3\text{N}$ ) is given by the following reaction:



A 150.-L reactor is charged to the following partial pressures at 25°C:

$$P_{\text{C}_3\text{H}_6} = 0.500 \text{ MPa}$$

$$P_{\text{NH}_3} = 0.800 \text{ MPa}$$

$$P_{\text{O}_2} = 1.500 \text{ MPa}$$

What mass of acrylonitrile can be produced from this mixture (Mpa =  $10^6$  Pa)?

115. A chemist weighed out 5.14 g of a mixture containing unknown amounts of  $\text{BaO}(s)$  and  $\text{CaO}(s)$  and placed the sample in a 1.50-L flask containing  $\text{CO}_2(g)$  at 30.0°C and 750. torr. After the reaction to form  $\text{BaCO}_3(s)$  and  $\text{CaCO}_3(s)$  was completed, the pressure of  $\text{CO}_2(g)$  remaining was 230. torr. Calculate the mass percentages of  $\text{CaO}(s)$  and  $\text{BaO}(s)$  in the mixture.

116. A mixture of chromium and zinc weighing 0.362 g was reacted with an excess of hydrochloric acid. After all the metals in the mixture reacted, 225 mL of dry hydrogen gas was collected at 27°C and 750. torr. Determine the mass percent Zn in the metal sample. [Zinc reacts with hydrochloric acid to produce zinc chloride and hydrogen gas; chromium reacts with hydrochloric acid to produce chromium(III) chloride and hydrogen gas.]

117. Consider a sample of a hydrocarbon (a compound consisting of only carbon and hydrogen) at 0.959 atm and 298 K. Upon combusting the entire sample in oxygen, you collect a mixture of gaseous carbon dioxide and water vapor at 1.51 atm and 375 K. This mixture has a density of 1.391 g/L and occupies a volume four times as large as that of the pure hydrocarbon. Determine the molecular formula of the hydrocarbon.

118. You have an equimolar mixture of the gases  $\text{SO}_2$  and  $\text{O}_2$ , along with some He, in a container fitted with a piston. The density of this mixture at STP is 1.924 g/L. Assume ideal behavior and constant temperature and pressure.

- a. What is the mole fraction of He in the original mixture?  
b. The  $\text{SO}_2$  and  $\text{O}_2$  react to completion to form  $\text{SO}_3$ . What is the density of the gas mixture after the reaction is complete?

119. Methane ( $\text{CH}_4$ ) gas flows into a combustion chamber at a rate of 200. L/min at 1.50 atm and ambient temperature. Air is added to the chamber at 1.00 atm and the same temperature, and the gases are ignited.

- a. To ensure complete combustion of  $\text{CH}_4$  to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ , three times as much oxygen as is necessary is reacted. Assuming air is 21 mole percent  $\text{O}_2$  and 79 mole percent  $\text{N}_2$ , calculate the flow rate of air necessary to deliver the required amount of oxygen.

- b. Under the conditions in part a, combustion of methane was not complete as a mixture of  $\text{CO}_2(g)$  and  $\text{CO}(g)$  was produced. It was determined that 95.0% of the carbon in the exhaust gas was present in  $\text{CO}_2$ . The remainder was present as carbon in CO. Calculate the composition of the exhaust gas in terms of mole fraction of CO,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . Assume  $\text{CH}_4$  is completely reacted and  $\text{N}_2$  is unreacted.

120. A steel cylinder contains 5.00 mol of graphite (pure carbon) and 5.00 mol of  $\text{O}_2$ . The mixture is ignited and all the graphite reacts. Combustion produces a mixture of CO gas and  $\text{CO}_2$  gas. After the cylinder has cooled to its original temperature, it is found that the pressure of the cylinder has increased by 17.0%. Calculate the mole fractions of CO,  $\text{CO}_2$ , and  $\text{O}_2$  in the final gaseous mixture.

121. The total mass that can be lifted by a balloon is given by the difference between the mass of air displaced by the balloon and the mass of the gas inside the balloon. Consider a hot-air balloon that approximates a sphere 5.00 m in diameter and contains air heated to 65°C. The surrounding air temperature is 21°C. The pressure in the balloon is equal to the atmospheric pressure, which is 745 torr.

- a. What total mass can the balloon lift? Assume that the average molar mass of air is 29.0 g/mol. (Hint: Heated air is less dense than cool air.)

- b. If the balloon is filled with enough helium at 21°C and 745 torr to achieve the same volume as in part a, what total mass can the balloon lift?

- c. What mass could the hot-air balloon in part a lift if it were on the ground in Denver, Colorado, where a typical atmospheric pressure is 630. torr?

122. You have a sealed, flexible balloon filled with argon gas. The atmospheric pressure is 1.00 atm and the temperature is

## 226 Chapter Five Gases

25°C. The air has a mole fraction of nitrogen of 0.790, the rest being oxygen.

- Explain why the balloon would float when heated. Make sure to discuss which factors change and which remain constant, and why this matters. Be complete.
  - Above what temperature would you heat the balloon so that it would float?
- 123.** You have a helium balloon at 1.00 atm and 25°C. You want to make a hot-air balloon with the same volume and same lift as the helium balloon. Assume air is 79.0% nitrogen, 21.0% oxygen by volume. The “lift” of a balloon is given by the difference between the mass of air displaced by the balloon and the mass of gas inside the balloon.
- Will the temperature in the hot-air balloon have to be higher or lower than 25°C? Explain.
  - Calculate the temperature of the air required for the hot-air balloon to provide the same lift as the helium balloon at 1.00 atm and 25°C. Assume atmospheric conditions are 1.00 atm and 25°C.
- 124.** We state that the ideal gas law tends to hold best at low pressures and high temperatures. Show how the van der Waals equation simplifies to the ideal gas law under these conditions.
- 125.** Atmospheric scientists often use mixing ratios to express the concentrations of trace compounds in air. Mixing ratios are often expressed as ppmv (parts per million volume):

$$\text{ppmv of } X = \frac{\text{vol. of } X \text{ at STP}}{\text{total vol. of air at STP}} \times 10^6$$

On a recent autumn day, the concentration of carbon monoxide in the air in downtown Denver, Colorado, reached  $3.0 \times 10^2$  ppmv. The atmospheric pressure at that time was 628 torr, and the temperature was 0°C.

- What was the partial pressure of CO?
  - What was the concentration of CO in molecules per cubic centimeter?
- 126.** Nitrogen gas ( $N_2$ ) reacts with hydrogen gas ( $H_2$ ) to form ammonia gas ( $NH_3$ ). You have nitrogen and hydrogen gases in a 15.0-L container fitted with a movable piston (the piston allows the container volume to change so as to keep the pressure constant inside the container). Initially the partial pressure of each reactant gas is 1.00 atm. Assume the temperature is constant and that the reaction goes to completion.
- Calculate the partial pressure of ammonia in the container after the reaction has reached completion.
  - Calculate the volume of the container after the reaction has reached completion.

## Integrative Problems

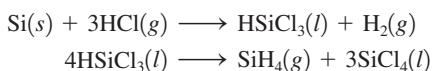
These problems require the integration of multiple concepts to find the solutions.

- 127.** In the presence of nitric acid,  $UO^{2+}$  undergoes a redox process. It is converted to  $UO_2^{2+}$  and nitric oxide (NO) gas is produced according to the following unbalanced equation:



If  $2.55 \times 10^2$  mL of  $NO(g)$  is isolated at 29°C and 1.5 atm, what amount (moles) of  $UO^{2+}$  was used in the reaction?

- 128.** Silane,  $SiH_4$ , is the silicon analogue of methane,  $CH_4$ . It is prepared industrially according to the following equations:



- If 156 mL of  $HSiCl_3$  ( $d = 1.34$  g/mL) is isolated when 15.0 L of  $HCl$  at 10.0 atm and 35°C is used, what is the percent yield of  $HSiCl_3$ ?

- When 156 mL of  $HSiCl_3$  is heated, what volume of  $SiH_4$  at 10.0 atm and 35°C will be obtained if the percent yield of the reaction is 93.1%?

- 129.** Solid thorium(IV) fluoride has a boiling point of 1680°C. What is the density of a sample of gaseous thorium(IV) fluoride at its boiling point under a pressure of 2.5 atm in a 1.7-L container? Which gas will effuse faster at 1680°C, thorium(IV) fluoride or uranium(III) fluoride? How much faster?

- 130.** Natural gas is a mixture of hydrocarbons, primarily methane ( $CH_4$ ) and ethane ( $C_2H_6$ ). A typical mixture might have  $\chi_{\text{methane}} = 0.915$  and  $\chi_{\text{ethane}} = 0.085$ . What are the partial pressures of the two gases in a 15.00-L container of natural gas at 20.°C and 1.44 atm? Assuming complete combustion of both gases in the natural gas sample, what is the total mass of water formed?

## Marathon Problem\*

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

- 131.** Use the following information to identify element A and compound B, then answer questions a and b.

An empty glass container has a mass of 658.572 g. It has a mass of 659.452 g after it has been filled with nitrogen gas at a pressure of 790. torr and a temperature of 15°C. When the container is evacuated and refilled with a certain element (A) at a pressure of 745 torr and a temperature of 26°C, it has a mass of 660.59 g.

Compound B, a gaseous organic compound that consists of 85.6% carbon and 14.4% hydrogen by mass, is placed in a stainless steel vessel (10.68 L) with excess oxygen gas. The vessel is placed in a constant-temperature bath at 22°C. The pressure in the vessel is 11.98 atm. In the bottom of the vessel is a container that is packed with Ascarite and a desiccant. Ascarite is asbestos impregnated with sodium hydroxide; it quantitatively absorbs carbon dioxide:




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The desiccant is anhydrous magnesium perchlorate, which quantitatively absorbs the water produced by the combustion reaction as well as the water produced by the above reaction. Neither the Ascarite nor the desiccant reacts with compound B or oxygen. The total mass of the container with the Ascarite and desiccant is 765.3 g.

The combustion reaction of compound B is initiated by a spark. The pressure immediately rises, then begins to decrease, and finally reaches a steady value of 6.02 atm. The stainless steel vessel is carefully opened, and the mass of the container inside the vessel is found to be 846.7 g.

A and B react quantitatively in a 1:1 mole ratio to form one mole of the single product, gas C.

- a. How many grams of C will be produced if 10.0 L of A and 8.60 L of B (each at STP) are reacted by opening a stopcock connecting the two samples?
- b. What will be the total pressure in the system?



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmcoc.com/PIC/zumdahl7e](http://college.hmcoc.com/PIC/zumdahl7e).

# 6 Thermochemistry

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*Hot lava flowing into the ocean in Hawaii Volcanoes National Park creates clouds of steam.*



**E**nergy is the essence of our very existence as individuals and as a society. The food that we eat furnishes the energy to live, work, and play, just as the coal and oil consumed by manufacturing and transportation systems power our modern industrialized civilization.

In the past, huge quantities of carbon-based fossil fuels have been available for the taking. This abundance of fuels has led to a world society with a voracious appetite for energy, consuming millions of barrels of petroleum every day. We are now dangerously dependent on the dwindling supplies of oil, and this dependence is an important source of tension among nations in today's world. In an incredibly short time we have moved from a period of ample and cheap supplies of petroleum to one of high prices and uncertain supplies. If our present standard of living is to be maintained, we must find alternatives to petroleum. To do this, we need to know the relationship between chemistry and energy, which we explore in this chapter.

There are additional problems with fossil fuels. The waste products from burning fossil fuels significantly affect our environment. For example, when a carbon-based fuel is burned, the carbon reacts with oxygen to form carbon dioxide, which is released into the atmosphere. Although much of this carbon dioxide is consumed in various natural processes such as photosynthesis and the formation of carbonate materials, the amount of carbon dioxide in the atmosphere is steadily increasing. This increase is significant because atmospheric carbon dioxide absorbs heat radiated from the earth's surface and radiates it back toward the earth. Since this is an important mechanism for controlling the earth's temperature, many scientists fear that an increase in the concentration of carbon dioxide will warm the earth, causing significant changes in climate. In addition, impurities in the fossil fuels react with components of the air to produce air pollution. We discussed some aspects of this problem in Chapter 5.

Just as energy is important to our society on a macroscopic scale, it is critically important to each living organism on a microscopic scale. The living cell is a miniature chemical factory powered by energy from chemical reactions. The process of cellular respiration extracts the energy stored in sugars and other nutrients to drive the various tasks of the cell. Although the extraction process is more complex and more subtle, the energy obtained from "fuel" molecules by the cell is the same as would be obtained from burning the fuel to power an internal combustion engine.

Whether it is an engine or a cell that is converting energy from one form to another, the processes are all governed by the same principles, which we will begin to explore in this chapter. Additional aspects of energy transformation will be covered in Chapter 16.

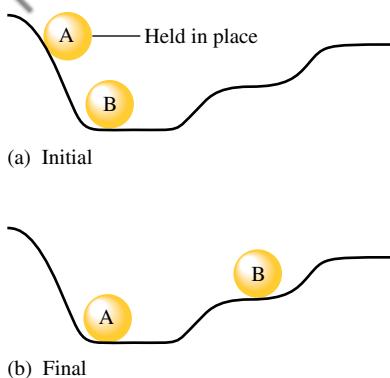
## 6.1 The Nature of Energy

Although the concept of energy is quite familiar, energy itself is rather difficult to define precisely. We will define **energy** as the *capacity to do work or to produce heat*. In this chapter we will concentrate specifically on the heat transfer that accompanies chemical processes.

One of the most important characteristics of energy is that it is conserved. The **law of conservation of energy** states that *energy can be converted from one form to another but can be neither created nor destroyed*. That is, the energy of the universe is constant. Energy can be classified as either potential or kinetic energy. **Potential energy** is energy due to position or composition. For example, water behind a dam has potential energy that can be converted to work when the water flows down through turbines, thereby creating

One interesting definition of energy is that which is needed to oppose natural attractions (for example, gravity and electrostatic attractions).

The total energy content of the universe is constant.

**FIGURE 6.1**

(a) In the initial positions, ball A has a higher potential energy than ball B. (b) After A has rolled down the hill, the potential energy lost by A has been converted to random motions of the components of the hill (frictional heating) and to the increase in the potential energy of B.

**Heat involves a transfer of energy.**



This infrared photo of a house shows where energy leaks occur. The more red the color, the more energy (heat) is leaving the house.



**Visualization: Coffee Creamer Flammability**

electricity. Attractive and repulsive forces also lead to potential energy. The energy released when gasoline is burned results from differences in attractive forces between the nuclei and electrons in the reactants and products. The **kinetic energy** of an object is energy due to the motion of the object and depends on the mass of the object  $m$  and its velocity  $v$ :  $KE = \frac{1}{2}mv^2$ .

Energy can be converted from one form to another. For example, consider the two balls in Fig. 6.1(a). Ball A, because of its higher position initially, has more potential energy than ball B. When A is released, it moves down the hill and strikes B. Eventually, the arrangement shown in Fig. 6.1(b) is achieved. What has happened in going from the initial to the final arrangement? The potential energy of A has decreased, but since energy is conserved, all the energy lost by A must be accounted for. How is this energy distributed?

Initially, the potential energy of A is changed to kinetic energy as the ball rolls down the hill. Part of this kinetic energy is then transferred to B, causing it to be raised to a higher final position. Thus the potential energy of B has been increased. However, since the final position of B is lower than the original position of A, some of the energy is still unaccounted for. Both balls in their final positions are at rest, so the missing energy cannot be due to their motions. What has happened to the remaining energy?

The answer lies in the interaction between the hill's surface and the ball. As ball A rolls down the hill, some of its kinetic energy is transferred to the surface of the hill as heat. This transfer of energy is called *frictional heating*. The temperature of the hill increases very slightly as the ball rolls down.

Before we proceed further, it is important to recognize that heat and temperature are decidedly different. As we saw in Chapter 5, *temperature* is a property that reflects the random motions of the particles in a particular substance. **Heat**, on the other hand, involves the *transfer* of energy between two objects due to a temperature difference. Heat is not a substance contained by an object, although we often talk of heat as if this were true.

Note that in going from the initial to the final arrangements in Fig. 6.1, ball B gains potential energy because work was done by ball A on B. **Work** is defined as force acting over a distance. Work is required to raise B from its original position to its final one. Part of the original energy stored as potential energy in A has been transferred through work to B, thereby increasing B's potential energy. Thus there are two ways to transfer energy: through work and through heat.

In rolling to the bottom of the hill shown in Fig. 6.1, ball A will always lose the same amount of potential energy. However, the way that this energy transfer is divided between work and heat depends on the specific conditions—the **pathway**. For example, the surface of the hill might be so rough that the energy of A is expended completely through frictional heating; A is moving so slowly when it hits B that it cannot move B to the next level. In this case, no work is done. Regardless of the condition of the hill's surface, the *total energy* transferred will be constant. However, the amounts of heat and work will differ. Energy change is independent of the pathway; however, work and heat are both dependent on the pathway.

This brings us to a very important concept: the **state function or state property**. A state function refers to a property of the system that depends only on its *present state*. A state function (property) does not depend in any way on the system's past (or future). In other words, the value of a state function does not depend on how the system arrived at the present state; it depends only on the characteristics of the present state. This leads to a very important characteristic of a state function: A change in this function (property) in going from one state to another state is independent of the particular pathway taken between the two states.

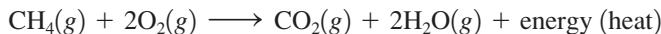
A nonscientific analogy that illustrates the difference between a state function and a nonstate function is elevation on the earth's surface and distance between two points. In traveling from Chicago (elevation 674 ft) to Denver (elevation 5280 ft), the change in elevation is always  $5280 - 674 = 4606$  ft regardless of the route taken between the two cities. The distance traveled, however, depends on how you make the trip. Thus elevation is a function that does not depend on the route (pathway) but distance is pathway dependent. Elevation is a state function and distance is not.

Energy is a state function; work and heat are not.

Of the functions considered in our present example, energy is a state function, but work and heat are not state functions.

## Chemical Energy

The ideas we have just illustrated using mechanical examples also apply to chemical systems. The combustion of methane, for example, is used to heat many homes in the United States:



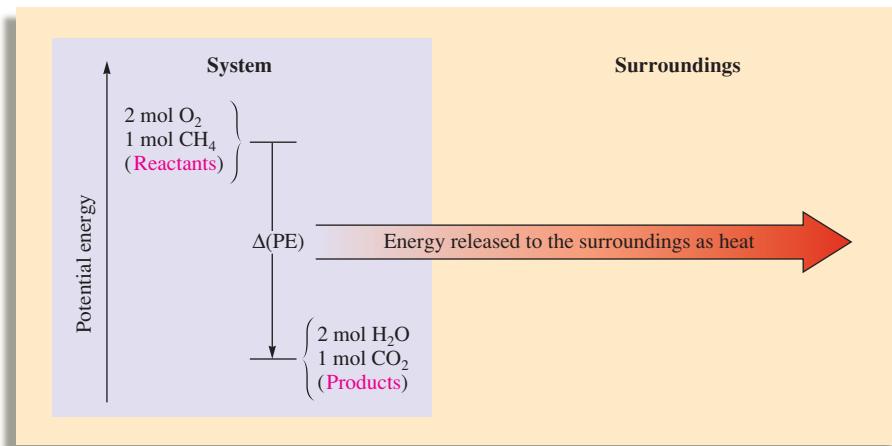
To discuss this reaction, we divide the universe into two parts: the system and the surroundings. The **system** is the part of the universe on which we wish to focus attention; the **surroundings** include everything else in the universe. In this case we define the system as the reactants and products of the reaction. The surroundings consist of the reaction container (a furnace, for example), the room, and anything else other than the reactants and products.

When a reaction results in the evolution of heat, it is said to be **exothermic** (*exo-* is a prefix meaning “out of”); that is, energy flows *out of the system*. For example, in the combustion of methane, energy flows out of the system as heat. Reactions that absorb energy from the surroundings are said to be **endothermic**. When the heat flow is *into a system*, the process is endothermic. For example, the formation of nitric oxide from nitrogen and oxygen is endothermic:



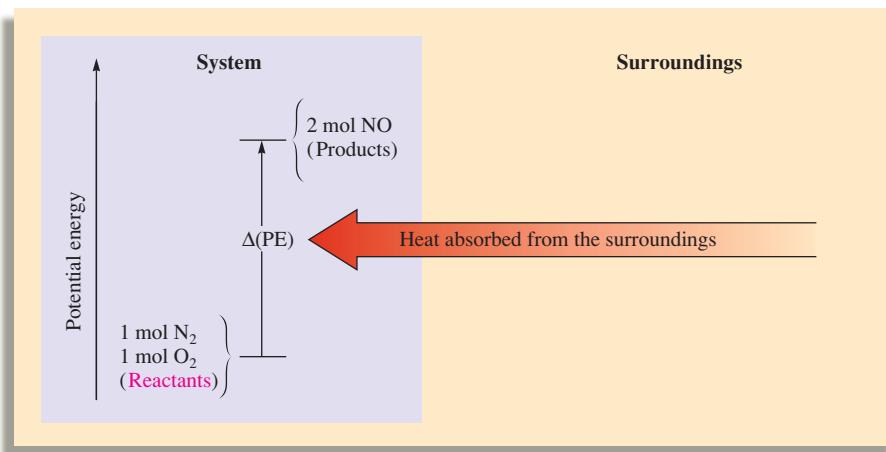
Where does the energy, released as heat, come from in an exothermic reaction? The answer lies in the difference in potential energies between the products and the reactants. Which has lower potential energy, the reactants or the products? We know that total energy is conserved and that energy flows from the system into the surroundings in an exothermic reaction. This means that *the energy gained by the surroundings must be equal to the energy lost by the system*. In the combustion of methane, the energy content of the system decreases, which means that 1 mole of CO<sub>2</sub> and 2 moles of H<sub>2</sub>O molecules (the products) possess less potential energy than do 1 mole of CH<sub>4</sub> and 2 moles of O<sub>2</sub> molecules (the reactants). The heat flow into the surroundings results from a lowering of the potential energy of the reaction system. This always holds true. *In any exothermic reaction, some of the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.*

The energy diagram for the combustion of methane is shown in Fig. 6.2, where  $\Delta(\text{PE})$  represents the *change* in potential energy stored in the bonds of the products as compared with the bonds of the reactants. In other words, this quantity represents the difference between



**FIGURE 6.2**

The combustion of methane releases the quantity of energy  $\Delta(\text{PE})$  to the surroundings via heat flow. This is an exothermic process.

**FIGURE 6.3**

The energy diagram for the reaction of nitrogen and oxygen to form nitric oxide. This is an endothermic process: Heat [equal in magnitude to  $\Delta(\text{PE})$ ] flows into the system from the surroundings.

the energy required to break the bonds in the reactants and the energy released when the bonds in the products are formed. In an exothermic process, the bonds in the products are stronger (on average) than those of the reactants. That is, more energy is released by forming the new bonds in the products than is consumed to break the bonds in the reactants. The net result is that the quantity of energy  $\Delta(\text{PE})$  is transferred to the surroundings through heat.

For an endothermic reaction, the situation is reversed, as shown in Fig. 6.3. Energy that flows into the system as heat is used to increase the potential energy of the system. In this case the products have higher potential energy (weaker bonds on average) than the reactants.

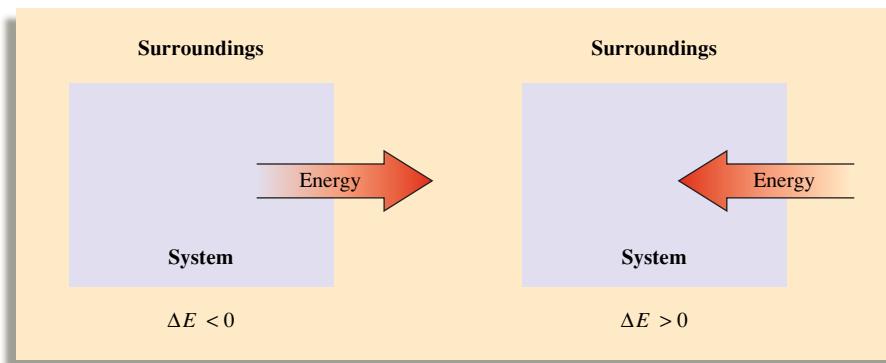
The study of energy and its interconversions is called **thermodynamics**. The law of conservation of energy is often called the **first law of thermodynamics** and is stated as follows: *The energy of the universe is constant*.

The **internal energy**  $E$  of a system can be defined most precisely as the sum of the kinetic and potential energies of all the “particles” in the system. The internal energy of a system can be changed by a flow of work, heat, or both. That is,

$$\Delta E = q + w$$

where  $\Delta E$  represents the change in the system’s internal energy,  $q$  represents heat, and  $w$  represents work.

Thermodynamic quantities always consist of two parts: a *number*, giving the magnitude of the change, and a *sign*, indicating the direction of the flow. *The sign reflects the system’s point of view*. For example, if a quantity of energy flows *into* the system via heat (an endothermic process),  $q$  is equal to  $+x$ , where the *positive* sign indicates that the *system’s energy is increasing*. On the other hand, when energy flows *out of* the system via heat (an exothermic process),  $q$  is equal to  $-x$ , where the *negative* sign indicates that the *system’s energy is decreasing*.



The convention in this text is to take the system's point of view;  $q = -x$  denotes an exothermic process, and  $q = +x$  denotes an endothermic one.

In this text the same conventions also apply to the flow of work. If the system does work on the surroundings (energy flows out of the system),  $w$  is negative. If the surroundings do work on the system (energy flows into the system),  $w$  is positive. We define work from the system's point of view to be consistent for all thermodynamic quantities. That is, in this convention the signs of both  $q$  and  $w$  reflect what happens to the system; thus we use  $\Delta E = q + w$ .

In this text we *always* take the system's point of view. This convention is not followed in every area of science. For example, engineers are in the business of designing machines to do work, that is, to make the system (the machine) transfer energy to its surroundings through work. Consequently, engineers define work from the surroundings' point of view. In their convention, work that flows out of the system is treated as positive because the energy of the surroundings has increased. The first law of thermodynamics is then written  $\Delta E = q - w'$ , where  $w'$  signifies work from the surroundings' point of view.

### Sample Exercise 6.1

The joule (J) is the fundamental SI unit for energy:

$$J = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

One kilojoule (kJ) =  $10^3$  J.

### Internal Energy

Calculate  $\Delta E$  for a system undergoing an endothermic process in which 15.6 kJ of heat flows and where 1.4 kJ of work is done on the system.

#### Solution

We use the equation

$$\Delta E = q + w$$

where  $q = +15.6$  kJ, since the process is endothermic, and  $w = +1.4$  kJ, since work is done on the system. Thus

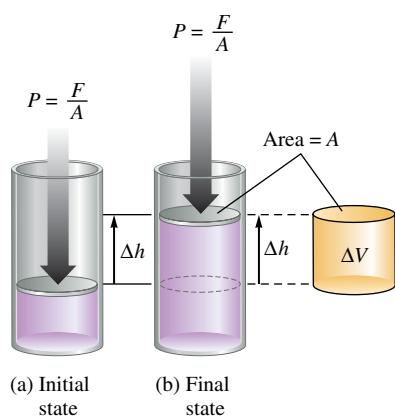
$$\Delta E = 15.6 \text{ kJ} + 1.4 \text{ kJ} = 17.0 \text{ kJ}$$

The system has gained 17.0 kJ of energy.

**See Exercises 6.21 and 6.22.**



Visualization: Work versus Energy Flow



**FIGURE 6.4**

(a) The piston, moving a distance  $\Delta h$  against a pressure  $P$ , does work on the surroundings. (b) Since the volume of a cylinder is the area of the base times its height, the change in volume of the gas is given by  $\Delta h \times A = \Delta V$ .

A common type of work associated with chemical processes is work done by a gas (through *expansion*) or work done to a gas (through *compression*). For example, in an automobile engine, the heat from the combustion of the gasoline expands the gases in the cylinder to push back the piston, and this motion is then translated into the motion of the car.

Suppose we have a gas confined to a cylindrical container with a movable piston as shown in Fig. 6.4, where  $F$  is the force acting on a piston of area  $A$ . Since pressure is defined as force per unit area, the pressure of the gas is

$$P = \frac{F}{A}$$

Work is defined as force applied over a distance, so if the piston moves a distance  $\Delta h$ , as shown in Fig. 6.4, then the work done is

$$\text{Work} = \text{force} \times \text{distance} = F \times \Delta h$$

Since  $P = F/A$  or  $F = P \times A$ , then

$$\text{Work} = F \times \Delta h = P \times A \times \Delta h$$

Since the volume of a cylinder equals the area of the piston times the height of the cylinder (Fig. 6.4), the change in volume  $\Delta V$  resulting from the piston moving a distance  $\Delta h$  is

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

Substituting  $\Delta V = A \times \Delta h$  into the expression for work gives

$$\text{Work} = P \times A \times \Delta h = P\Delta V$$

This gives us the *magnitude* (size) of the work required to expand a gas  $\Delta V$  against a pressure  $P$ .

What about the sign of the work? The gas (the system) is expanding, moving the piston against the pressure. Thus the system is doing work on the surroundings, so from the system's point of view the sign of the work should be negative.

For an *expanding* gas,  $\Delta V$  is a positive quantity because the volume is increasing. Thus  $\Delta V$  and  $w$  must have opposite signs, which leads to the equation

$$w = -P\Delta V$$

Note that for a gas expanding against an external pressure  $P$ ,  $w$  is a negative quantity as required, since work flows out of the system. When a gas is *compressed*,  $\Delta V$  is a negative quantity (the volume decreases), which makes  $w$  a positive quantity (work flows into the system).

### Sample Exercise 6.2

### PV Work

Calculate the work associated with the expansion of a gas from 46 L to 64 L at a constant external pressure of 15 atm.

#### Solution

For a gas at constant pressure,

$$w = -P\Delta V$$

In this case  $P = 15$  atm and  $\Delta V = 64 - 46 = 18$  L. Hence

$$w = -15 \text{ atm} \times 18 \text{ L} = -270 \text{ L} \cdot \text{atm}$$

Note that since the gas expands, it does work on its surroundings.

**Reality Check:** Energy flows out of the gas, so  $w$  is a negative quantity.

**See Exercises 6.25 through 6.27.**

For an ideal gas, work can occur only when its volume changes. Thus, if a gas is heated at constant volume, the pressure increases but no work occurs.

In dealing with "PV work," keep in mind that the  $P$  in  $P\Delta V$  always refers to the external pressure—the pressure that causes a compression or that resists an expansion.

### Sample Exercise 6.3

### Internal Energy, Heat, and Work

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from  $4.00 \times 10^6$  L to  $4.50 \times 10^6$  L by the addition of  $1.3 \times 10^8$  J of energy as heat. Assuming that the balloon expands against a constant pressure of 1.0 atm, calculate  $\Delta E$  for the process. (To convert between L · atm and J, use  $1 \text{ L} \cdot \text{atm} = 101.3 \text{ J}$ .)

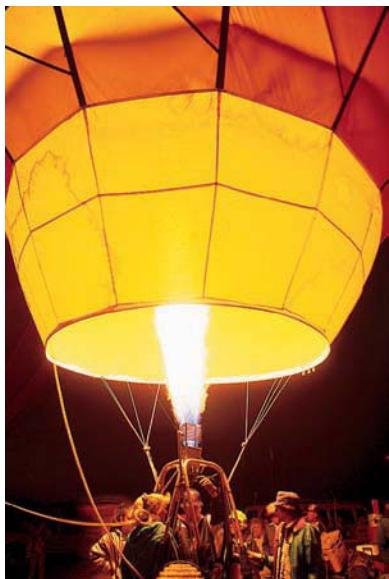
#### Solution

To calculate  $\Delta E$ , we use the equation

$$\Delta E = q + w$$

Since the problem states that  $1.3 \times 10^8$  J of energy is *added* as heat,

$$q = +1.3 \times 10^8 \text{ J}$$



A propane burner is used to heat the air in a hot-air balloon.

The work done can be calculated from the expression

$$w = -P\Delta V$$

In this case  $P = 1.0 \text{ atm}$  and

$$\begin{aligned}\Delta V &= V_{\text{final}} - V_{\text{initial}} \\ &= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L} = 5.0 \times 10^5 \text{ L}\end{aligned}$$

Thus

$$w = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L} \cdot \text{atm}$$

Note that the negative sign for  $w$  makes sense, since the gas is expanding and thus doing work on the surroundings.

To calculate  $\Delta E$ , we must sum  $q$  and  $w$ . However, since  $q$  is given in units of J and  $w$  is given in units of  $\text{L} \cdot \text{atm}$ , we must change the work to units of joules:

$$w = -5.0 \times 10^5 \text{ L} \cdot \text{atm} \times \frac{101.3 \text{ J}}{\text{L} \cdot \text{atm}} = -5.1 \times 10^7 \text{ J}$$

Then

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

**Reality Check:** Since more energy is added through heating than the gas expends doing work, there is a net increase in the internal energy of the gas in the balloon. Hence  $\Delta E$  is positive.

*See Exercises 6.28 through 6.30.*

## 6.2 Enthalpy and Calorimetry

### Enthalpy

So far we have discussed the internal energy of a system. A less familiar property of a system is its **enthalpy**,  $H$ , which is defined as

$$H = E + PV$$

where  $E$  is the internal energy of the system,  $P$  is the pressure of the system, and  $V$  is the volume of the system.

Since internal energy, pressure, and volume are all state functions, *enthalpy is also a state function*. But what exactly is enthalpy? To help answer this question, consider a process carried out at constant pressure and where the only work allowed is pressure-volume work ( $w = -P\Delta V$ ). Under these conditions, the expression

$$\Delta E = q_P + w$$

becomes

$$\Delta E = q_P - P\Delta V$$

or

$$q_P = \Delta E + P\Delta V$$

where  $q_P$  is the heat at constant pressure.

We will now relate  $q_P$  to a change in enthalpy. The definition of enthalpy is  $H = E + PV$ . Therefore, we can say

$$\text{Change in } H = (\text{change in } E) + (\text{change in } PV)$$

**Enthalpy is a state function. A change in enthalpy does not depend on the pathway between two states.**

Recall from the previous section that  $w$  and  $P\Delta V$  have opposite signs:

$$w = -P\Delta V$$

or

$$\Delta H = \Delta E + \Delta(PV)$$

Since  $P$  is constant, the change in  $PV$  is due only to a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

$$\Delta H = \Delta E + P\Delta V$$

This expression is identical to the one we obtained for  $q_P$ :

$$q_P = \Delta E + P\Delta V$$

Thus, for a process carried out at constant pressure and where the only work allowed is that from a volume change, we have

$$\Delta H = q_P$$

$\Delta H = q$  only at constant pressure.

The change in enthalpy of a system has no easily interpreted meaning except at constant pressure, where  $\Delta H$  = heat.

At constant pressure, exothermic means  $\Delta H$  is negative; endothermic means  $\Delta H$  is positive.

*At constant pressure (where only PV work is allowed), the change in enthalpy  $\Delta H$  of the system is equal to the energy flow as heat.* This means that for a reaction studied at constant pressure, the flow of heat is a measure of the change in enthalpy for the system. For this reason, the terms *heat of reaction* and *change in enthalpy* are used interchangeably for reactions studied at constant pressure.

For a chemical reaction, the enthalpy change is given by the equation

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

In a case in which the products of a reaction have a greater enthalpy than the reactants,  $\Delta H$  will be positive. Thus heat will be absorbed by the system, and the reaction is endothermic. On the other hand, if the enthalpy of the products is less than that of the reactants,  $\Delta H$  will be negative. In this case the overall decrease in enthalpy is achieved by the generation of heat, and the reaction is exothermic.

### Sample Exercise 6.4

### Enthalpy

When 1 mole of methane ( $\text{CH}_4$ ) is burned at constant pressure, 890 kJ of energy is released as heat. Calculate  $\Delta H$  for a process in which a 5.8-g sample of methane is burned at constant pressure.

#### Solution

At constant pressure, 890 kJ of energy per mole of  $\text{CH}_4$  is produced as heat:

$$q_P = \Delta H = -890 \text{ kJ/mol CH}_4$$

Note that the minus sign indicates an exothermic process. In this case, a 5.8-g sample of  $\text{CH}_4$  (molar mass = 16.0 g/mol) is burned. Since this amount is smaller than 1 mole, less than 890 kJ will be released as heat. The actual value can be calculated as follows:

$$5.8 \text{ g CH}_4 \times \frac{1 \text{ mol CH}_4}{16.0 \text{ g CH}_4} = 0.36 \text{ mol CH}_4$$

and

$$0.36 \text{ mol CH}_4 \times \frac{-890 \text{ kJ}}{\text{mol CH}_4} = -320 \text{ kJ}$$

Thus, when a 5.8-g sample of  $\text{CH}_4$  is burned at constant pressure,

$$\Delta H = \text{heat flow} = -320 \text{ kJ}$$

*See Exercises 6.35 through 6.38.*

**TABLE 6.1 The Specific Heat Capacities of Some Common Substances**

Substance	Specific Heat Capacity ( $\text{J}/\text{C} \cdot \text{g}$ )
$\text{H}_2\text{O}(l)$	4.18
$\text{H}_2\text{O}(s)$	2.03
$\text{Al}(s)$	0.89
$\text{Fe}(s)$	0.45
$\text{Hg}(l)$	0.14
$\text{C}(s)$	0.71

**Specific heat capacity:** the energy required to raise the temperature of one gram of a substance by one degree Celsius.

**Molar heat capacity:** the energy required to raise the temperature of one mole of a substance by one degree Celsius.

## Calorimetry

The device used experimentally to determine the heat associated with a chemical reaction is called a **calorimeter**. **Calorimetry**, the science of measuring heat, is based on observing the temperature change when a body absorbs or discharges energy as heat. Substances respond differently to being heated. One substance might require a great deal of heat energy to raise its temperature by one degree, whereas another will exhibit the same temperature change after absorbing relatively little heat. The **heat capacity**  $C$  of a substance, which is a measure of this property, is defined as

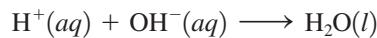
$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

When an element or a compound is heated, the energy required will depend on the amount of the substance present (for example, it takes twice as much energy to raise the temperature of two grams of water by one degree than it takes to raise the temperature of one gram of water by one degree). Thus, in defining the heat capacity of a substance, the amount of substance must be specified. If the heat capacity is given *per gram* of substance, it is called the **specific heat capacity**, and its units are  $\text{J}/\text{C} \cdot \text{g}$  or  $\text{J}/\text{K} \cdot \text{g}$ . If the heat capacity is given *per mole* of the substance, it is called the **molar heat capacity**, and it has the units  $\text{J}/\text{C} \cdot \text{mol}$  or  $\text{J}/\text{K} \cdot \text{mol}$ . The specific heat capacities of some common substances are given in Table 6.1. Note from this table that the heat capacities of metals are very different from that of water. It takes much less energy to change the temperature of a gram of a metal by  $1^\circ\text{C}$  than for a gram of water.

Although the calorimeters used for highly accurate work are precision instruments, a very simple calorimeter can be used to examine the fundamentals of calorimetry. All we need are two nested Styrofoam cups with a cover through which a stirrer and thermometer can be inserted, as shown in Fig. 6.5. This device is called a “coffee-cup calorimeter.” The outer cup is used to provide extra insulation. The inner cup holds the solution in which the reaction occurs.

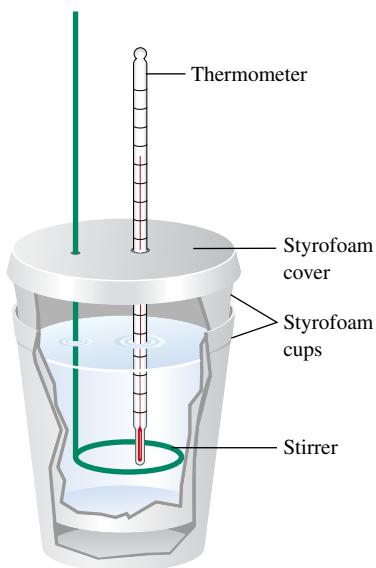
The measurement of heat using a simple calorimeter such as that shown in Fig. 6.5 is an example of **constant-pressure calorimetry**, since the pressure (atmospheric pressure) remains constant during the process. Constant-pressure calorimetry is used in determining the changes in enthalpy (heats of reactions) for reactions occurring in solution. Recall that under these conditions, the change in enthalpy equals the heat.

For example, suppose we mix 50.0 mL of 1.0  $M$  HCl at  $25.0^\circ\text{C}$  with 50.0 mL of 1.0  $M$  NaOH also at  $25^\circ\text{C}$  in a calorimeter. After the reactants are mixed by stirring, the temperature is observed to increase to  $31.9^\circ\text{C}$ . As we saw in Section 4.8, the net ionic equation for this reaction is



When these reactants (each originally at the same temperature) are mixed, the temperature of the mixed solution is observed to increase. Therefore, the chemical reaction must be releasing energy as heat. This released energy increases the random motions of the solution components, which in turn increases the temperature. The quantity of energy released can be determined from the temperature increase, the mass of solution, and the specific heat capacity of the solution. For an approximate result, we will assume that the calorimeter does not absorb or leak any heat and that the solution can be treated as if it were pure water with a density of 1.0 g/mL.

We also need to know the heat required to raise the temperature of a given amount of water by  $1^\circ\text{C}$ . Table 6.1 lists the specific heat capacity of water as 4.18  $\text{J}/\text{C} \cdot \text{g}$ . This means that 4.18 J of energy is required to raise the temperature of 1 gram of water by  $1^\circ\text{C}$ .



**FIGURE 6.5**

A coffee-cup calorimeter made of two Styrofoam cups.



## CHEMICAL IMPACT

### Nature Has Hot Plants

The voodoo lily is a beautiful, seductive—and foul-smelling—plant. The exotic-looking lily features an elaborate reproductive mechanism—a purple spike that can reach nearly 3 feet in length and is cloaked by a hoodlike leaf. But approach to the plant reveals bad news—it smells terrible!

Despite its antisocial odor, this putrid plant has fascinated biologists for many years because of its ability to generate heat. At the peak of its metabolic activity, the plant's blossom can be as much as  $15^{\circ}\text{C}$  above its ambient temperature. To generate this much heat, the metabolic rate of the plant must be close to that of a flying hummingbird!

What's the purpose of this intense heat production? For a plant faced with limited food supplies in the very competitive tropical climate where it grows, heat production seems like a great waste of energy. The answer to this mystery is that the voodoo lily is pollinated mainly by carrion-loving insects. Thus the lily prepares a malodorous

mixture of chemicals characteristic of rotting meat, which it then “cooks” off into the surrounding air to attract flesh-eating beetles and flies. Then, once the insects enter the pollination chamber, the high temperatures there (as high as  $110^{\circ}\text{F}$ ) cause the insects to remain very active to better carry out their pollination duties.

The voodoo lily is only one of many such thermogenic (heat-producing) plants. Another interesting example is the eastern skunk cabbage, which produces enough heat to bloom inside of a snow bank by creating its own ice caves. These plants are of special interest to biologists because they provide opportunities to study metabolic reactions that are quite subtle in “normal” plants. For example, recent studies have shown that salicylic acid, the active form of aspirin, is probably very important in producing the metabolic bursts in thermogenic plants.

Besides studying the dramatic heat effects in thermogenic plants, biologists are also interested in calorimetric

If two reactants at the same temperature are mixed and the resulting solution gets warmer, this means the reaction taking place is exothermic. An endothermic reaction cools the solution.

From these assumptions and definitions, we can calculate the heat (change in enthalpy) for the neutralization reaction:

Energy released by the reaction

= energy absorbed by the solution

= specific heat capacity  $\times$  mass of solution  $\times$  increase in temperature

=  $s \times m \times \Delta T$

In this case the increase in temperature ( $\Delta T$ ) =  $31.9^{\circ}\text{C} - 25.0^{\circ}\text{C} = 6.9^{\circ}\text{C}$ , and the mass of solution ( $m$ ) =  $100.0 \text{ mL} \times 1.0 \text{ g/mL} = 1.0 \times 10^2 \text{ g}$ . Thus

$$\text{Energy released} = s \times m \times \Delta T$$

$$= \left( 4.18 \frac{\text{J}}{\text{C} \cdot \text{g}} \right) (1.0 \times 10^2 \text{ g}) (6.9^{\circ}\text{C}) \\ = 2.9 \times 10^3 \text{ J}$$

How much energy would have been released if twice these amounts of solutions had been mixed? The answer is that twice as much energy would have been produced. The heat of a reaction is an *extensive property*; it depends directly on the amount of substance, in this case on the amounts of reactants. In contrast, an *intensive property* is not related to the amount of a substance. For example, temperature is an intensive property.

Enthalpies of reaction are often expressed in terms of moles of reacting substances. The number of moles of  $\text{H}^+$  ions consumed in the preceding experiment is

$$50.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.0 \text{ mol}}{\text{L}} \text{H}^+ = 5.0 \times 10^{-2} \text{ mol H}^+$$

Thus  $2.9 \times 10^3 \text{ J}$  heat was released when  $5.0 \times 10^{-2} \text{ mol H}^+$  ions reacted, or

$$\frac{2.9 \times 10^3 \text{ J}}{5.0 \times 10^{-2} \text{ mol H}^+} = 5.8 \times 10^4 \text{ J/mol}$$

studies of regular plants. For example, very precise calorimeters have been designed that can be used to study the heat produced, and thus the metabolic activities, of clumps of cells no larger than a bread crumb. Several scientists have suggested that a single calorimetric measurement taking just a few minutes on a tiny plant might be useful in predicting the growth rate of the mature plant throughout its lifetime. If true, this would provide a very efficient method for selecting the plants most likely to thrive as adults.

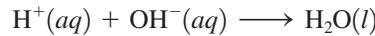
Because the study of the heat production by plants is an excellent way to learn about plant metabolism, this continues to be a “hot” area of research.



The voodoo lily attracts pollinating insects with its foul odor.

Notice that in this example we mentally keep track of the direction of the energy flow and assign the correct sign at the end of the calculation.

of heat released per 1.0 mol  $\text{H}^+$  ions neutralized. Thus the *magnitude* of the enthalpy change per mole for the reaction



is 58 kJ/mol. Since heat is *evolved*,  $\Delta H = -58 \text{ kJ/mol}$ .

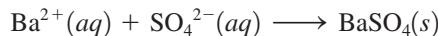
### Sample Exercise 6.5

### Constant-Pressure Calorimetry

When 1.00 L of 1.00 M  $\text{Ba}(\text{NO}_3)_2$  solution at 25.0°C is mixed with 1.00 L of 1.00 M  $\text{Na}_2\text{SO}_4$  solution at 25°C in a calorimeter, the white solid  $\text{BaSO}_4$  forms and the temperature of the mixture increases to 28.1°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 J/ $^\circ\text{C} \cdot \text{g}$ , and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of  $\text{BaSO}_4$  formed.

#### Solution

The ions present before any reaction occurs are  $\text{Ba}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ . The  $\text{Na}^+$  and  $\text{NO}_3^-$  ions are spectator ions, since  $\text{NaNO}_3$  is very soluble in water and will not precipitate under these conditions. The net ionic equation for the reaction is therefore



Since the temperature increases, formation of the solid  $\text{BaSO}_4$  must be exothermic;  $\Delta H$  will be negative.

Heat evolved by reaction

$$= \text{heat absorbed by solution}$$

$$= \text{specific heat capacity} \times \text{mass of solution} \times \text{increase in temperature}$$

Since 1.00 L of each solution is used, the total solution volume is 2.00 L, and

$$\text{Mass of solution} = 2.00 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.0 \text{ g}}{1 \text{ mL}} = 2.0 \times 10^3 \text{ g}$$

$$\text{Temperature increase} = 28.1^\circ\text{C} - 25.0^\circ\text{C} = 3.1^\circ\text{C}$$

$$\text{Heat evolved} = (4.18 \text{ J}/^\circ\text{C} \cdot \text{g})(2.0 \times 10^3 \text{ g})(3.1^\circ\text{C}) = 2.6 \times 10^4 \text{ J}$$

Thus

$$q = q_P = \Delta H = -2.6 \times 10^4 \text{ J}$$

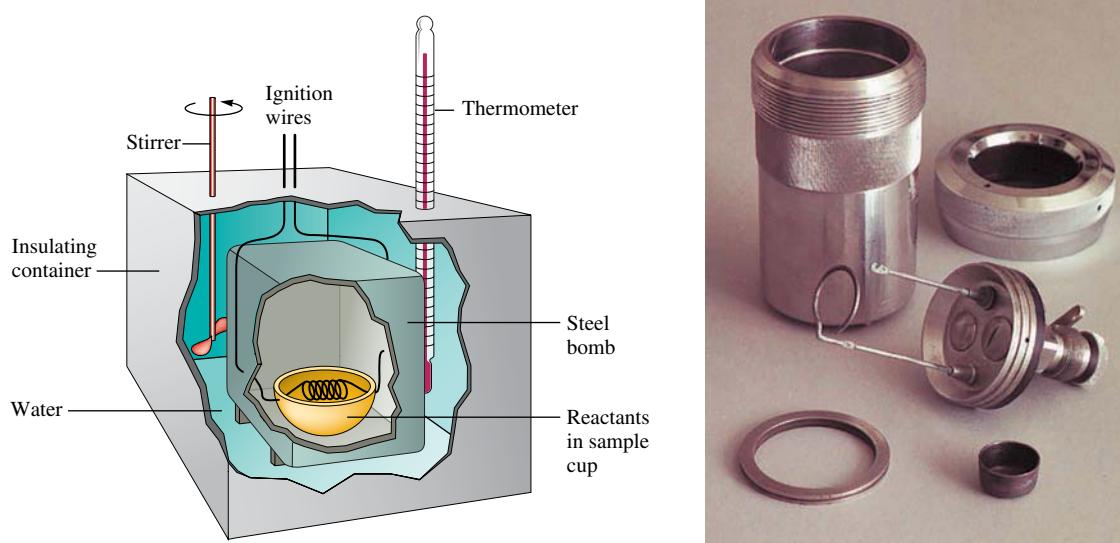
Since 1.0 L of 1.0 M  $\text{Ba}(\text{NO}_3)_2$  contains 1 mol  $\text{Ba}^{2+}$  ions and 1.0 L of 1.0 M  $\text{Na}_2\text{SO}_4$  contains 1.0 mol  $\text{SO}_4^{2-}$  ions, 1.0 mol solid  $\text{BaSO}_4$  is formed in this experiment. Thus the enthalpy change per mole of  $\text{BaSO}_4$  formed is

$$\Delta H = -2.6 \times 10^4 \text{ J/mol} = -26 \text{ kJ/mol}$$

*See Exercises 6.51 through 6.54.*

Calorimetry experiments also can be performed at **constant volume**. For example, when a photographic flashbulb flashes, the bulb becomes very hot, because the reaction of the zirconium or magnesium wire with the oxygen inside the bulb is exothermic. The reaction occurs inside the flashbulb, which is rigid and does not change volume. Under these conditions, no work is done (because the volume must change for pressure–volume work to be performed). To study the energy changes in reactions under conditions of constant volume, a “bomb calorimeter” (Fig. 6.6) is used. Weighed reactants are placed inside a rigid steel container (the “bomb”) and ignited. The energy change is determined by measuring the increase in the temperature of the water and other calorimeter parts. For a constant-volume process, the change in volume  $\Delta V$  is equal to zero, so work (which is  $-P\Delta V$ ) is also equal to zero. Therefore,

$$\Delta E = q + w = q = q_V \quad (\text{constant volume})$$



**FIGURE 6.6**

A bomb calorimeter. The reaction is carried out inside a rigid steel “bomb” (photo of actual disassembled “bomb” shown on right), and the heat evolved is absorbed by the surrounding water and other calorimeter parts. The quantity of energy produced by the reaction can be calculated from the temperature increase.



## CHEMICAL IMPACT

### Firewalking: Magic or Science?

**F**or millennia people have been amazed at the ability of Eastern mystics to walk across beds of glowing coals without any apparent discomfort. Even in the United States, thousands of people have performed feats of firewalking as part of motivational seminars. How is this possible? Do firewalkers have supernatural powers?

Actually, there are good scientific explanations, based on the concepts covered in this chapter, of why firewalking is possible. The first important factor concerns the heat capacity of feet. Because human tissue is mainly composed of water, it has a relatively large specific heat capacity. This means that a large amount of energy must be transferred from the coals to significantly change the temperature of the feet. During the brief contact between feet and coals, there is relatively little time for energy flow so the feet do not reach a high enough temperature to cause damage.

Second, although the surface of the coals has a very high temperature, the red hot layer is very thin. Therefore, the quantity of energy available to heat the feet is smaller than might be expected. This factor points to the difference between temperature and heat. Temperature reflects the *intensity* of the random kinetic energy in a given sample of matter. The amount of energy available for heat flow, on the other hand, depends on the quantity of matter at a given temperature—10 grams of matter at a given temperature contains 10 times as much thermal



A group of firewalkers in Japan.

energy as 1 gram of the same matter. This is why the tiny spark from a sparkler does not hurt when it hits your hand. The spark has a very high temperature but has so little mass that no significant energy transfer occurs to your hand. This same argument applies to the very thin hot layer on the coals.

Thus, although firewalking is an impressive feat, there are several sound scientific reasons why it is possible (with the proper training and a properly prepared bed of coals).

Suppose we wish to measure the energy of combustion of octane ( $C_8H_{18}$ ), a component of gasoline. A 0.5269-g sample of octane is placed in a bomb calorimeter known to have a heat capacity of  $11.3 \text{ kJ}^\circ\text{C}$ . This means that  $11.3 \text{ kJ}$  of energy is required to raise the temperature of the water and other parts of the calorimeter by  $1^\circ\text{C}$ . The octane is ignited in the presence of excess oxygen, and the temperature increase of the calorimeter is  $2.25^\circ\text{C}$ . The amount of energy released is calculated as follows:

Energy released by the reaction

$$\begin{aligned} &= \text{temperature increase} \times \text{energy required to change the temperature by } 1^\circ\text{C} \\ &= \Delta T \times \text{heat capacity of calorimeter} \\ &= 2.25^\circ\text{C} \times 11.3 \text{ kJ}^\circ\text{C} = 25.4 \text{ kJ} \end{aligned}$$

This means that 25.4 kJ of energy was released by the combustion of 0.5269 g octane.

The number of moles of octane is

$$0.5269 \text{ g octane} \times \frac{1 \text{ mol octane}}{114.2 \text{ g octane}} = 4.614 \times 10^{-3} \text{ mol octane}$$

Since  $25.4 \text{ kJ}$  of energy was released for  $4.614 \times 10^{-3} \text{ mol}$  octane, the energy released per mole is

$$\frac{25.4 \text{ kJ}}{4.614 \times 10^{-3} \text{ mol}} = 5.50 \times 10^3 \text{ kJ/mol}$$

Since the reaction is exothermic,  $\Delta E$  is negative:

$$\Delta E_{\text{combustion}} = -5.50 \times 10^3 \text{ kJ/mol}$$

Note that since no work is done in this case,  $\Delta E$  is equal to the heat.

$$\Delta E = q + w = q \quad \text{since } w = 0$$

Thus  $q = -5.50 \times 10^3 \text{ kJ/mol}$ .

### Sample Exercise 6.6

### Constant-Volume Calorimetry

Hydrogen's potential as a fuel is discussed in Section 6.6.

It has been suggested that hydrogen gas obtained by the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out using a bomb calorimeter with a heat capacity of  $11.3 \text{ kJ}/^\circ\text{C}$ . When a  $1.50\text{-g}$  sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by  $7.3^\circ\text{C}$ . When a  $1.15\text{-g}$  sample of hydrogen gas was burned with excess oxygen, the temperature increase was  $14.3^\circ\text{C}$ . Calculate the energy of combustion (per gram) for hydrogen and methane.

#### Solution

We calculate the energy of combustion for methane using the heat capacity of the calorimeter ( $11.3 \text{ kJ}/^\circ\text{C}$ ) and the observed temperature increase of  $7.3^\circ\text{C}$ :

$$\begin{aligned} \text{Energy released in the combustion of } 1.5 \text{ g CH}_4 &= (11.3 \text{ kJ}/^\circ\text{C})(7.3^\circ\text{C}) \\ &= 83 \text{ kJ} \end{aligned}$$

$$\text{Energy released in the combustion of } 1 \text{ g CH}_4 = \frac{83 \text{ kJ}}{1.5 \text{ g}} = 55 \text{ kJ/g}$$

Similarly, for hydrogen

$$\begin{aligned} \text{Energy released in the combustion of } 1.15 \text{ g H}_2 &= (11.3 \text{ kJ}/^\circ\text{C})(14.3^\circ\text{C}) \\ &= 162 \text{ kJ} \end{aligned}$$

$$\text{Energy released in the combustion of } 1 \text{ g H}_2 = \frac{162 \text{ kJ}}{1.15 \text{ g}} = 141 \text{ kJ/g}$$

The energy released in the combustion of  $1 \text{ g}$  hydrogen is approximately 2.5 times that for  $1 \text{ g}$  methane, indicating that hydrogen gas is a potentially useful fuel.

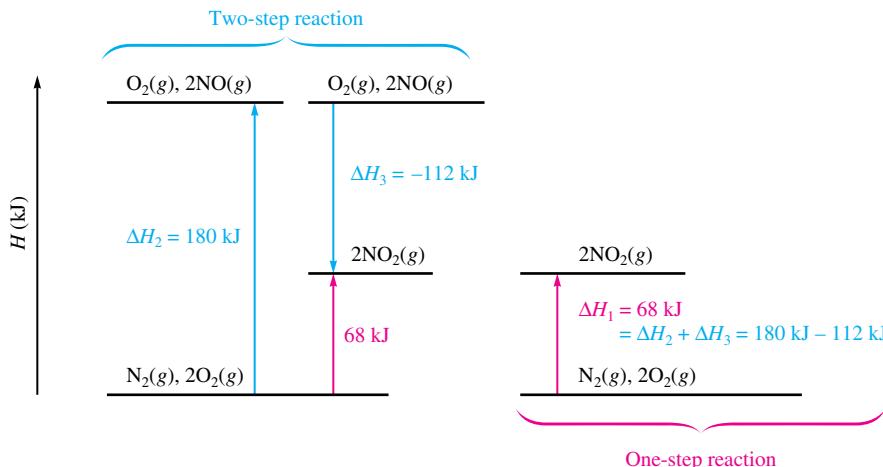
*See Exercises 6.55 and 6.56.*

### 6.3 Hess's Law

Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. This means that *in going from a particular set of reactants to a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps*. This principle is known as **Hess's law** and can be illustrated by examining the oxidation of nitrogen to produce nitrogen dioxide. The overall reaction can be written in one step, where the enthalpy change is represented by  $\Delta H_1$ .



$\Delta H$  is not dependent on the reaction pathway.

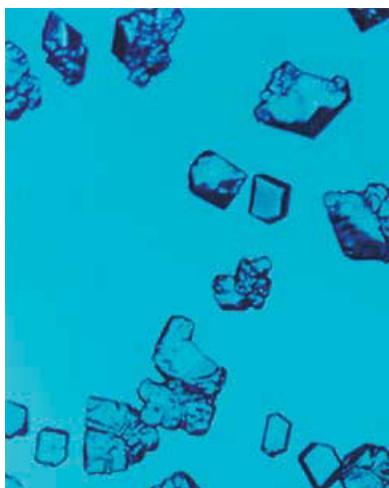
**FIGURE 6.7**

The principle of Hess's law. The same change in enthalpy occurs when nitrogen and oxygen react to form nitrogen dioxide, regardless of whether the reaction occurs in one (red) or two (blue) steps.



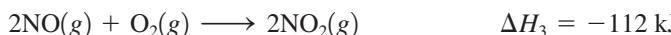
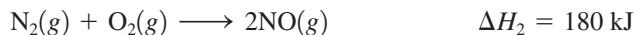
Visualization: Hess's Law

Reversing the direction of a reaction changes the sign of  $\Delta H$ .



Crystals of xenon tetrafluoride, the first reported binary compound containing a noble gas element.

This reaction also can be carried out in two distinct steps, with enthalpy changes designated by  $\Delta H_2$  and  $\Delta H_3$ :



Note that the sum of the two steps gives the net, or overall, reaction and that

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \text{ kJ}$$

The principle of Hess's law is shown schematically in Fig. 6.7.

### Characteristics of Enthalpy Changes

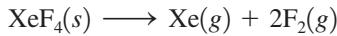
To use Hess's law to compute enthalpy changes for reactions, it is important to understand two characteristics of  $\Delta H$  for a reaction:

1. If a reaction is reversed, the sign of  $\Delta H$  is also reversed.
2. The magnitude of  $\Delta H$  is directly proportional to the quantities of reactants and products in a reaction. If the coefficients in a balanced reaction are multiplied by an integer, the value of  $\Delta H$  is multiplied by the same integer.

Both these rules follow in a straightforward way from the properties of enthalpy changes. The first rule can be explained by recalling that the *sign* of  $\Delta H$  indicates the *direction* of the heat flow at constant pressure. If the direction of the reaction is reversed, the direction of the heat flow also will be reversed. To see this, consider the preparation of xenon tetrafluoride, which was the first binary compound made from a noble gas:

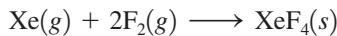


This reaction is exothermic, and 251 kJ of energy flows into the surroundings as heat. On the other hand, if the colorless  $XeF_4$  crystals are decomposed into the elements, according to the equation

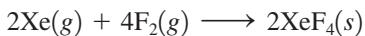


the opposite energy flow occurs because 251 kJ of energy must be added to the system to produce this endothermic reaction. Thus, for this reaction,  $\Delta H = +251 \text{ kJ}$ .

The second rule comes from the fact that  $\Delta H$  is an extensive property, depending on the amount of substances reacting. For example, since 251 kJ of energy is evolved for the reaction



then for a preparation involving twice the quantities of reactants and products, or



twice as much heat would be evolved:

$$\Delta H = 2(-251 \text{ kJ}) = -502 \text{ kJ}$$

### Sample Exercise 6.7

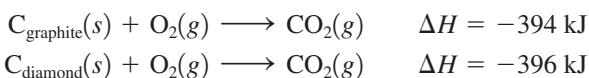
### Hess's Law I

Two forms of carbon are *graphite*, the soft, black, slippery material used in “lead” pencils and as a lubricant for locks, and *diamond*, the brilliant, hard gemstone. Using the enthalpies of combustion for graphite ( $-394 \text{ kJ/mol}$ ) and diamond ( $-396 \text{ kJ/mol}$ ), calculate  $\Delta H$  for the conversion of graphite to diamond:

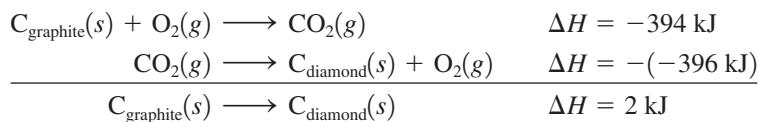


#### Solution

The combustion reactions are

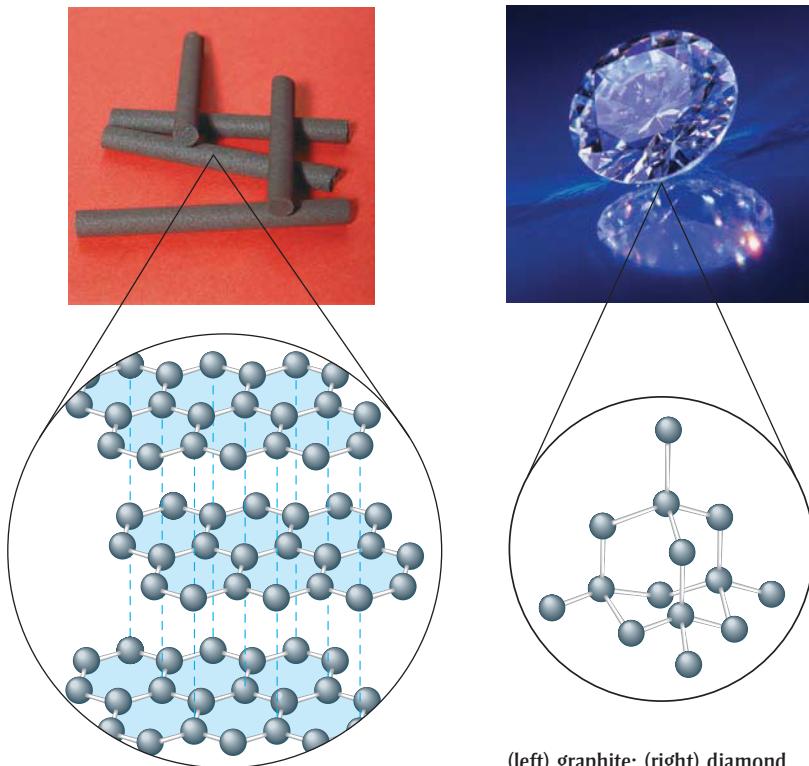


Note that if we reverse the second reaction (which means we must change the sign of  $\Delta H$ ) and sum the two reactions, we obtain the desired reaction:



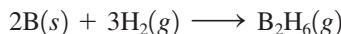
Thus 2 kJ of energy is required to change 1 mol graphite to diamond. This process is endothermic.

*See Exercises 6.57 and 6.58.*



**Sample Exercise 6.8****Hess's Law II**

Diborane ( $\text{B}_2\text{H}_6$ ) is a highly reactive boron hydride that was once considered as a possible rocket fuel for the U.S. space program. Calculate  $\Delta H$  for the synthesis of diborane from its elements, according to the equation



using the following data:

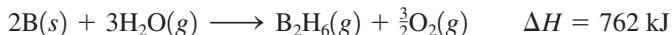
Reaction	$\Delta H$
(a) $2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s)$	−1273 kJ
(b) $\text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g)$	−2035 kJ
(c) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)$	−286 kJ
(d) $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44 kJ

**Solution**

To obtain  $\Delta H$  for the required reaction, we must somehow combine equations (a), (b), (c), and (d) to produce that reaction and add the corresponding  $\Delta H$  values. This can best be done by focusing on the reactants and products of the required reaction. The reactants are  $\text{B}(s)$  and  $\text{H}_2(g)$ , and the product is  $\text{B}_2\text{H}_6(g)$ . How can we obtain the correct equation? Reaction (a) has  $\text{B}(s)$  as a reactant, as needed in the required equation. Thus reaction (a) will be used as it is. Reaction (b) has  $\text{B}_2\text{H}_6(g)$  as a reactant, but this substance is needed as a product. Thus reaction (b) must be reversed, and the sign of  $\Delta H$  must be changed accordingly. Up to this point we have

(a)	$2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \longrightarrow \text{B}_2\text{O}_3(s)$	$\Delta H = -1273 \text{ kJ}$
−(b)	$\text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + 3\text{O}_2(g)$	$\Delta H = -(-2035 \text{ kJ})$
Sum: $\text{B}_2\text{O}_3(s) + 2\text{B}(s) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{O}_3(s) + \text{B}_2\text{H}_6(g) + 3\text{O}_2(g)$		$\Delta H = 762 \text{ kJ}$

Deleting the species that occur on both sides gives



We are closer to the required reaction, but we still need to remove  $\text{H}_2\text{O}(g)$  and  $\text{O}_2(g)$  and introduce  $\text{H}_2(g)$  as a reactant. We can do this using reactions (c) and (d). If we multiply reaction (c) and its  $\Delta H$  value by 3 and add the result to the preceding equation, we have

3 × (c)	$3[\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{H}_2\text{O}(l)]$	$\Delta H = 3(-286 \text{ kJ})$
Sum: $2\text{B}(s) + 3\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(g) \longrightarrow \text{B}_2\text{H}_6(g) + \frac{3}{2}\text{O}_2(g) + 3\text{H}_2\text{O}(l)$		$\Delta H = -96 \text{ kJ}$

We can cancel the  $\frac{3}{2}\text{O}_2(g)$  on both sides, but we cannot cancel the  $\text{H}_2\text{O}$  because it is gaseous on one side and liquid on the other. This can be solved by adding reaction (d), multiplied by 3:

3 × (d)	$3[\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)]$	$\Delta H = 3(44 \text{ kJ})$
2B(s) + 3H <sub>2</sub> (g) + 3H <sub>2</sub> O(g) + 3H <sub>2</sub> O(l) → B <sub>2</sub> H <sub>6</sub> (g) + 3H <sub>2</sub> O(l) + 3H <sub>2</sub> O(g)		$\Delta H = +36 \text{ kJ}$

This gives the reaction required by the problem:



Thus  $\Delta H$  for the synthesis of 1 mol diborane from the elements is +36 kJ.

*See Exercises 6.59 through 6.64.*

### Hints for Using Hess's Law

Calculations involving Hess's law typically require that several reactions be manipulated and combined to finally give the reaction of interest. In doing this procedure you should

- Work *backward* from the required reaction, using the reactants and products to decide how to manipulate the other given reactions at your disposal
- Reverse any reactions as needed to give the required reactants and products
- Multiply reactions to give the correct numbers of reactants and products

This process involves some trial and error, but it can be very systematic if you always allow the final reaction to guide you.

## 6.4 Standard Enthalpies of Formation

For a reaction studied under conditions of constant pressure, we can obtain the enthalpy change using a calorimeter. However, this process can be very difficult. In fact, in some cases it is impossible, since certain reactions do not lend themselves to such study. An example is the conversion of solid carbon from its graphite form to its diamond form:



The value of  $\Delta H$  for this process cannot be obtained by direct measurement in a calorimeter because the process is much too slow under normal conditions. However, as we saw in Sample Exercise 6.7,  $\Delta H$  for this process can be calculated from heats of combustion. This is only one example of how useful it is to be able to *calculate*  $\Delta H$  values for chemical reactions. We will next show how to do this using standard enthalpies of formation.

The **standard enthalpy of formation** ( $\Delta H_f^\circ$ ) of a compound is defined as the *change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states*.

A *degree symbol* on a thermodynamic function, for example,  $\Delta H^\circ$ , indicates that the corresponding process has been carried out under standard conditions. The **standard state** for a substance is a precisely defined reference state. Because thermodynamic functions often depend on the concentrations (or pressures) of the substances involved, we must use a common reference state to properly compare the thermodynamic properties of two substances. This is especially important because, for most thermodynamic properties, we can measure only *changes* in the property. For example, we have no method for determining absolute values of enthalpy. We can measure enthalpy changes ( $\Delta H$  values) only by performing heat-flow experiments.

### Conventional Definitions of Standard States

#### For a Compound

- The standard state of a gaseous substance is a pressure of exactly 1 atmosphere.
- For a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.
- For a substance present in a solution, the standard state is a concentration of exactly 1 M.

#### For an Element

- The standard state of an element is the form in which the element exists under conditions of 1 atmosphere and 25°C. (The standard state for oxygen is O<sub>2</sub>(g) at a pressure of 1 atmosphere; the standard state for sodium is Na(s); the standard state for mercury is Hg(l); and so on.)

Recently, the International Union of Pure and Applied Chemists (IUPAC) has adopted 1 bar (100,000 Pa) as the standard pressure instead of 1 atm (101,305 Pa). Both standards are now in wide use.

Standard state is *not* the same as the standard temperature and pressure (STP) for a gas (discussed in Section 5.4).



Brown nitrogen dioxide gas.

**TABLE 6.2 Standard Enthalpies of Formation for Several Compounds at 25°C**

Compound	$\Delta H_f^\circ$ (kJ/mol)
$\text{NH}_3(g)$	-46
$\text{NO}_2(g)$	34
$\text{H}_2\text{O}(l)$	-286
$\text{Al}_2\text{O}_3(s)$	-1676
$\text{Fe}_2\text{O}_3(s)$	-826
$\text{CO}_2(g)$	-394
$\text{CH}_3\text{OH}(l)$	-239
$\text{C}_8\text{H}_{18}(l)$	-269

Several important characteristics of the definition of the enthalpy of formation will become clearer if we again consider the formation of nitrogen dioxide from the elements in their standard states:



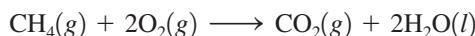
Note that the reaction is written so that both elements are in their standard states, and 1 mole of product is formed. Enthalpies of formation are *always* given per mole of product with the product in its standard state.

The formation reaction for methanol is written as



The standard state of carbon is graphite, the standard states for oxygen and hydrogen are the diatomic gases, and the standard state for methanol is the liquid.

The  $\Delta H_f^\circ$  values for some common substances are shown in Table 6.2. More values are found in Appendix 4. The importance of the tabulated  $\Delta H_f^\circ$  values is that enthalpies for many reactions can be calculated using these numbers. To see how this is done, we will calculate the standard enthalpy change for the combustion of methane:

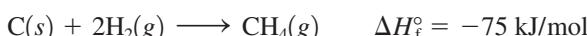


Enthalpy is a state function, so we can invoke Hess's law and choose *any* convenient pathway from reactants to products and then sum the enthalpy changes along the chosen pathway. A convenient pathway, shown in Fig. 6.8, involves taking the reactants apart to the respective elements in their standard states in reactions (a) and (b) and then forming the products from these elements in reactions (c) and (d). This general pathway will work for any reaction, since atoms are conserved in a chemical reaction.

Note from Fig. 6.8 that reaction (a), where methane is taken apart into its elements,

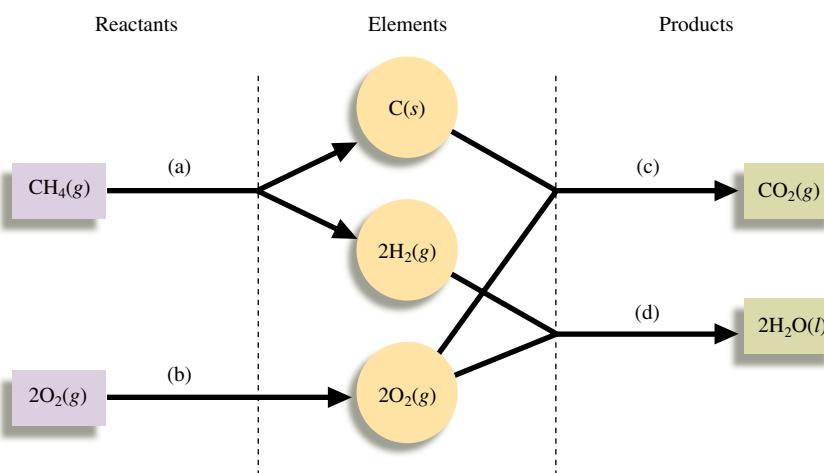


is just the reverse of the formation reaction for methane:



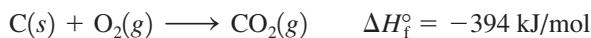
Since reversing a reaction means changing the sign of  $\Delta H$  but keeping the magnitude the same,  $\Delta H$  for reaction (a) is  $-\Delta H_f^\circ$ , or 75 kJ. Thus  $\Delta H_{(a)}^\circ = 75 \text{ kJ}$ .

Next we consider reaction (b). Here oxygen is already an element in its standard state, so no change is needed. Thus  $\Delta H_{(b)}^\circ = 0$ .

**FIGURE 6.8**

In this pathway for the combustion of methane, the reactants are first taken apart in reactions (a) and (b) to form the constituent elements in their standard states, which are then used to assemble the products in reactions (c) and (d).

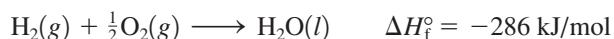
The next steps, reactions (c) and (d), use the elements formed in reactions (a) and (b) to form the products. Note that reaction (c) is simply the formation reaction for carbon dioxide:



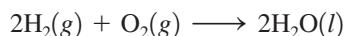
and

$$\Delta H_{(c)}^\circ = \Delta H_f^\circ \text{ for } \text{CO}_2(g) = -394 \text{ kJ}$$

Reaction (d) is the formation reaction for water:



However, since 2 moles of water are required in the balanced equation, we must form 2 moles of water from the elements:



Thus

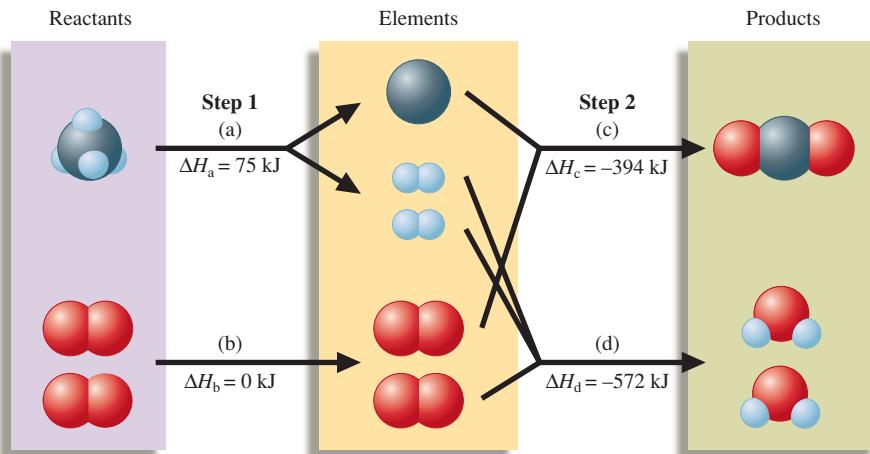
$$\Delta H_{(d)}^\circ = 2 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l) = 2(-286 \text{ kJ}) = -572 \text{ kJ}$$

We have now completed the pathway from the reactants to the products. The change in enthalpy for the reaction is the sum of the  $\Delta H$  values (including their signs) for the steps:

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= \Delta H_{(a)}^\circ + \Delta H_{(b)}^\circ + \Delta H_{(c)}^\circ + \Delta H_{(d)}^\circ \\ &= [-\Delta H_f^\circ \text{ for } \text{CH}_4(g)] + 0 + [\Delta H_f^\circ \text{ for } \text{CO}_2(g)] + [2 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l)] \\ &= -(-75 \text{ kJ}) + 0 + (-394 \text{ kJ}) + (-572 \text{ kJ}) \\ &= -891 \text{ kJ} \end{aligned}$$

This process is diagrammed in Fig. 6.9. Notice that the reactants are taken apart and converted to elements [not necessary for  $\text{O}_2(g)$ ] that are then used to form products. You can see that this is a very exothermic reaction because very little energy is required to convert the reactants to the respective elements but a great deal of energy is released when these elements form the products. This is why this reaction is so useful for producing heat to warm homes and offices.

Let's examine carefully the pathway we used in this example. First, the reactants were broken down into the elements in their standard states. This process involved reversing



**FIGURE 6.9**

A schematic diagram of the energy changes for the reaction  $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$ .

**Subtraction means to reverse the sign and add.**

**Elements in their standard states are not included in enthalpy calculations using  $\Delta H_f^\circ$  values.**

the formation reactions and thus switching the signs of the enthalpies of formation. The products were then constructed from these elements. This involved formation reactions and thus enthalpies of formation. We can summarize this entire process as follows: *The enthalpy change for a given reaction can be calculated by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products.* Remember to multiply the enthalpies of formation by integers as required by the balanced equation. This statement can be represented symbolically as follows:

$$\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants}) \quad (6.1)$$

where the symbol  $\Sigma$  (sigma) means “to take the sum of the terms,” and  $n_p$  and  $n_r$  represent the moles of each product or reactant, respectively.

*Elements are not included in the calculation because elements require no change in form.* We have in effect defined the enthalpy of formation of an element in its standard state as zero, since we have chosen this as our reference point for calculating enthalpy changes in reactions.

### Keep in Mind the Following Key Concepts When Doing Enthalpy Calculations:

- When a reaction is reversed, the magnitude of  $\Delta H$  remains the same, but its sign changes.
- When the balanced equation for a reaction is multiplied by an integer, the value of  $\Delta H$  for that reaction must be multiplied by the same integer.
- The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants and products:

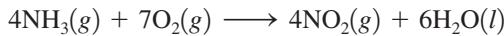
$$\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

- Elements in their standard states are not included in the  $\Delta H_{\text{reaction}}$  calculations. That is,  $\Delta H_f^\circ$  for an element in its standard state is zero.

### Sample Exercise 6.9

### Enthalpies from Standard Enthalpies of Formation I

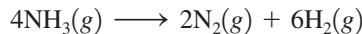
Using the standard enthalpies of formation listed in Table 6.2, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.



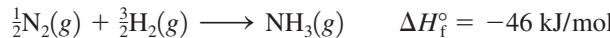
#### Solution

We will use the pathway in which the reactants are broken down into elements in their standard states, which are then used to form the products (see Fig. 6.10).

► 1 *Decomposition of  $\text{NH}_3(g)$  into elements* (reaction (a) in Fig. 6.10). The first step is to decompose 4 moles of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$ :

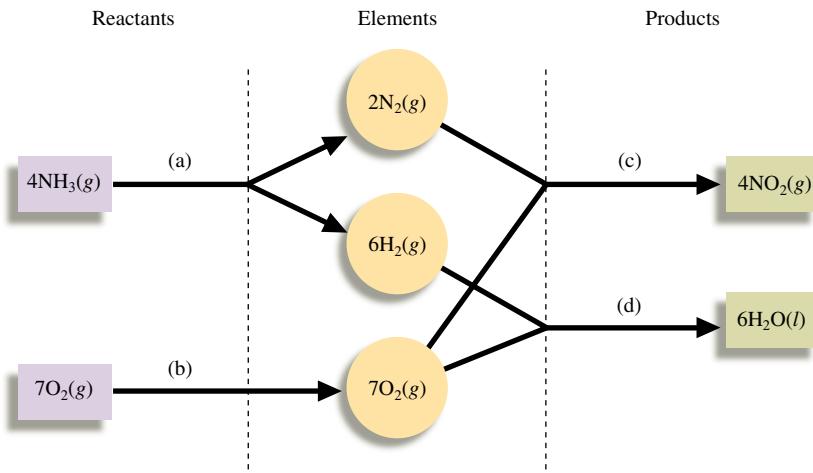


The preceding reaction is 4 times the *reverse* of the formation reaction for  $\text{NH}_3$ :



Thus

$$\Delta H_{(a)}^\circ = 4 \text{ mol} [ -(-46 \text{ kJ/mol}) ] = 184 \text{ kJ}$$

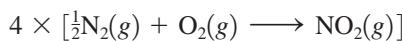
**FIGURE 6.10**

A pathway for the combustion of ammonia.

→ 2 *Elemental oxygen* (reaction (b) in Fig. 6.10). Since  $O_2(g)$  is an element in its standard state,  $\Delta H^\circ_{(b)} = 0$ .

We now have the elements  $N_2(g)$ ,  $H_2(g)$ , and  $O_2(g)$ , which can be combined to form the products of the overall reaction.

→ 3 *Synthesis of  $NO_2(g)$  from elements* (reaction (c) in Fig. 6.10). The overall reaction equation has 4 moles of  $NO_2$ . Thus the required reaction is 4 times the formation reaction for  $NO_2$ :



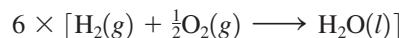
and

$$\Delta H^\circ_{(c)} = 4 \times \Delta H_f^\circ \text{ for } NO_2(g)$$

From Table 6.2,  $\Delta H_f^\circ$  for  $NO_2(g) = 34 \text{ kJ/mol}$  and

$$\Delta H^\circ_{(c)} = 4 \text{ mol} \times 34 \text{ kJ/mol} = 136 \text{ kJ}$$

→ 4 *Synthesis of  $H_2O(l)$  from elements* (reaction (d) in Fig. 6.10). Since the overall equation for the reaction has 6 moles of  $H_2O(l)$ , the required reaction is 6 times the formation reaction for  $H_2O(l)$ :



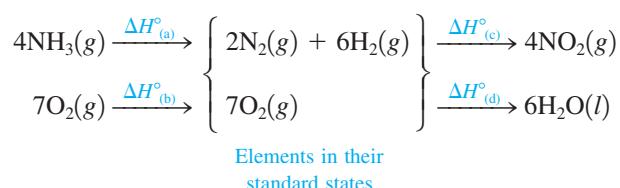
and

$$\Delta H^\circ_{(d)} = 6 \times \Delta H_f^\circ \text{ for } H_2O(l)$$

From Table 6.2,  $\Delta H_f^\circ$  for  $H_2O(l) = -286 \text{ kJ/mol}$  and

$$\Delta H^\circ_{(d)} = 6 \text{ mol} (-286 \text{ kJ/mol}) = -1716 \text{ kJ}$$

To summarize, we have done the following:



We add the  $\Delta H^\circ$  values for the steps to get  $\Delta H^\circ$  for the overall reaction:

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)} \\ &= [4 \times -\Delta H_f^\circ \text{ for } \text{NH}_3(g)] + 0 + [4 \times \Delta H_f^\circ \text{ for } \text{NO}_2(g)] \\ &\quad + [6 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l)] \\ &= [4 \times \Delta H_f^\circ \text{ for } \text{NO}_2(g)] + [6 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l)] \\ &\quad - [4 \times \Delta H_f^\circ \text{ for } \text{NH}_3(g)] \\ &= \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})\end{aligned}$$

Remember that elemental reactants and products do not need to be included, since  $\Delta H_f^\circ$  for an element in its standard state is zero. Note that we have again obtained Equation (6.1). The final solution is

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= [4 \times (34 \text{ kJ})] + [6 \times (-286 \text{ kJ})] - [4 \times (-46 \text{ kJ})] \\ &= -1396 \text{ kJ}\end{aligned}$$

*See Exercises 6.67 and 6.68.*

Now that we have shown the basis for Equation (6.1), we will make direct use of it to calculate  $\Delta H$  for reactions in succeeding exercises.

### Sample Exercise 6.10

### Enthalpies from Standard Enthalpies of Formation II



Visualization: Thermite Reaction



The thermite reaction is one of the most energetic chemical reactions known.

Using enthalpies of formation, calculate the standard change in enthalpy for the thermite reaction:



This reaction occurs when a mixture of powdered aluminum and iron(III) oxide is ignited with a magnesium fuse.

#### Solution

We use Equation (6.1):

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})$$

where

$$\Delta H_f^\circ \text{ for } \text{Fe}_2\text{O}_3(s) = -826 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for } \text{Al}_2\text{O}_3(s) = -1676 \text{ kJ/mol}$$

$$\Delta H_f^\circ \text{ for } \text{Al}(s) = \Delta H_f^\circ \text{ for } \text{Fe}(s) = 0$$

Thus

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= \Delta H_f^\circ \text{ for } \text{Al}_2\text{O}_3(s) - \Delta H_f^\circ \text{ for } \text{Fe}_2\text{O}_3(s) \\ &= -1676 \text{ kJ} - (-826 \text{ kJ}) = -850 \text{ kJ}\end{aligned}$$

This reaction is so highly exothermic that the iron produced is initially molten. This process is often used as a lecture demonstration and also has been used in welding massive steel objects such as ships' propellers.

*See Exercises 6.71 and 6.72.*

**Sample Exercise 6.11****Enthalpies from Standard Enthalpies of Formation III**

Methanol ( $\text{CH}_3\text{OH}$ ) is often used as a fuel in high-performance engines in race cars. Using the data in Table 6.2, compare the standard enthalpy of combustion per gram of methanol with that per gram of gasoline. Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane ( $\text{C}_8\text{H}_{18}$ ).

**Solution**

The combustion reaction for methanol is



Using the standard enthalpies of formation from Table 6.2 and Equation (6.1), we have

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 2 \times \Delta H_f^\circ \text{ for } \text{CO}_2(g) + 4 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l) - \\ &\quad 2 \times \Delta H_f^\circ \text{ for } \text{CH}_3\text{OH}(l) \\ &= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ}) \\ &= -1454 \text{ kJ}\end{aligned}$$

Thus 1454 kJ of heat is evolved when 2 moles of methanol burn. The molar mass of methanol is 32.0 g/mol. This means that 1454 kJ of energy is produced when 64.0 g methanol burns. The enthalpy of combustion per gram of methanol is

$$\frac{-1454 \text{ kJ}}{64.0 \text{ g}} = -22.7 \text{ kJ/g}$$

The combustion reaction for octane is



Using the standard enthalpies of information from Table 6.2 and Equation (6.1), we have

$$\begin{aligned}\Delta H^\circ_{\text{reaction}} &= 16 \times \Delta H_f^\circ \text{ for } \text{CO}_2(g) + 18 \times \Delta H_f^\circ \text{ for } \text{H}_2\text{O}(l) - \\ &\quad 2 \times \Delta H_f^\circ \text{ for } \text{C}_8\text{H}_{18}(l) \\ &= 16 \times (-394 \text{ kJ}) + 18 \times (-286 \text{ kJ}) - 2 \times (-269 \text{ kJ}) \\ &= -1.09 \times 10^4 \text{ kJ}\end{aligned}$$

This is the amount of heat evolved when 2 moles of octane burn. Since the molar mass of octane is 114.2 g/mol, the enthalpy of combustion per gram of octane is

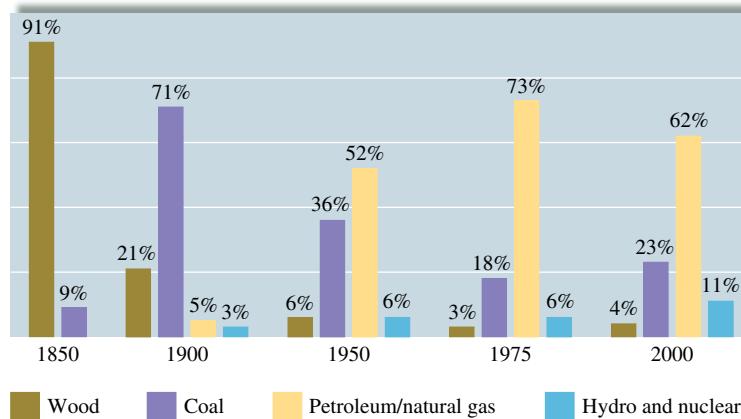
$$\frac{-1.09 \times 10^4 \text{ kJ}}{2(114.2 \text{ g})} = -47.8 \text{ kJ/g}$$

The enthalpy of combustion per gram of octane is approximately twice that per gram of methanol. On this basis, gasoline appears to be superior to methanol for use in a racing car, where weight considerations are usually very important. Why, then, is methanol used in racing cars? The answer is that methanol burns much more smoothly than gasoline in high-performance engines, and this advantage more than compensates for its weight disadvantage.

*See Exercise 6.77.*

## 6.5 Present Sources of Energy

Woody plants, coal, petroleum, and natural gas hold a vast amount of energy that originally came from the sun. By the process of photosynthesis, plants store energy that can be claimed by burning the plants themselves or the decay products that have been converted

**FIGURE 6.11**

Energy sources used in the United States.



This oil rig in Norway is the largest in the world.

over millions of years to **fossil fuels**. Although the United States currently depends heavily on petroleum for energy, this dependency is a relatively recent phenomenon, as shown in Fig. 6.11. In this section we discuss some sources of energy and their effects on the environment.

### Petroleum and Natural Gas

Although how they were produced is not completely understood, petroleum and natural gas were most likely formed from the remains of marine organisms that lived approximately 500 million years ago. **Petroleum** is a thick, dark liquid composed mostly of compounds called *hydrocarbons* that contain carbon and hydrogen. (Carbon is unique among elements in the extent to which it can bond to itself to form chains of various lengths.) Table 6.3 gives the formulas and names for several common hydrocarbons. **Natural gas**, usually associated with petroleum deposits, consists mostly of methane, but it also contains significant amounts of ethane, propane, and butane.

The composition of petroleum varies somewhat, but it consists mostly of hydrocarbons having chains that contain from 5 to more than 25 carbons. To be used efficiently, the petroleum must be separated into fractions by boiling. The lighter molecules (having the lowest boiling points) can be boiled off, leaving the heavier ones behind. The commercial uses of various petroleum fractions are shown in Table 6.4.

The petroleum era began when the demand for lamp oil during the Industrial Revolution outstripped the traditional sources: animal fats and whale oil. In response to this increased demand, Edwin Drake drilled the first oil well in 1859 at Titusville, Pennsylvania. The petroleum from this well was refined to produce *kerosene* (fraction C<sub>10</sub>–C<sub>18</sub>), which served as an excellent lamp oil. *Gasoline* (fraction C<sub>5</sub>–C<sub>10</sub>) had limited use and was often discarded. However, this situation soon changed. The development of the electric light decreased the need for kerosene, and the advent of the “horseless carriage” with its gasoline-powered engine signaled the birth of the gasoline age.

As gasoline became more important, new ways were sought to increase the yield of gasoline obtained from each barrel of petroleum. William Burton invented a process at Standard Oil of Indiana called *pyrolytic (high-temperature) cracking*. In this process, the heavier molecules of the kerosene fraction are heated to about 700°C, causing them to break (crack) into the smaller molecules of hydrocarbons in the gasoline fraction. As cars became larger, more efficient internal combustion engines were designed. Because of the uneven burning of the gasoline then available, these engines “knocked,” producing unwanted noise and even engine damage. Intensive research to find additives that would promote smoother burning produced tetraethyl lead, (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Pb, a very effective “anti-knock” agent.

**TABLE 6.3 Names and Formulas for Some Common Hydrocarbons**

Formula	Name
CH <sub>4</sub>	Methane
C <sub>2</sub> H <sub>6</sub>	Ethane
C <sub>3</sub> H <sub>8</sub>	Propane
C <sub>4</sub> H <sub>10</sub>	Butane
C <sub>5</sub> H <sub>12</sub>	Pentane
C <sub>6</sub> H <sub>14</sub>	Hexane
C <sub>7</sub> H <sub>16</sub>	Heptane
C <sub>8</sub> H <sub>18</sub>	Octane

**TABLE 6.4 Uses of the Various Petroleum Fractions**

Petroleum Fraction in Terms of Numbers of Carbon Atoms	Major Uses
C <sub>5</sub> –C <sub>10</sub>	Gasoline
C <sub>10</sub> –C <sub>18</sub>	Kerosene
	Jet fuel
C <sub>15</sub> –C <sub>25</sub>	Diesel fuel
	Heating oil
	Lubricating oil
>C <sub>25</sub>	Asphalt

Coal has variable composition depending on both its age and location.

The addition of tetraethyl lead to gasoline became a common practice, and by 1960, gasoline contained as much as 3 grams of lead per gallon. As we have discovered so often in recent years, technological advances can produce environmental problems. To prevent air pollution from automobile exhaust, catalytic converters have been added to car exhaust systems. The effectiveness of these converters, however, is destroyed by lead. The use of leaded gasoline also greatly increased the amount of lead in the environment, where it can be ingested by animals and humans. For these reasons, the use of lead in gasoline has been phased out, requiring extensive (and expensive) modifications of engines and of the gasoline refining process.

## Coal

**Coal** was formed from the remains of plants that were buried and subjected to high pressure and heat over long periods of time. Plant materials have a high content of cellulose, a complex molecule whose empirical formula is CH<sub>2</sub>O but whose molar mass is around 500,000 g/mol. After the plants and trees that flourished on the earth at various times and places died and were buried, chemical changes gradually lowered the oxygen and hydrogen content of the cellulose molecules. Coal “matures” through four stages: lignite, subbituminous, bituminous, and anthracite. Each stage has a higher carbon-to-oxygen and carbon-to-hydrogen ratio; that is, the relative carbon content gradually increases. Typical elemental compositions of the various coals are given in Table 6.5. The energy available from the combustion of a given mass of coal increases as the carbon content increases. Therefore, anthracite is the most valuable coal, and lignite the least valuable.

Coal is an important and plentiful fuel in the United States, currently furnishing approximately 23% of our energy. As the supply of petroleum dwindles, the share of the energy supply from coal is expected to increase. However, coal is expensive and dangerous to mine underground, and the strip mining of fertile farmland in the Midwest or of scenic land in the West causes obvious problems. In addition, the burning of coal, especially high-sulfur coal, yields air pollutants such as sulfur dioxide, which, in turn, can lead to acid rain, as we learned in Chapter 5. However, even if coal were pure carbon, the carbon dioxide produced when it was burned would still have significant effects on the earth’s climate.

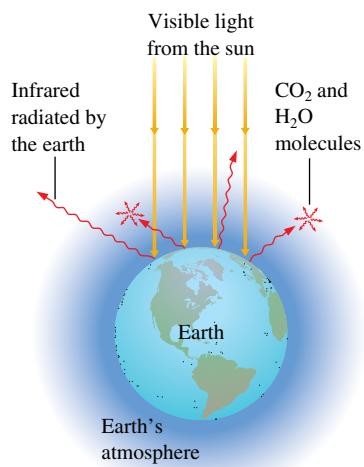
## Effects of Carbon Dioxide on Climate

The earth receives a tremendous quantity of radiant energy from the sun, about 30% of which is reflected back into space by the earth’s atmosphere. The remaining energy passes through the atmosphere to the earth’s surface. Some of this energy is absorbed by plants for photosynthesis and some by the oceans to evaporate water, but most of it is absorbed by soil, rocks, and water, increasing the temperature of the earth’s surface. This energy is in turn radiated from the heated surface mainly as *infrared radiation*, often called *heat radiation*.

**TABLE 6.5 Elemental Composition of Various Types of Coal**

Type of Coal	Mass Percent of Each Element				
	C	H	O	N	S
Lignite	71	4	23	1	1
Subbituminous	77	5	16	1	1
Bituminous	80	6	8	1	5
Anthracite	92	3	3	1	1

The electromagnetic spectrum, including visible and infrared radiation, is discussed in Chapter 7.

**FIGURE 6.12**

The earth's atmosphere is transparent to visible light from the sun. This visible light strikes the earth, and part of it is changed to infrared radiation. The infrared radiation from the earth's surface is strongly absorbed by CO<sub>2</sub>, H<sub>2</sub>O, and other molecules present in smaller amounts (for example, CH<sub>4</sub> and N<sub>2</sub>O) in the atmosphere. In effect, the atmosphere traps some of the energy, acting like the glass in a greenhouse and keeping the earth warmer than it would otherwise be.

**The average temperature of the earth's surface is 298 K. It would be 255 K without the "greenhouse gases."**

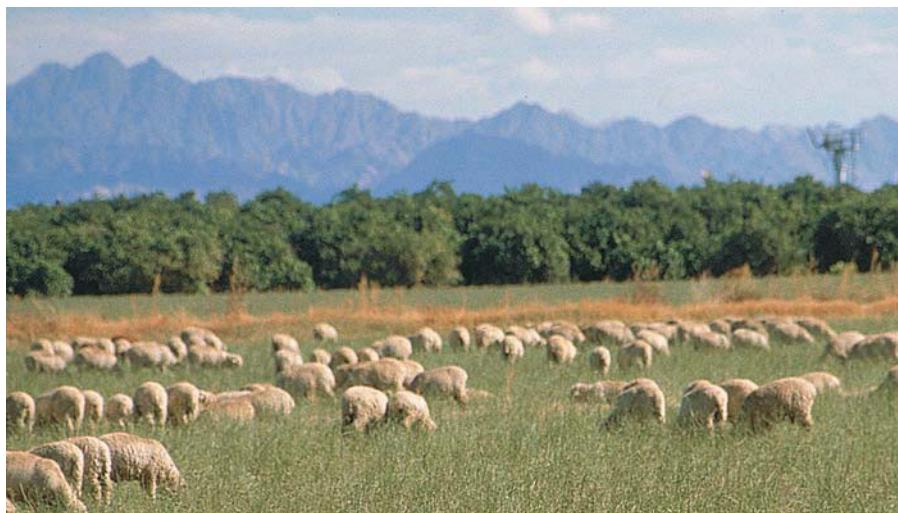
The atmosphere, like window glass, is transparent to visible light but does not allow all the infrared radiation to pass back into space. Molecules in the atmosphere, principally H<sub>2</sub>O and CO<sub>2</sub>, strongly absorb infrared radiation and radiate it back toward the earth, as shown in Fig. 6.12, so a net amount of thermal energy is retained by the earth's atmosphere, causing the earth to be much warmer than it would be without its atmosphere. In a way, the atmosphere acts like the glass of a greenhouse, which is transparent to visible light but absorbs infrared radiation, thus raising the temperature inside the building. This **greenhouse effect** is seen even more spectacularly on Venus, where the dense atmosphere is thought to be responsible for the high surface temperature of that planet.

Thus the temperature of the earth's surface is controlled to a significant extent by the carbon dioxide and water content of the atmosphere. The effect of atmospheric moisture (humidity) is apparent in the Midwest. In summer, when the humidity is high, the heat of the sun is retained well into the night, giving very high nighttime temperatures. On the other hand, in winter, the coldest temperatures always occur on clear nights, when the low humidity allows efficient radiation of energy back into space.

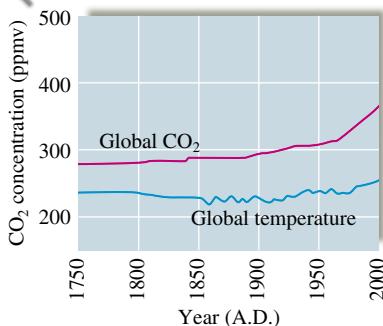
The atmosphere's water content is controlled by the water cycle (evaporation and precipitation), and the average remains constant over the years. However, as fossil fuels have been used more extensively, the carbon dioxide concentration has increased by about 16% from 1880 to 1980. Comparisons of satellite data have now produced evidence that the greenhouse effect has significantly warmed the earth's atmosphere. The data compare the same areas in both 1979 and 1997. The analysis shows that more infrared radiation was blocked by CO<sub>2</sub>, methane, and other greenhouse gases. This *could* increase the earth's average temperature by as much as 3°C, causing dramatic changes in climate and greatly affecting the growth of food crops.

How well can we predict long-term effects? Because weather has been studied for a period of time that is minuscule compared with the age of the earth, the factors that control the earth's climate in the long range are not clearly understood. For example, we do not understand what causes the earth's periodic ice ages. So it is difficult to estimate the impact of the increasing carbon dioxide levels.

In fact, the variation in the earth's average temperature over the past century is somewhat confusing. In the northern latitudes during the past century, the average temperature rose by 0.8°C over a period of 60 years, then cooled by 0.5°C during the next 25 years, and finally warmed by 0.2°C in the succeeding 15 years. Such fluctuations do not match the steady increase in carbon dioxide. However, in southern latitudes and near the equator during the past century, the average temperature showed a steady rise totaling 0.4°C.



Sheep grazing on a ranch in Australia.

**FIGURE 6.13**

The atmospheric CO<sub>2</sub> concentration and the average global temperature over the last 250 years. Note the significant increase in CO<sub>2</sub> concentration in the last 50 years.

(Source: National Assessment Synthesis Team, *Climate Change Impacts on the United States: The Potential Consequences of Climate, Variability and Change, Overview*, Report for the U.S. Global Change Research Program, Cambridge University Press, Cambridge, UK, p. 13, 2000.)

This figure is in reasonable agreement with the predicted effect of the increasing carbon dioxide concentration over that period. Another significant fact is that the past 10 years constitute the warmest decade on record.

Although the exact relationship between the carbon dioxide concentration in the atmosphere and the earth's temperature is not known at present, one thing is clear: The increase in the atmospheric concentration of carbon dioxide is quite dramatic (see Fig. 6.13). We must consider the implications of this increase as we consider our future energy needs.

Methane is another greenhouse gas that is 21 times more potent than carbon dioxide. This fact is particularly significant for countries with lots of animals, because methane is produced by methanogenic archae that live in the animals' rumen. For example, sheep and cattle produce about 14% of Australia's total greenhouse emissions. To reduce this level, Australia has initiated a program to vaccinate sheep and cattle to lower the number of archae present in their digestive systems. It is hoped that this effort will reduce by 20% the amount of methane emitted by these animals.

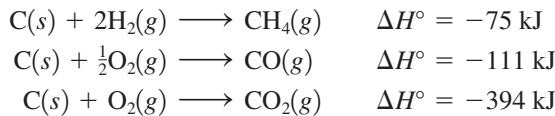
## 6.6 New Energy Sources

As we search for the energy sources of the future, we need to consider economic, climatic, and supply factors. There are several potential energy sources: the sun (solar), nuclear processes (fission and fusion), biomass (plants), and synthetic fuels. Direct use of the sun's radiant energy to heat our homes and run our factories and transportation systems seems a sensible long-term goal. But what do we do now? Conservation of fossil fuels is one obvious step, but substitutes for fossil fuels also must be found. We will discuss some alternative sources of energy here. Nuclear power will be considered in Chapter 21.

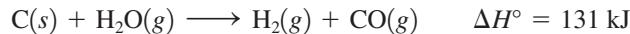
### Coal Conversion

One alternative energy source involves using a traditional fuel—coal—in new ways. Since transportation costs for solid coal are high, more energy-efficient fuels are being developed from coal. One possibility is to produce a gaseous fuel. Substances like coal that contain large molecules have high boiling points and tend to be solids or thick liquids. To convert coal from a solid to a gas therefore requires reducing the size of the molecules; the coal structure must be broken down in a process called *coal gasification*. This is done by treating the coal with oxygen and steam at high temperatures to break many of the carbon–carbon bonds. These bonds are replaced by carbon–hydrogen and carbon–oxygen bonds as the coal fragments react with the water and oxygen. The process is represented in Fig. 6.14. The desired product is a mixture of carbon monoxide and hydrogen called *synthetic gas*, or *syngas*, and methane (CH<sub>4</sub>) gas. Since all the components of this product can react with oxygen to release heat in a combustion reaction, this gas is a useful fuel.

One of the most important considerations in designing an industrial process is efficient use of energy. In coal gasification, some of the reactions are exothermic:

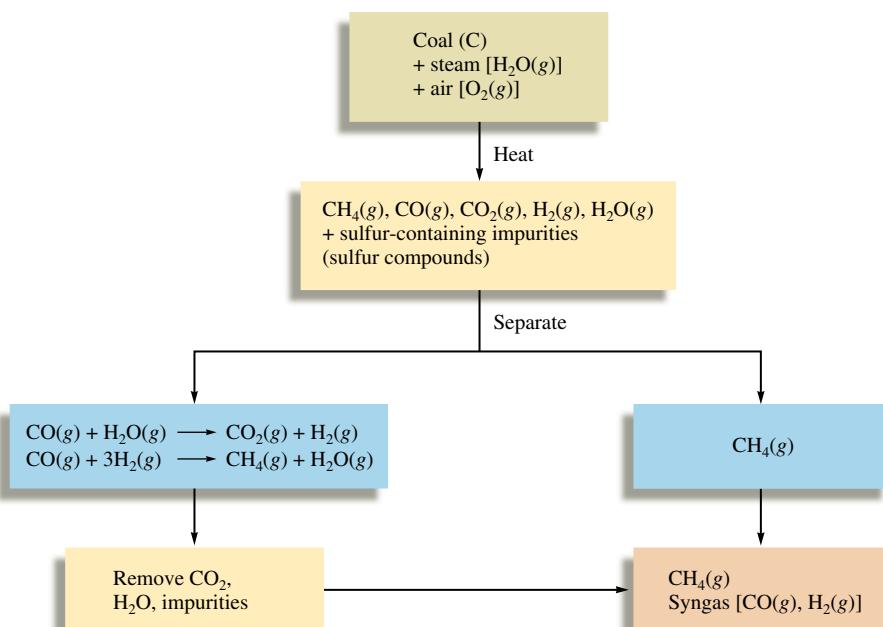


Other gasification reactions are endothermic, for example:



An industrial process must be energy efficient.

If such conditions as the rate of feed of coal, air, and steam are carefully controlled, the correct temperature can be maintained in the process without using any external energy source. That is, an energy balance is maintained.

**FIGURE 6.14**

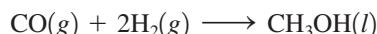
Coal gasification. Reaction of coal with a mixture of steam and air breaks down the large hydrocarbon molecules in the coal to smaller gaseous molecules, which can be used as fuels.



The main engines in the space shuttle Endeavour use hydrogen and oxygen as fuel.

Presently only a few plants in the United States use syngas produced on site to produce electricity. These plants are being used to evaluate the economic feasibility of producing electrical power by coal gasification.

Although syngas can be used directly as a fuel, it is also important as a raw material to produce other fuels. For example, syngas can be converted directly to methanol:

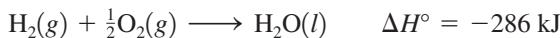


Methanol is used in the production of synthetic fibers and plastics and also can be used as a fuel. In addition, it can be converted directly to gasoline. Approximately half of South Africa's gasoline supply comes from methanol produced from syngas.

In addition to coal gasification, the formation of *coal slurries* is another new use of coal. A slurry is a suspension of fine particles in a liquid, and coal must be pulverized and mixed with water to form a slurry. The slurry can be handled, stored, and burned in ways similar to those used for *residual oil*, a heavy fuel oil from petroleum accounting for almost 15% of U.S. petroleum imports. One hope is that coal slurries might replace solid coal and residual oil as fuels for electricity-generating power plants. However, the water needed for slurries might place an unacceptable burden on water resources, especially in the western states.

### Hydrogen as a Fuel

If you have ever seen a lecture demonstration where hydrogen–oxygen mixtures were ignited, you have witnessed a demonstration of hydrogen's potential as a fuel. The combustion reaction is



As we saw in Sample Exercise 6.6, the heat of combustion of H<sub>2</sub>(g) per gram is approximately 2.5 times that of natural gas. In addition, hydrogen has a real advantage over fossil fuels in that the only product of hydrogen combustion is water; fossil fuels also produce carbon dioxide. However, even though it appears that hydrogen is a very logical choice as a major fuel for the future, there are three main problems: the cost of production, storage, and transport.



## CHEMICAL IMPACT

### Farming the Wind

In the Midwest the wind blows across fields of corn, soybeans, wheat, and wind turbines—wind turbines? It turns out that the wind that seems to blow almost continuously across the plains is now becoming the latest cash crop. One of these new-breed wind farmers is Daniel Juhl, who recently erected 17 wind turbines on six acres of land near Woodstock, Minnesota. These turbines can generate as much as 10 megawatts (MW) of electricity, which Juhl sells to the local electrical utility.

There is plenty of untapped wind-power in the United States. Wind mappers rate regions on a scale of 1 to 6 (with 6 being the best) to indicate the quality of the wind resource. Wind farms are now being developed in areas rated from 4 to 6. The farmers who own the land welcome the increased income derived from the wind blowing across their land. Economists estimate that each acre devoted to wind turbines

can pay royalties to the farmers of as much as \$8000 per year, or many times the revenue from growing corn on that same land. Daniel Juhl claims that farmers who construct the turbines themselves can realize as much as \$20,000 per year per turbine. Globally, wind generation of electricity has nearly quadrupled in the last five years and is expected to increase by about 60% per year in the United States. The economic feasibility of wind-generated electricity has greatly improved in the last 30 years as the wind turbines have become more efficient. Today's turbines can produce electricity that costs about the same as that from other sources. The most impressive thing about wind power is the magnitude of the supply. According to the American Wind Energy Association in Washington, D.C., the wind-power potential in the United States is comparable or larger than the energy resources under the sands of Saudi Arabia.

First let's look at the production problem. Although hydrogen is very abundant on earth, virtually none of it exists as the free gas. Currently, the main source of hydrogen gas is from the treatment of natural gas with steam:



We can calculate  $\Delta H$  for this reaction using Equation (6.1):

$$\begin{aligned}\Delta H^\circ &= \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants}) \\ &= \Delta H_f^\circ \text{ for CO}(g) - \Delta H_f^\circ \text{ for CH}_4(g) - \Delta H_f^\circ \text{ for H}_2\text{O}(g) \\ &= -111 \text{ kJ} - (-75 \text{ kJ}) - (-242 \text{ kJ}) = 206 \text{ kJ}\end{aligned}$$

Note that this reaction is highly endothermic; treating methane with steam is not an efficient way to obtain hydrogen for fuel. It would be much more economical to burn the methane directly.

A virtually inexhaustible supply of hydrogen exists in the waters of the world's oceans. However, the reaction



requires 286 kJ of energy per mole of liquid water, and under current circumstances, large-scale production of hydrogen from water is not economically feasible. However, several methods for such production are currently being studied: electrolysis of water, thermal decomposition of water, thermochemical decomposition of water, and biological decomposition of water.

Electrolysis of water involves passing an electric current through it, as shown in Fig. 1.16 in Chapter 1. The present cost of electricity makes the hydrogen produced by electrolysis too expensive to be competitive as a fuel. However, if in the future we develop more efficient sources of electricity, this situation could change.

Recent research at the University of Minnesota by Lanny Schmidt and his coworkers suggests that corn could be a feasible source of hydrogen. In this process the starch from the corn is fermented to produce alcohol, which is then decomposed in a special

Electrolysis will be discussed in Chapter 17.

The biggest hurdle that must be overcome before wind power can become a significant electricity producer in the United States is construction of the transmission infrastructure—the power lines needed to move the electricity from the rural areas to the cities where most of the power is used. For example, the hundreds of turbines planned in southwest Minnesota in a development called Buffalo Ridge could supply enough electricity to power 1 million homes if transmission problems can be solved.

Another possible scenario for wind farms is to use the electrical power generated to decompose water to produce hydrogen gas that could be carried to cities by pipelines and used as a fuel. One real benefit of hydrogen is that it produces water as its only combustion product. Thus, it is essentially pollution-free.

Within a few years wind power could be a major source of electricity. There could be a fresh wind blowing across the energy landscape of the United States in the near future.

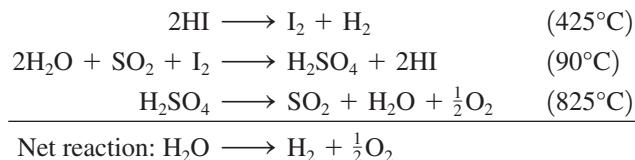


This State Line Wind Project along the Oregon-Washington border uses approximately 399 wind turbines to create enough electricity to power some 70,000 households.

reactor at 140°C with a rhodium and cerium oxide catalyst to give hydrogen. These scientists indicate that enough hydrogen gas can be obtained from a few ounces of ethanol to generate electricity to run six 60-watt bulbs for an hour.

Thermal decomposition is another method for producing hydrogen from water. This involves heating the water to several thousand degrees, where it spontaneously decomposes into hydrogen and oxygen. However, attaining temperatures in this range would be very expensive even if a practical heat source and a suitable reaction container were available.

In the thermochemical decomposition of water, chemical reactions, as well as heat, are used to “split” water into its components. One such system involves the following reactions (the temperature required for each is given in parentheses):



Note that the HI is not consumed in the net reaction. Note also that the maximum temperature required is 825°C, a temperature that is feasible if a nuclear reactor is used as a heat source. A current research goal is to find a system for which the required temperatures are low enough that sunlight can be used as the energy source.

But what about the organisms that decompose water without the aid of electricity or high temperatures? In the process of photosynthesis, green plants absorb carbon dioxide and water and use them along with energy from the sun to produce the substances needed for growth. Scientists have studied photosynthesis for years, hoping to get answers to humanity’s food and energy shortages. At present, much of this research involves attempts to modify the photosynthetic process so that plants will release hydrogen gas from water instead of using the hydrogen to produce complex compounds. Small-scale experiments have shown that under certain conditions plants do produce hydrogen gas, but the yields

are far from being commercially useful. At this point the economical production of hydrogen gas remains unrealized.

The storage and transportation of hydrogen also present problems. First, on metal surfaces the H<sub>2</sub> molecule decomposes to atoms. Since the atoms are so small, they can migrate into the metal, causing structural changes that make it brittle. This might lead to a pipeline failure if hydrogen were pumped under high pressure.

An additional problem is the relatively small amount of energy that is available *per unit volume* of hydrogen gas. Although the energy available per gram of hydrogen is significantly greater than that per gram of methane, the energy available per given volume of hydrogen is about one-third that available from the same volume of methane. This is demonstrated in Sample Exercise 6.12.

Although the use of hydrogen as a fuel solves some of the problems associated with fossil fuels, it does present some potential environmental problems of its own. Studies by John M. Eiler and his colleagues at California Institute of Technology indicate that, if hydrogen becomes a major source of energy, accidental leakage of the gas into the atmosphere could pose a threat. The Cal Tech scientists calculate that leakage could raise the concentration of H<sub>2</sub> in the atmosphere from its natural level of 0.5 part per million to more than 2 parts per million. As some of the H<sub>2</sub> eventually finds its way into the upper atmosphere, it would react with O<sub>2</sub> to form water, which would increase the number of ice crystals. This could lead to the destruction of some of the protective ozone because many of the chemical reactions that destroy ozone occur on the surfaces of ice crystals. However, as is the usual case with environmental issues, the situation is complicated. The scenario suggested by Eiler's team may not happen because the leaked H<sub>2</sub> could be consumed by soil microbes that use hydrogen as a nutrient. In fact, Eiler's studies show that 90% of the H<sub>2</sub> emitted into the atmosphere today from sources such as motor vehicles and forest fires is eventually absorbed by soil organisms.

The evaluation of hydrogen as a fuel illustrates how complex and interconnected the economic and environmental issues are.

### Sample Exercise 6.12

### Enthalpies of Combustion

Compare the energy available from the combustion of a given volume of methane and the same volume of hydrogen at the same temperature and pressure.

#### Solution

In Sample Exercise 6.6 we calculated the heat released for the combustion of methane and hydrogen: 55 kJ/g CH<sub>4</sub> and 141 kJ/g H<sub>2</sub>. We also know from our study of gases that 1 mol H<sub>2</sub>(g) has the same volume as 1 mol CH<sub>4</sub>(g) at the same temperature and pressure (assuming ideal behavior). Thus, for molar volumes of both gases under the same conditions of temperature and pressure,

$$\frac{\text{Enthalpy of combustion of 1 molar volume of H}_2\text{(g)}}{\text{Enthalpy of combustion of 1 molar volume of CH}_4\text{(g)}}$$

$$\begin{aligned} &= \frac{\text{enthalpy of combustion per mole of H}_2}{\text{enthalpy of combustion per mole of CH}_4} \\ &= \frac{(-141 \text{ kJ/g})(2.02 \text{ g H}_2/\text{mol H}_2)}{(-55 \text{ kJ/g})(16.04 \text{ g CH}_4/\text{mol CH}_4)} \\ &= \frac{-285}{-882} \approx \frac{1}{3} \end{aligned}$$

Thus about three times the volume of hydrogen gas is needed to furnish the same energy as a given volume of methane.

*See Exercise 6.78.*

Could hydrogen be considered as a potential fuel for automobiles? This is an intriguing question. The internal combustion engines in automobiles can be easily adapted to burn hydrogen. In fact, BMW is now experimenting with a fleet of cars powered by hydrogen-burning internal combustion engines. However, the primary difficulty is the storage of enough hydrogen to give an automobile a reasonable range. This is illustrated by Sample Exercise 6.13.

**Sample Exercise 6.13**

### Comparing Enthalpies of Combustion

Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H<sub>2</sub> (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gal) of gasoline (density = 0.740 g/mL). Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C.

**Solution**

The mass of 80.0 L gasoline is

$$80.0 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.740 \text{ g}}{1 \text{ mL}} = 59,200 \text{ g}$$

Since H<sub>2</sub> furnishes three times as much energy per gram as gasoline, only a third as much liquid hydrogen is needed to furnish the same energy:

$$\text{Mass of H}_2(l) \text{ needed} = \frac{59,200 \text{ g}}{3} = 19,700 \text{ g}$$

Since density = mass/volume, then volume = mass/density, and the volume of H<sub>2</sub>(l) needed is

$$V = \frac{19,700 \text{ g}}{0.0710 \text{ g/mL}} = 2.77 \times 10^5 \text{ mL} = 277 \text{ L}$$

Thus 277 L of liquid H<sub>2</sub> is needed to furnish the same energy of combustion as 80.0 L of gasoline.

To calculate the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C, we use the ideal gas law:

$$PV = nRT$$

In this case

$$P = 1.00 \text{ atm}, T = 273 + 25^\circ\text{C} = 298 \text{ K}, \text{ and } R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}.$$

Also,

$$n = 19,700 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} = 9.75 \times 10^3 \text{ mol H}_2$$

Thus

$$V = \frac{nRT}{P} = \frac{(9.75 \times 10^3 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})}{1.00 \text{ atm}} = 2.38 \times 10^5 \text{ L} = 238,000 \text{ L}$$

At 1 atm and 25°C, the hydrogen gas needed to replace 20 gal of gasoline occupies a volume of 238,000 L.

*See Exercises 6.79 and 6.80.*



## CHEMICAL IMPACT

### Veggie Gasoline?

**G**asoline usage is as high as ever, and world petroleum supplies will eventually dwindle. One possible alternative to petroleum as a source of fuels and lubricants is vegetable oil—the same vegetable oil we now use to cook french fries. Researchers believe that the oils from soybeans, corn, canola, and sunflowers all have the potential to be used in cars as well as on salads.

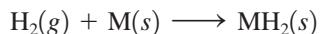
The use of vegetable oil for fuel is not a new idea. Rudolf Diesel reportedly used peanut oil to run one of his engines at the Paris Exposition in 1900. In addition, ethyl alcohol has been used widely as a fuel in South America and as a fuel additive in the United States.



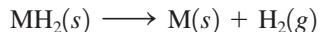
This promotion bus both advertises biodiesel and demonstrates its usefulness

You can see from Sample Exercise 6.13 that an automobile would need a huge tank to hold enough hydrogen gas (at 1 atm) to have a typical mileage range. Clearly, hydrogen must be stored as a liquid or in some other way. Is this feasible? Because of its very low boiling point (20 K), storage of liquid hydrogen requires a superinsulated container that can withstand high pressures. Storage in this manner would be both expensive and hazardous because of the potential for explosion. Thus storage of hydrogen in the individual automobile as a liquid does not seem practical.

A much better alternative seems to be the use of metals that absorb hydrogen to form solid metal hydrides:



To use this method of storage, hydrogen gas would be pumped into a tank containing the solid metal in powdered form, where it would be absorbed to form the hydride, whose volume would be little more than that of the metal alone. This hydrogen would then be available for combustion in the engine by release of  $\text{H}_2(g)$  from the hydride as needed:



Several types of solids that absorb hydrogen to form hydrides are being studied for use in hydrogen-powered vehicles. The most likely use of hydrogen in automobiles will be to power fuel cells (see Section 17.5). Ford, Honda, and Toyota are all experimenting with cars powered by hydrogen fuel cells.

### Other Energy Alternatives

Many other energy sources are being considered for future use. The western states, especially Colorado, contain huge deposits of *oil shale*, which consists of a complex carbon-based material called *kerogen* contained in porous rock formations. These deposits have the potential of being a larger energy source than the vast petroleum deposits of the Middle East. The main problem with oil shale is that the trapped fuel is not fluid and cannot

Metal hydrides are discussed in Chapter 18.

Biodiesel, a fuel made by esterifying the fatty acids found in vegetable oil, has some real advantages over regular diesel fuel. Biodiesel produces fewer pollutants such as particulates, carbon monoxide, and complex organic molecules, and since vegetable oils have no sulfur, there is no noxious sulfur dioxide in the exhaust gases. Also, biodiesel can run in existing engines with little modification. In addition, biodiesel is much more biodegradable than petroleum-based fuels, so spills cause less environmental damage.

Of course, biodiesel also has some serious drawbacks. The main one is that it costs about three times as much as regular diesel fuel. Biodiesel also produces more nitrogen oxides in the exhaust than conventional diesel fuel and is less stable in storage. Biodiesel also can leave more gummy deposits in engines and must be "winterized" by removing components that tend to solidify at low temperatures.

The best solution may be to use biodiesel as an additive to regular diesel fuel. One such fuel is known as B20 because it is 20% biodiesel and 80% conventional diesel

fuel. B20 is especially attractive because of the higher lubricating ability of vegetable oils, thus reducing diesel engine wear.

Vegetable oils are also being looked at as replacements for motor oils and hydraulic fluids. Tests of a sunflower seed-based engine lubricant manufactured by Renewable Lubricants of Hartville, Ohio, have shown satisfactory lubricating ability while lowering particle emissions. In addition, Lou Honary and his colleagues at the University of Northern Iowa have developed BioSOY, a vegetable oil-based hydraulic fluid for use in heavy machinery.

Veggie oil fuels and lubricants seem to have a growing market as petroleum supplies wane and as environmental laws become more stringent. In Germany's Black Forest region, for example, environmental protection laws require that farm equipment use only vegetable oil fuels and lubricants. In the near future there may be veggie oil in your garage as well as in your kitchen.

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Adapted from "Fill 'Er Up . . . with Veggie Oil," by Corinna Wu, as appeared in *Science News*, Vol. 154, December 5, 1998, p. 364.

be pumped. To recover the fuel, the rock must be heated to a temperature of 250°C or higher to decompose the kerogen to smaller molecules that produce gaseous and liquid products. This process is expensive and yields large quantities of waste rock, which have a negative environmental impact.

*Ethanol* ( $C_2H_5OH$ ) is another fuel with the potential to supplement, if not replace, gasoline. The most common method of producing ethanol is fermentation, a process in which sugar is changed to alcohol by the action of yeast. The sugar can come from virtually any source, including fruits and grains, although fuel-grade ethanol would probably come mostly from corn. Car engines can burn pure alcohol or *gasohol*, an alcohol–gasoline mixture (10% ethanol in gasoline), with little modification. Gasohol is now widely available in the United States. The use of pure alcohol as a motor fuel is not feasible in most of the United States because it does not vaporize easily when temperatures are low. However, pure ethanol could be a very practical fuel in warm climates. For example, in Brazil, large quantities of ethanol fuel are being produced for cars.

*Methanol* ( $CH_3OH$ ), an alcohol similar to ethanol, which has been used successfully for many years in race cars, is now being evaluated as a motor fuel in California. A major gasoline retailer has agreed to install pumps at 25 locations to dispense a fuel that is 85% methanol and 15% gasoline for use in specially prepared automobiles. The California Energy Commission feels that methanol has great potential for providing a secure, long-term energy supply that would alleviate air quality problems. Arizona and Colorado are also considering methanol as a major source of portable energy.

Another potential source of liquid fuels is oil squeezed from seeds (*seed oil*). For example, some farmers in North Dakota, South Africa, and Australia are now using sunflower oil to replace diesel fuel. Oil seeds, found in a wide variety of plants, can be processed to produce an oil composed mainly of carbon and hydrogen, which of course reacts with oxygen to produce carbon dioxide, water, and heat. It is hoped that oil-seed plants can be developed that will thrive under soil and climatic conditions unsuitable for corn and wheat. The main advantage of seed oil as a fuel is that it is renewable. Ideally, fuel would be grown just like food crops.



The sugars in corn are fermented and used to produce ethanol, an additive for gasoline.

## Key Terms

### Section 6.1

energy  
 law of conservation of energy  
 potential energy  
 kinetic energy  
 heat  
 work  
 pathway  
 state function (property)  
 system  
 surroundings  
 exothermic  
 endothermic  
 thermodynamics  
 first law of thermodynamics  
 internal energy

### Section 6.2

enthalpy  
 calorimeter  
 calorimetry  
 heat capacity  
 specific heat capacity  
 molar heat capacity  
 constant-pressure calorimetry  
 constant-volume calorimetry

### Section 6.3

Hess's law

### Section 6.4

standard enthalpy of formation  
 standard state

### Section 6.5

fossil fuels  
 petroleum  
 natural gas  
 coal  
 greenhouse effect

### Section 6.6

syngas

## For Review

### Energy

- The capacity to do work or produce heat
- Is conserved (first law of thermodynamics)
- Can be converted from one form to another
- Is a state function
- Potential energy: stored energy
- Kinetic energy: energy due to motion
- The internal energy for a system is the sum of its potential and kinetic energies
- The internal energy of a system can be changed by work and heat:

$$\Delta E = q + w$$

### Work

- Force applied over a distance
- For an expanding/contracting gas
- Not a state function

$$w = -P\Delta V$$

### Heat

- Energy flow due to a temperature difference
- Exothermic: energy as heat flows out of a system
- Endothermic: energy as heat flows into a system
- Not a state function
- Measured for chemical reactions by calorimetry

### Enthalpy

- $H = E + PV$
- Is a state function
- Hess's law: the change in enthalpy in going from a given set of reactants to a given set of products is the same whether the process takes place in one step or a series of steps
- Standard enthalpies of formation ( $\Delta H_f^\circ$ ) can be used to calculate  $\Delta H$  for a chemical reaction

$$\Delta H_{\text{reaction}}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H^\circ(\text{reactants})$$

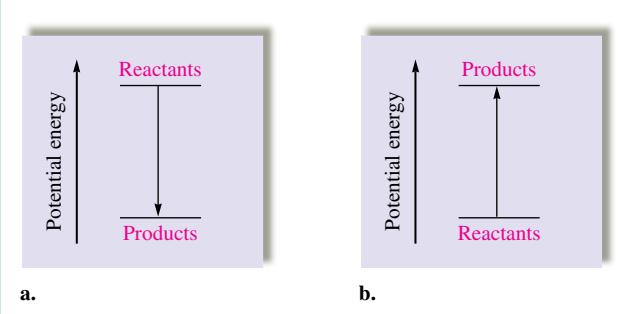
### Energy use

- Energy sources from fossil fuels are associated with difficult supply and environmental impact issues
- The greenhouse effect results from release into the atmosphere of gases, including carbon dioxide, that strongly absorb infrared radiation, thus warming the earth
- Alternative fuels are being sought to replace fossil fuels:
  - Hydrogen
  - Syngas from coal
  - Biofuels from plants such as corn and certain seed-producing plants

### REVIEW QUESTIONS

1. Define the following terms: potential energy, kinetic energy, path-dependent function, state function, system, surroundings.

2. Consider the following potential energy diagrams for two different reactions.



Which plot represents an exothermic reaction? In plot a, do the reactants on average have stronger or weaker bonds than the products? In plot b, reactants must gain potential energy to convert to products. How does this occur?

3. What is the first law of thermodynamics? How can a system change its internal energy,  $E$ ? What are the sign conventions for thermodynamic quantities used in this text?
4. When a gas expands, what is the sign of  $w$ ? Why? When a gas contracts, what is the sign of  $w$ ? Why? What are the signs of  $q$  and  $w$  for the process of boiling water?
5. What is the heat gained/released at constant pressure equal to ( $q_p = ?$ )? What is the heat gained/released at constant volume equal to ( $q_v = ?$ )? Explain why  $\Delta H$  is obtained directly from a coffee-cup calorimeter, whereas  $\Delta E$  is obtained directly from a bomb calorimeter.
6. High-quality audio amplifiers generate large amounts of heat. To dissipate the heat and prevent damage to the electronic components, heat-radiating metal fins are used. Would it be better to make these fins out of iron or aluminum? Why? (See Table 6.1 for specific heat capacities.)
7. Explain how calorimetry works to calculate  $\Delta H$  or  $\Delta E$  for a reaction. Does the temperature of the calorimeter increase or decrease for an endothermic reaction? For an exothermic reaction? Explain.
8. What is Hess's law? When a reaction is reversed, what happens to the sign and magnitude of  $\Delta H$  for that reversed reaction? When the coefficients in a balanced reaction are multiplied by a factor  $n$ , what happens to the sign and magnitude of  $\Delta H$  for that multiplied reaction?
9. Define the standard enthalpy of formation. What are standard states for elements and for compounds? Using Hess's law, illustrate why the formula  $\Delta H_{\text{reaction}}^{\circ} = \sum n_p \Delta H_f^{\circ} (\text{products}) - \sum n_r \Delta H_f^{\circ} (\text{reactants})$  works to calculate  $\Delta H^{\circ}$  for a reaction.
10. What are some of the problems associated with the world's dependence on fossil fuels? What are some alternative fuels for petroleum products?

## Active Learning Questions

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

1. Objects placed together eventually reach the same temperature. When you go into a room and touch a piece of metal in that room, it feels colder than a piece of plastic. Explain.

2. What is meant by the term *lower in energy*? Which is lower in energy, a mixture of hydrogen and oxygen gases or liquid water? How do you know? Which of the two is more stable? How do you know?
3. A fire is started in a fireplace by striking a match and lighting crumpled paper under some logs. Explain all the energy transfers in this scenario using the terms *exothermic*, *endothermic*, *system*, *surroundings*, *potential energy*, and *kinetic energy* in the discussion.

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4. Liquid water turns to ice. Is this process endothermic or exothermic? Explain what is occurring using the terms *system*, *surroundings*, *heat*, *potential energy*, and *kinetic energy* in the discussion.
5. Consider the following statements: "Heat is a form of energy, and energy is conserved. The heat lost by a system must be equal to the amount of heat gained by the surroundings. Therefore, heat is conserved." Indicate everything you think is correct in these statements. Indicate everything you think is incorrect. Correct the incorrect statements and explain.
6. Consider 5.5 L of a gas at a pressure of 3.0 atm in a cylinder with a movable piston. The external pressure is changed so that the volume changes to 10.5 L.
  - a. Calculate the work done, and indicate the correct sign.
  - b. Use the preceding data but consider the process to occur in two steps. At the end of the first step, the volume is 7.0 L. The second step results in a final volume of 10.5 L. Calculate the work done, and indicate the correct sign.
  - c. Calculate the work done if after the first step the volume is 8.0 L and the second step leads to a volume of 10.5 L. Does the work differ from that in part b? Explain.
7. In Question 6 the work calculated for the different conditions in the various parts of the question was different even though the system had the same initial and final conditions. Based on this information, is work a state function?
  - a. Explain how you know that work is not a state function.
  - b. Why does the work increase with an increase in the number of steps?
  - c. Which two-step process resulted in more work, when the first step had the bigger change in volume or when the second step had the bigger change in volume? Explain.
8. Photosynthetic plants use the following reaction to produce glucose, cellulose, and so forth:
 
$$6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \xrightarrow{\text{Sunlight}} \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$$

How might extensive destruction of forests exacerbate the greenhouse effect?

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

## Questions

9. Consider an airplane trip from Chicago, Illinois to Denver, Colorado. List some path-dependent functions and some state functions for the plane trip
10. How is average bond strength related to relative potential energies of the reactants and the products?
11. Assuming gasoline is pure C<sub>8</sub>H<sub>18</sub>(l), predict the signs of q and w for the process of combusting gasoline into CO<sub>2</sub>(g) and H<sub>2</sub>O(g).
12. What is the difference between ΔH and ΔE?
13. The enthalpy of combustion of CH<sub>4</sub>(g) when H<sub>2</sub>O(l) is formed is ~891 kJ/mol and the enthalpy of combustion of CH<sub>4</sub>(g) when H<sub>2</sub>O(g) is formed is ~803 kJ/mol. Use these data and Hess's law to determine the enthalpy of vaporization for water.

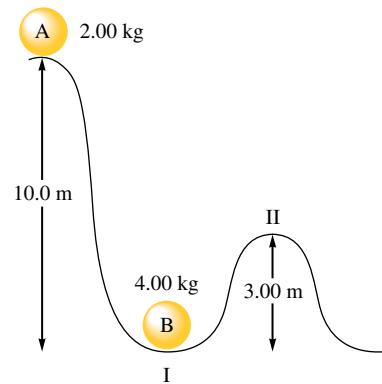
14. Standard enthalpies of formation are relative values. What are ΔH<sub>f</sub><sup>°</sup> values relative to?
15. What is incomplete combustion of fossil fuels? Why can this be a problem?
16. Explain the advantages and disadvantages of hydrogen as an alternative fuel.

## Exercises

In this section similar exercises are paired.

### Potential and Kinetic Energy

17. Calculate the kinetic energy of a baseball (mass = 5.25 oz) with a velocity of  $1.0 \times 10^2$  mi/h.
18. Calculate the kinetic energy of a  $1.0 \times 10^{-5}$ -g object with a velocity of  $2.0 \times 10^5$  cm/s.
19. Which has the greater kinetic energy, an object with a mass of 2.0 kg and a velocity of 1.0 m/s or an object with a mass of 1.0 kg and a velocity of 2.0 m/s?
20. Consider the accompanying diagram. Ball A is allowed to fall and strike ball B. Assume that all of ball A's energy is transferred to ball B, at point I, and that there is no loss of energy to other sources. What is the kinetic energy and the potential energy of ball B at point II? The potential energy is given by PE = mgz, where m is the mass in kilograms, g is the gravitational constant ( $9.81 \text{ m/s}^2$ ), and z is the distance in meters.



### Heat and Work

21. Calculate ΔE for each of the following.
  - a.  $q = -47 \text{ kJ}$ ,  $w = +88 \text{ kJ}$
  - b.  $q = +82 \text{ kJ}$ ,  $w = -47 \text{ kJ}$
  - c.  $q = +47 \text{ kJ}$ ,  $w = 0$
  - d. In which of these cases do the surroundings do work on the system?
22. A system undergoes a process consisting of the following two steps:  
Step 1: The system absorbs 72 J of heat while 35 J of work is done on it.

Step 2: The system absorbs 35 J of heat while performing 72 J of work.

Calculate  $\Delta E$  for the overall process.

- 23.** If the internal energy of a thermodynamic system is increased by 300. J while 75 J of expansion work is done, how much heat was transferred and in which direction, to or from the system?
- 24.** Calculate the internal energy change for each of the following.
  - a. One hundred (100.) joules of work are required to compress a gas. At the same time, the gas releases 23 J of heat.
  - b. A piston is compressed from a volume of 8.30 L to 2.80 L against a constant pressure of 1.90 atm. In the process, there is a heat gain by the system of 350. J.
  - c. A piston expands against 1.00 atm of pressure from 11.2 L to 29.1 L. In the process, 1037 J of heat is absorbed.
- 25.** A sample of an ideal gas at 15.0 atm and 10.0 L is allowed to expand against a constant external pressure of 2.00 atm at a constant temperature. Calculate the work in units of kJ for the gas expansion. (*Hint:* Boyle's law applies.)
- 26.** A piston performs work of 210. L atm on the surroundings, while the cylinder in which it is placed expands from 10. L to 25 L. At the same time, 45 J of heat is transferred from the surroundings to the system. Against what pressure was the piston working?
- 27.** Consider a mixture of air and gasoline vapor in a cylinder with a piston. The original volume is 40. cm<sup>3</sup>. If the combustion of this mixture releases 950. J of energy, to what volume will the gases expand against a constant pressure of 650. torr if all the energy of combustion is converted into work to push back the piston?
- 28.** As a system increases in volume, it absorbs 52.5 J of energy in the form of heat from the surroundings. The piston is working against a pressure of 0.500 atm. The final volume of the system is 58.0 L. What was the initial volume of the system if the internal energy of the system decreased by 102.5 J?
- 29.** A balloon filled with 39.1 mol helium has a volume of 876 L at 0.0°C and 1.00 atm pressure. The temperature of the balloon is increased to 38.0°C as it expands to a volume of 998 L, the pressure remaining constant. Calculate  $q$ ,  $w$ , and  $\Delta E$  for the helium in the balloon. (The molar heat capacity for helium gas is 20.8 J/°C · mol.)
- 30.** One mole of H<sub>2</sub>O(g) at 1.00 atm and 100.°C occupies a volume of 30.6 L. When one mole of H<sub>2</sub>O(g) is condensed to one mole of H<sub>2</sub>O(l) at 1.00 atm and 100.°C, 40.66 kJ of heat is released. If the density of H<sub>2</sub>O(l) at this temperature and pressure is 0.996 g/cm<sup>3</sup>, calculate  $\Delta E$  for the condensation of one mole of water at 1.00 atm and 100.°C.

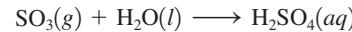
### Properties of Enthalpy

- 31.** One of the components of polluted air is NO. It is formed in the high-temperature environment of internal combustion engines by the following reaction:



Why are high temperatures needed to convert N<sub>2</sub> and O<sub>2</sub> to NO?

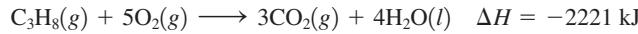
- 32.** The reaction



is the last step in the commercial production of sulfuric acid. The enthalpy change for this reaction is  $-227 \text{ kJ}$ . In designing a sulfuric acid plant, is it necessary to provide for heating or cooling of the reaction mixture? Explain.

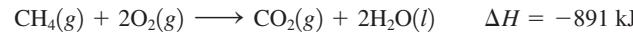
- 33.** Are the following processes exothermic or endothermic?
    - a. When solid KBr is dissolved in water, the solution gets colder.
    - b. Natural gas (CH<sub>4</sub>) is burned in a furnace.
    - c. When concentrated H<sub>2</sub>SO<sub>4</sub> is added to water, the solution gets very hot.
    - d. Water is boiled in a teakettle.
  - 34.** Are the following processes exothermic or endothermic?
    - a. the combustion of gasoline in a car engine
    - b. water condensing on a cold pipe
    - c. CO<sub>2</sub>(s)  $\longrightarrow$  CO<sub>2</sub>(g)
    - d. F<sub>2</sub>(g)  $\longrightarrow$  2F(g)
  - 35.** The overall reaction in a commercial heat pack can be represented as
- $$4\text{Fe}(\text{s}) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Fe}_2\text{O}_3(\text{s}) \quad \Delta H = -1652 \text{ kJ}$$
- a.** How much heat is released when 4.00 mol iron is reacted with excess O<sub>2</sub>?
  - b.** How much heat is released when 1.00 mol Fe<sub>2</sub>O<sub>3</sub> is produced?
  - c.** How much heat is released when 1.00 g iron is reacted with excess O<sub>2</sub>?
  - d.** How much heat is released when 10.0 g Fe and 2.00 g O<sub>2</sub> are reacted?
- 36.** Consider the following reaction:
- $$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -572 \text{ kJ}$$
- a.** How much heat is evolved for the production of 1.00 mol of H<sub>2</sub>O(l)?
  - b.** How much heat is evolved when 4.03 g of hydrogen is reacted with excess oxygen?
  - c.** How much heat is evolved when 186 g of oxygen is reacted with excess hydrogen?
  - d.** The total volume of hydrogen gas needed to fill the *Hindenburg* was  $2.0 \times 10^8 \text{ L}$  at 1.0 atm and 25°C. How much heat was evolved when the *Hindenburg* exploded, assuming all of the hydrogen reacted?

- 37.** Consider the combustion of propane:



Assume that all the heat in Sample Exercise 6.3 comes from the combustion of propane. What mass of propane must be burned to furnish this amount of energy assuming the heat transfer process is 60.% efficient?

- 38.** Consider the following reaction:



Calculate the enthalpy change for each of the following cases:

- a.** 1.00 g methane is burned in excess oxygen.
- b.**  $1.00 \times 10^3 \text{ L}$  methane gas at 740. torr and 25°C is burned in excess oxygen.

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**39.** For the process  $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$  at 298 K and 1.0 atm,  $\Delta H$  is more positive than  $\Delta E$  by 2.5 kJ/mol. What does the 2.5 kJ/mol quantity represent?

**40.** For the following reactions at constant pressure, predict if  $\Delta H > \Delta E$ ,  $\Delta H < \Delta E$ , or  $\Delta H = \Delta E$ .

- $2\text{HF}(g) \longrightarrow \text{H}_2(g) + \text{F}_2(g)$
- $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
- $4\text{NH}_3(g) + 5\text{O}_2(g) \longrightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$

### Calorimetry and Heat Capacity

**41.** Consider the substances in Table 6.1. Which substance requires the largest amount of energy to raise the temperature of 25.0 g of the substance from 15.0°C to 37.0°C? Calculate the energy. Which substance in Table 6.1 has the largest temperature change when 550. g of the substance absorbs 10.7 kJ of energy? Calculate the temperature change.

**42.** The specific heat capacity of silver is 0.24 J°C · g.

- Calculate the energy required to raise the temperature of 150.0 g Ag from 273 K to 298 K.
- Calculate the energy required to raise the temperature of 1.0 mol Ag by 1.0°C (called the *molar heat capacity* of silver).
- It takes 1.25 kJ of energy to heat a sample of pure silver from 12.0°C to 15.2°C. Calculate the mass of the sample of silver.

**43.** A 5.00-g sample of one of the substances listed in Table 6.1 was heated from 25.2°C to 55.1°C, requiring 133 J to do so. What substance was it?

**44.** It takes 585 J of energy to raise the temperature of 125.6 g mercury from 20.0°C to 53.5°C. Calculate the specific heat capacity and the molar heat capacity of mercury.

**45.** A 30.0-g sample of water at 280. K is mixed with 50.0 g of water at 330. K. Calculate the final temperature of the mixture assuming no heat loss to the surroundings.

**46.** A biology experiment requires the preparation of a water bath at 37.0°C (body temperature). The temperature of the cold tap water is 22.0°C, and the temperature of the hot tap water is 55.0°C. If a student starts with 90.0 g of cold water, what mass of hot water must be added to reach 37.0°C?

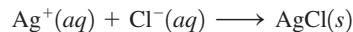
**47.** A 5.00-g sample of aluminum pellets (specific heat capacity = 0.89 J°C · g) and a 10.00-g sample of iron pellets (specific heat capacity = 0.45 J°C · g) are heated to 100.0°C. The mixture of hot iron and aluminum is then dropped into 97.3 g of water at 22.0°C. Calculate the final temperature of the metal and water mixture, assuming no heat loss to the surroundings.

**48.** Hydrogen gives off 120. J/g of energy when burned in oxygen, and methane gives off 50. J/g under the same circumstances. If a mixture of 5.0 g of hydrogen and 10. g of methane is burned, and the heat released is transferred to 50.0 g of water at 25.0°C, what final temperature will be reached by the water?

**49.** A 150.0-g sample of a metal at 75.0°C is added to 150.0 g of  $\text{H}_2\text{O}$  at 15.0°C. The temperature of the water rises to 18.3°C. Calculate the specific heat capacity of the metal, assuming that all the heat lost by the metal is gained by the water.

**50.** A 110.-g sample of copper (specific heat capacity = 0.20 J°C · g) is heated to 82.4°C and then placed in a container of water at 22.3°C. The final temperature of the water and copper is 24.9°C. What is the mass of the water in the container, assuming that all the heat lost by the copper is gained by the water?

**51.** In a coffee-cup calorimeter, 50.0 mL of 0.100 M  $\text{AgNO}_3$  and 50.0 mL of 0.100 M HCl are mixed to yield the following reaction:



The two solutions were initially at 22.60°C, and the final temperature is 23.40°C. Calculate the heat that accompanies this reaction in kJ/mol of  $\text{AgCl}$  formed. Assume that the combined solution has a mass of 100.0 g and a specific heat capacity of 4.18 J°C · g.

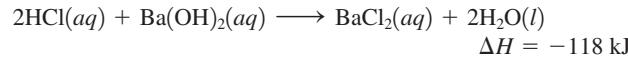
**52.** In a coffee-cup calorimeter, 1.60 g of  $\text{NH}_4\text{NO}_3$  is mixed with 75.0 g of water at an initial temperature of 25.00°C. After dissolution of the salt, the final temperature of the calorimeter contents is 23.34°C. Assuming the solution has a heat capacity of 4.18 J°C · g and assuming no heat loss to the calorimeter, calculate the enthalpy change for the dissolution of  $\text{NH}_4\text{NO}_3$  in units of kJ/mol.

**53.** Consider the dissolution of  $\text{CaCl}_2$ :



An 11.0-g sample of  $\text{CaCl}_2$  is dissolved in 125 g of water, with both substances at 25.0°C. Calculate the final temperature of the solution assuming no heat lost to the surroundings and assuming the solution has a specific heat capacity of 4.18 J°C · g.

**54.** Consider the reaction



Calculate the heat when 100.0 mL of 0.500 M HCl is mixed with 300.0 mL of 0.100 M  $\text{Ba}(\text{OH})_2$ . Assuming that the temperature of both solutions was initially 25.0°C and that the final mixture has a mass of 400.0 g and a specific heat capacity of 4.18 J°C · g, calculate the final temperature of the mixture.

**55.** The heat capacity of a bomb calorimeter was determined by burning 6.79 g of methane (energy of combustion = -802 kJ/mol  $\text{CH}_4$ ) in the bomb. The temperature changed by 10.8°C.

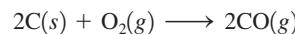
a. What is the heat capacity of the bomb?

b. A 12.6-g sample of acetylene,  $\text{C}_2\text{H}_2$ , produced a temperature increase of 16.9°C in the same calorimeter. What is the energy of combustion of acetylene (in kJ/mol)?

**56.** A 0.1964-g sample of quinone ( $\text{C}_6\text{H}_4\text{O}_2$ ) is burned in a bomb calorimeter that has a heat capacity of 1.56 kJ°C. The temperature of the calorimeter increases by 3.2°C. Calculate the energy of combustion of quinone per gram and per mole.

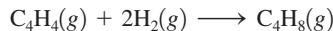
### Hess's Law

**57.** The enthalpy of combustion of solid carbon to form carbon dioxide is -393.7 kJ/mol carbon, and the enthalpy of combustion of carbon monoxide to form carbon dioxide is -283.3 kJ/mol CO. Use these data to calculate  $\Delta H$  for the reaction

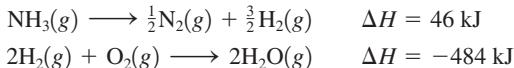


- 58.** Combustion reactions involve reacting a substance with oxygen.

When compounds containing carbon and hydrogen are combusted, carbon dioxide and water are the products. Using the enthalpies of combustion for  $\text{C}_4\text{H}_4$  ( $-2341 \text{ kJ/mol}$ ),  $\text{C}_4\text{H}_8$  ( $-2755 \text{ kJ/mol}$ ), and  $\text{H}_2$  ( $-286 \text{ kJ/mol}$ ), calculate  $\Delta H$  for the reaction



- 59.** Given the following data

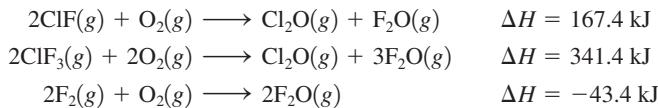


calculate  $\Delta H$  for the reaction

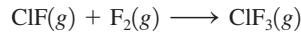


On the basis of the enthalpy change, is this a useful reaction for the synthesis of ammonia?

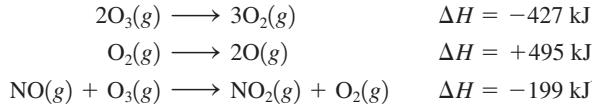
- 60.** Given the following data



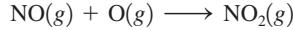
calculate  $\Delta H$  for the reaction



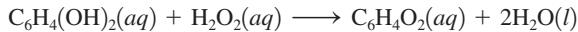
- 61.** Given the following data



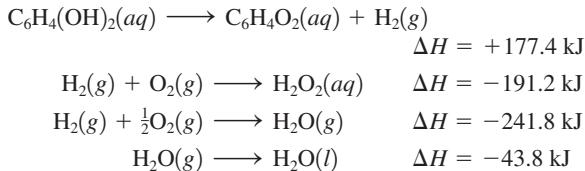
calculate  $\Delta H$  for the reaction



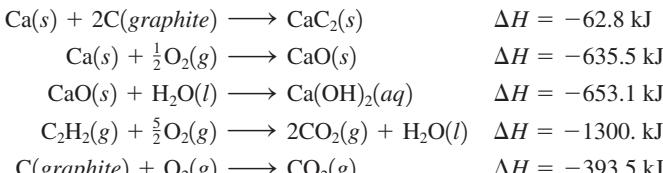
- 62.** The bombardier beetle uses an explosive discharge as a defensive measure. The chemical reaction involved is the oxidation of hydroquinone by hydrogen peroxide to produce quinone and water:



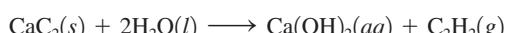
Calculate  $\Delta H$  for this reaction from the following data:



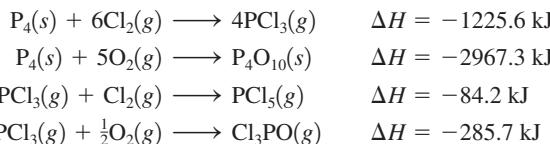
- 63.** Given the following data



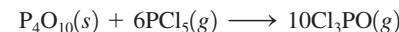
calculate  $\Delta H$  for the reaction



- 64.** Given the following data



calculate  $\Delta H$  for the reaction



### Standard Enthalpies of Formation

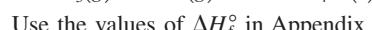
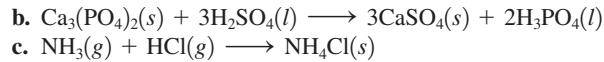
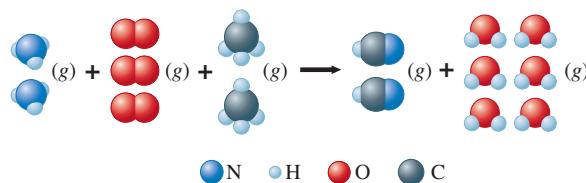
- 65.** Give the definition of the standard enthalpy of formation for a substance. Write separate reactions for the formation of  $\text{NaCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_{12}\text{O}_6$ , and  $\text{PbSO}_4$  that have  $\Delta H^\circ_f$  values equal to  $\Delta H^\circ_f$  for each compound.

- 66.** Write reactions for which the enthalpy change will be

- a.  $\Delta H^\circ_f$  for solid aluminum oxide.
- b. The standard enthalpy of combustion of liquid ethanol,  $\text{C}_2\text{H}_5\text{OH}(l)$ .
- c. The standard enthalpy of neutralization of sodium hydroxide solution by hydrochloric acid.
- d.  $\Delta H^\circ_f$  for gaseous vinyl chloride,  $\text{C}_2\text{H}_3\text{Cl}(g)$ .
- e. The enthalpy of combustion of liquid benzene,  $\text{C}_6\text{H}_6(l)$ .
- f. The enthalpy of solution of solid ammonium bromide.

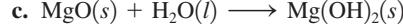
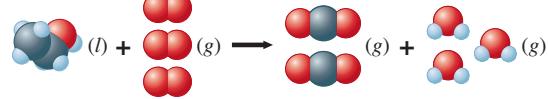
- 67.** Use the values of  $\Delta H^\circ_f$  in Appendix 4 to calculate  $\Delta H^\circ$  for the following reactions.

a.

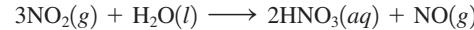
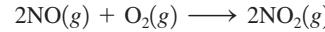


- 68.** Use the values of  $\Delta H^\circ_f$  in Appendix 4 to calculate  $\Delta H^\circ$  for the following reactions. (See Exercise 67.)

a.



- 69.** The Ostwald process for the commercial production of nitric acid from ammonia and oxygen involves the following steps:

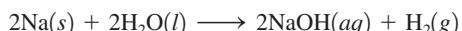
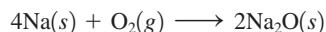


- a.** Use the values of  $\Delta H^\circ_f$  in Appendix 4 to calculate the value of  $\Delta H^\circ$  for each of the preceding reactions.

- b.** Write the overall equation for the production of nitric acid by the Ostwald process by combining the preceding equations. (Water is also a product.) Is the overall reaction exothermic or endothermic?

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70. Calculate  $\Delta H^\circ$  for each of the following reactions using the data in Appendix 4:



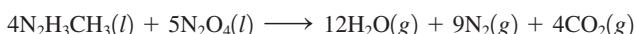
Explain why a water or carbon dioxide fire extinguisher might not be effective in putting out a sodium fire.

71. The reusable booster rockets of the space shuttle use a mixture of aluminum and ammonium perchlorate as fuel. A possible reaction is



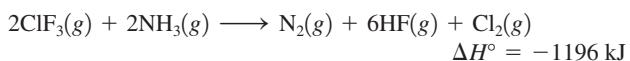
Calculate  $\Delta H^\circ$  for this reaction.

72. The space shuttle orbiter utilizes the oxidation of methylhydrazine by dinitrogen tetroxide for propulsion:



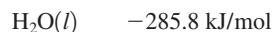
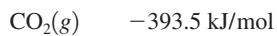
Calculate  $\Delta H^\circ$  for this reaction.

73. Consider the reaction



Calculate  $\Delta H_f^\circ$  for  $\text{ClF}_3(g)$ .

74. The standard enthalpy of combustion of ethene gas,  $\text{C}_2\text{H}_4(g)$ , is  $-1411.1 \text{ kJ/mol}$  at 298 K. Given the following enthalpies of formation, calculate  $\Delta H_f^\circ$  for  $\text{C}_2\text{H}_4(g)$ .



### Energy Consumption and Sources

75. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) has been proposed as an alternative fuel. Calculate the standard of enthalpy of combustion per gram of liquid ethanol.

76. Methanol ( $\text{CH}_3\text{OH}$ ) has also been proposed as an alternative fuel. Calculate the standard enthalpy of combustion per gram of liquid methanol and compare this answer to that for ethanol in Exercise 75.

77. Some automobiles and buses have been equipped to burn propane ( $\text{C}_3\text{H}_8$ ). Compare the amounts of energy that can be obtained per gram of  $\text{C}_3\text{H}_8(g)$  and per gram of gasoline, assuming that gasoline is pure octane,  $\text{C}_8\text{H}_{18}(l)$ . (See Sample Exercise 6.11.) Look up the boiling point of propane. What disadvantages are there to using propane instead of gasoline as a fuel?

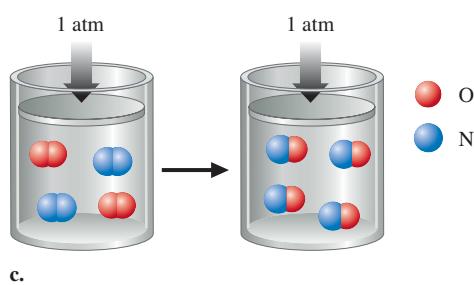
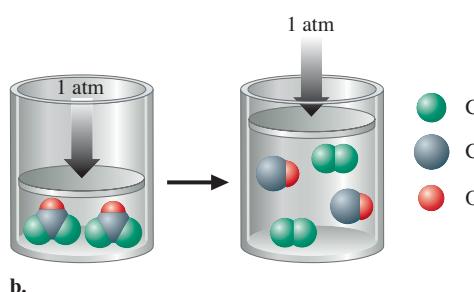
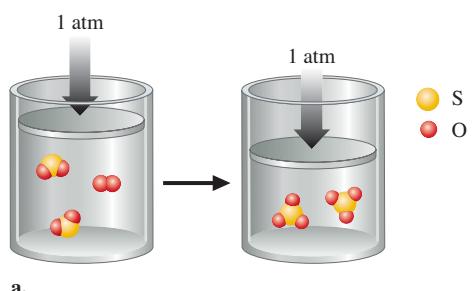
78. Acetylene ( $\text{C}_2\text{H}_2$ ) and butane ( $\text{C}_4\text{H}_{10}$ ) are gaseous fuels with enthalpies of combustion of  $-49.9 \text{ kJ/g}$  and  $-49.5 \text{ kJ/g}$ , respectively. Compare the energy available from the combustion of a given volume of acetylene to the combustion energy from the same volume of butane at the same temperature and pressure.

79. Assume that  $4.19 \times 10^6 \text{ kJ}$  of energy is needed to heat a home. If this energy is derived from the combustion of methane ( $\text{CH}_4$ ), what volume of methane, measured at STP, must be burned? ( $\Delta H_{\text{combustion}}^\circ$  for  $\text{CH}_4 = -891 \text{ kJ/mol}$ )

80. The complete combustion of acetylene,  $\text{C}_2\text{H}_2(g)$ , produces 1300. kJ of energy per mole of acetylene consumed. How many grams of acetylene must be burned to produce enough heat to raise the temperature of 1.00 gal of water by  $10.0^\circ\text{C}$  if the process is 80.0% efficient? Assume the density of water is  $1.00 \text{ g/cm}^3$ .

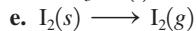
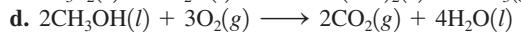
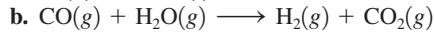
### Additional Exercises

81. Three gas-phase reactions were run in a constant-pressure piston apparatus as illustrated below. For each reaction, give the balanced reaction and predict the sign of  $w$  (the work done) for the reaction.



If just the balanced reactions were given, how could you predict the sign of  $w$  for a reaction?

82. Consider the following changes:



At constant temperature and pressure, in which of these changes is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?

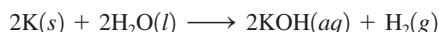
- 83.** Consider the following cyclic process carried out in two steps on a gas:

Step 1: 45 J of heat is added to the gas, and 10. J of expansion work is performed.

Step 2: 60. J of heat is removed from the gas as the gas is compressed back to the initial state.

Calculate the work for the gas compression in Step 2.

- 84.** Calculate  $\Delta H^\circ$  for the reaction



A 5.00-g chunk of potassium is dropped into 1.00 kg water at 24.0°C. What is the final temperature of the water after the preceding reaction occurs? Assume that all the heat is used to raise the temperature of the water. (Never run this reaction. It is very dangerous; it bursts into flame!)

- 85.** The enthalpy of neutralization for the reaction of a strong acid with a strong base is  $-56\text{ kJ/mol}$  of water produced. How much energy will be released when 200.0 mL of 0.400 M HCl is mixed with 150.0 mL of 0.500 M NaOH?

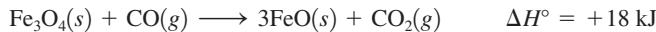
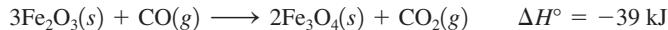
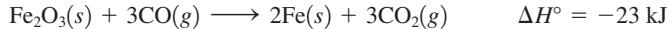
- 86.** When 1.00 L of 2.00 M  $\text{Na}_2\text{SO}_4$  solution at 30.0°C is added to 2.00 L of 0.750 M  $\text{Ba}(\text{NO}_3)_2$  solution at 30.0°C in a calorimeter, a white solid ( $\text{BaSO}_4$ ) forms. The temperature of the mixture increases to 42.0°C. Assuming that the specific heat capacity of the solution is  $6.37\text{ J}^\circ\text{C} \cdot \text{g}$  and that the density of the final solution is 2.00 g/mL, calculate the enthalpy change per mole of  $\text{BaSO}_4$  formed.

- 87.** If a student performs an endothermic reaction in a calorimeter, how does the calculated value of  $\Delta H$  differ from the actual value if the heat exchanged with the calorimeter is not taken into account?

- 88.** In a bomb calorimeter, the reaction vessel is surrounded by water that must be added for each experiment. Since the amount of water is not constant from experiment to experiment, the mass of water must be measured in each case. The heat capacity of the calorimeter is broken down into two parts: the water and the calorimeter components. If a calorimeter contains 1.00 kg water and has a total heat capacity of  $10.84\text{ kJ}^\circ\text{C}$ , what is the heat capacity of the calorimeter components?

- 89.** The bomb calorimeter in Exercise 88 is filled with 987 g of water. The initial temperature of the calorimeter contents is 23.32°C. A 1.056-g sample of benzoic acid ( $\Delta E_{\text{comb}} = -26.42\text{ kJ/g}$ ) is combusted in the calorimeter. What is the final temperature of the calorimeter contents?

- 90.** Given the following data

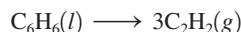


calculate  $\Delta H^\circ$  for the reaction



- 91.** At 298 K, the standard enthalpies of formation for  $\text{C}_2\text{H}_2(g)$  and  $\text{C}_6\text{H}_6(l)$  are 227 kJ/mol and 49 kJ/mol, respectively.

- a. Calculate  $\Delta H^\circ$  for



- b. Both acetylene ( $\text{C}_2\text{H}_2$ ) and benzene ( $\text{C}_6\text{H}_6$ ) can be used as fuels. Which compound would liberate more energy per gram when combusted in air?

- 92.** Using the following data, calculate the standard heat of formation of  $\text{ICl}(g)$  in kJ/mol:

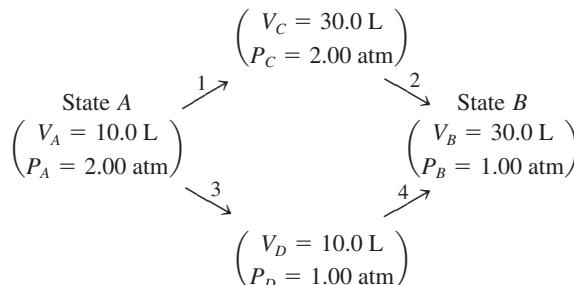
$\text{Cl}_2(g) \longrightarrow 2\text{Cl}(g)$	$\Delta H^\circ = 242.3\text{ kJ}$
$\text{I}_2(g) \longrightarrow 2\text{I}(g)$	$\Delta H^\circ = 151.0\text{ kJ}$
$\text{ICl}(g) \longrightarrow \text{I}(g) + \text{Cl}(g)$	$\Delta H^\circ = 211.3\text{ kJ}$
$\text{I}_2(s) \longrightarrow \text{I}_2(g)$	$\Delta H^\circ = 62.8\text{ kJ}$

- 93.** Calculate  $\Delta H^\circ$  for each of the following reactions, which occur in the atmosphere.

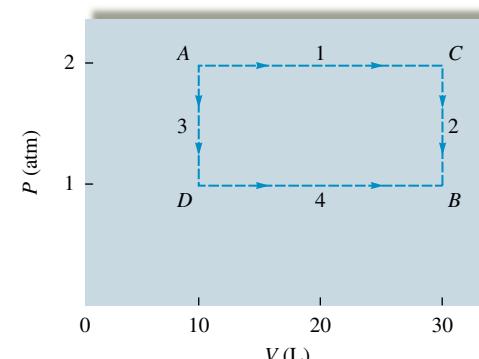
- a.  $\text{C}_2\text{H}_4(g) + \text{O}_3(g) \longrightarrow \text{CH}_3\text{CHO}(g) + \text{O}_2(g)$   
 b.  $\text{O}_3(g) + \text{NO}(g) \longrightarrow \text{NO}_2(g) + \text{O}_2(g)$   
 c.  $\text{SO}_3(g) + \text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{SO}_4(aq)$   
 d.  $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$

## Challenge Problems

- 94.** Consider 2.00 mol of an ideal gas that is taken from state A ( $P_A = 2.00\text{ atm}$ ,  $V_A = 10.0\text{ L}$ ) to state B ( $P_B = 1.00\text{ atm}$ ,  $V_B = 30.0\text{ L}$ ) by two different pathways:



These pathways are summarized on the following graph of  $P$  versus  $V$ :



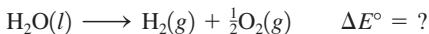
Calculate the work (in units of J) associated with the two pathways. Is work a state function? Explain.

- 95.** Combustion of table sugar produces  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . When 1.46 g of table sugar is combusted in a constant-volume (bomb) calorimeter, 24.00 kJ of heat is liberated.

- a. Assuming that table sugar is pure sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$ , write the balanced equation for the combustion reaction.

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- b.** Calculate  $\Delta E$  in kJ/mol  $C_{12}H_{22}O_{11}$  for the combustion reaction of sucrose.
- c.** Calculate  $\Delta H$  in kJ/mol  $C_{12}H_{22}O_{11}$  for the combustion reaction of sucrose at 25°C.
- 96.** The sun supplies energy at a rate of about 1.0 kilowatt per square meter of surface area (1 watt = 1 J/s). The plants in an agricultural field produce the equivalent of 20. kg of sucrose ( $C_{12}H_{22}O_{11}$ ) per hour per hectare (1 ha = 10,000 m<sup>2</sup>). Assuming that sucrose is produced by the reaction
- $$12CO_2(g) + 11H_2O(l) \longrightarrow C_{12}H_{22}O_{11}(s) + 12O_2(g) \quad \Delta H = 5640 \text{ kJ}$$
- calculate the percentage of sunlight used to produce the sucrose—that is, determine the efficiency of photosynthesis.
- 97.** The best solar panels currently available are about 13% efficient in converting sunlight to electricity. A typical home will use about 40. kWh of electricity per day (1 kWh = 1 kilowatt hour; 1 kW = 1000 J/s). Assuming 8.0 hours of useful sunlight per day, calculate the minimum solar panel surface area necessary to provide all of a typical home's electricity. (See Exercise 96 for the energy rate supplied by the sun.)
- 98.** On Easter Sunday, April 3, 1983, nitric acid spilled from a tank car near downtown Denver, Colorado. The spill was neutralized with sodium carbonate:
- $$2HNO_3(aq) + Na_2CO_3(s) \longrightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$$
- a.** Calculate  $\Delta H^\circ$  for this reaction. Approximately  $2.0 \times 10^4$  gal nitric acid was spilled. Assume that the acid was an aqueous solution containing 70.0%  $HNO_3$  by mass with a density of 1.42 g/cm<sup>3</sup>. How much sodium carbonate was required for complete neutralization of the spill, and how much heat was evolved? ( $\Delta H_f^\circ$  for  $NaNO_3(aq)$  = -467 kJ/mol)
- b.** According to *The Denver Post* for April 4, 1983, authorities feared that dangerous air pollution might occur during the neutralization. Considering the magnitude of  $\Delta H^\circ$ , what was their major concern?
- 99.** A piece of chocolate cake contains about 400 Calories. A nutritional Calorie is equal to 1000 calories (thermochemical calories), which is equal to 4.184 kJ. How many 8-in-high steps must a 180-lb man climb to expend the 400 Cal from the piece of cake? See Exercise 20 for the formula for potential energy.
- 100.** The standard enthalpy of formation of  $H_2O(l)$  at 298 K is -285.8 kJ/mol. Calculate the change in internal energy for the following process at 298 K and 1 atm:



(Hint: Using the ideal gas equation, derive an expression for work in terms of  $n$ ,  $R$ , and  $T$ .)

- 101.** You have a 1.00-mol sample of water at -30.0°C and you heat it until you have gaseous water at 140.0°C. Calculate  $q$  for the entire process. Use the following data.

Specific heat capacity of ice = 2.03 J/°C · g

Specific heat capacity of water = 4.18 J/°C · g

Specific heat capacity of steam = 2.02 J/°C · g

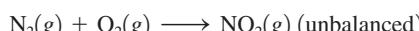


- 102.** A 500.0-g sample of an element at 195°C is dropped into an ice–water mixture; 109.5 g of ice melts and an ice–water mixture remains. Calculate the specific heat of the element. See Exercise 101 for pertinent information.

## Integrative Problems

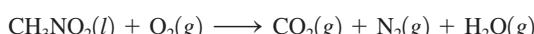
These problems require the integration of multiple concepts to find the solutions.

- 103.** The preparation of  $NO_2(g)$  from  $N_2(g)$  and  $O_2(g)$  is an endothermic reaction:



The enthalpy change of reaction for the balanced equation (with lowest whole-number coefficients) is  $\Delta H = 67.7$  kJ. If  $2.50 \times 10^2$  mL of  $N_2(g)$  at 100.0°C and 3.50 atm and  $4.50 \times 10^2$  mL of  $O_2(g)$  at 100.0°C and 3.50 atm are mixed, what amount of heat is necessary to synthesize  $NO_2(g)$ ?

- 104.** Nitromethane,  $CH_3NO_2$ , can be used as a fuel. When the liquid is burned, the (unbalanced) reaction is mainly



- a.** The standard enthalpy change of reaction ( $\Delta H_{\text{rxn}}^\circ$ ) for the balanced reaction (with lowest whole-number coefficients) is -1288.5 kJ. Calculate the  $\Delta H_f^\circ$  for nitromethane.

- b.** A 15.0-L flask containing a sample of nitromethane is filled with  $O_2$  and the flask is heated to 100.0°C. At this temperature, and after the reaction is complete, the total pressure of all the gases inside the flask is 950. torr. If the mole fraction of nitrogen ( $\chi_{\text{nitrogen}}$ ) is 0.134 after the reaction is complete, what mass of nitrogen was produced?

- 105.** A cubic piece of uranium metal (specific heat capacity = 0.117 J/°C · g) at 200.0°C is dropped into 1.00 L of deuterium oxide ("heavy water," specific heat capacity = 4.211 J/°C · g) at 25.5°C. The final temperature of the uranium and deuterium oxide mixture is 28.5°C. Given the densities of uranium (19.05 g/cm<sup>3</sup>) and deuterium oxide (1.11 g/mL), what is the edge length of the cube of uranium?

## Marathon Problems\*

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

- 106.** A sample consisting of 22.7 g of a nongaseous, unstable compound X is placed inside a metal cylinder with a radius of 8.00 cm, and a piston is carefully placed on the surface of the compound so that, for all practical purposes, the distance between the bottom of the cylinder and the piston is zero. (A hole in the piston allows trapped air to escape as the piston is placed on the compound; then this hole is plugged so that nothing in-

\*Used with permission from the *Journal of Chemical Education*, Vol. 68, No. 11, 1991, pp. 919–922; copyright © 1991, Division of Chemical Education, Inc.

side the cylinder can escape.) The piston-and-cylinder apparatus is carefully placed in 10.00 kg of water at 25.00°C. The barometric pressure is 778 torr.

When the compound spontaneously decomposes, the piston moves up, the temperature of the water reaches a maximum of 29.52°C, and then it gradually decreases as the water loses heat to the surrounding air. The distance between the piston and the bottom of the cylinder, at the maximum temperature, is 59.8 cm. Chemical analysis shows that the cylinder contains 0.300 mol carbon dioxide, 0.250 mol liquid water, 0.025 mol oxygen gas, and an undetermined amount of a gaseous element A.

It is known that the enthalpy change for the decomposition of X, according to the reaction described above, is  $-1893 \text{ kJ/mol}$  X. The standard enthalpies of formation for gaseous carbon dioxide and liquid water are  $-393.5 \text{ kJ/mol}$  and  $-286 \text{ kJ/mol}$ , respectively. The heat capacity for water is  $4.184 \text{ J}^{\circ}\text{C}^{-1} \cdot \text{g}$ . The conversion factor between  $\text{L} \cdot \text{atm}$  and  $\text{J}$  can be determined from the two values for the gas constant  $R$ , namely,  $0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K}$  and  $8.3145 \text{ J/mol} \cdot \text{K}$ . The vapor pressure of water at  $29.5^{\circ}\text{C}$  is 31 torr. Assume that the heat capacity of the piston-and-cylinder apparatus is negligible and that the piston has negligible mass.

Given the preceding information, determine

- The formula for X.
- The pressure–volume work (in kJ) for the decomposition of the 22.7-g sample of X.
- The *molar* change in internal energy for the decomposition of X and the approximate standard enthalpy of formation for X.

- 107.** A gaseous hydrocarbon reacts completely with oxygen gas to form carbon dioxide and water vapor. Given the following data, determine  $\Delta H_f^\circ$  for the hydrocarbon:

$$\Delta H_{\text{rxn}}^\circ = -2044.5 \text{ kJ/mol hydrocarbon}$$

$$\Delta H_f^\circ (\text{CO}_2) = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^\circ (\text{H}_2\text{O}) = -242 \text{ kJ/mol}$$

Density of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  product mixture at  $1.00 \text{ atm}$ ,  $200.0^{\circ}\text{C}$  =  $0.751 \text{ g/L}$

The density of the hydrocarbon is less than the density of Kr at the same conditions.

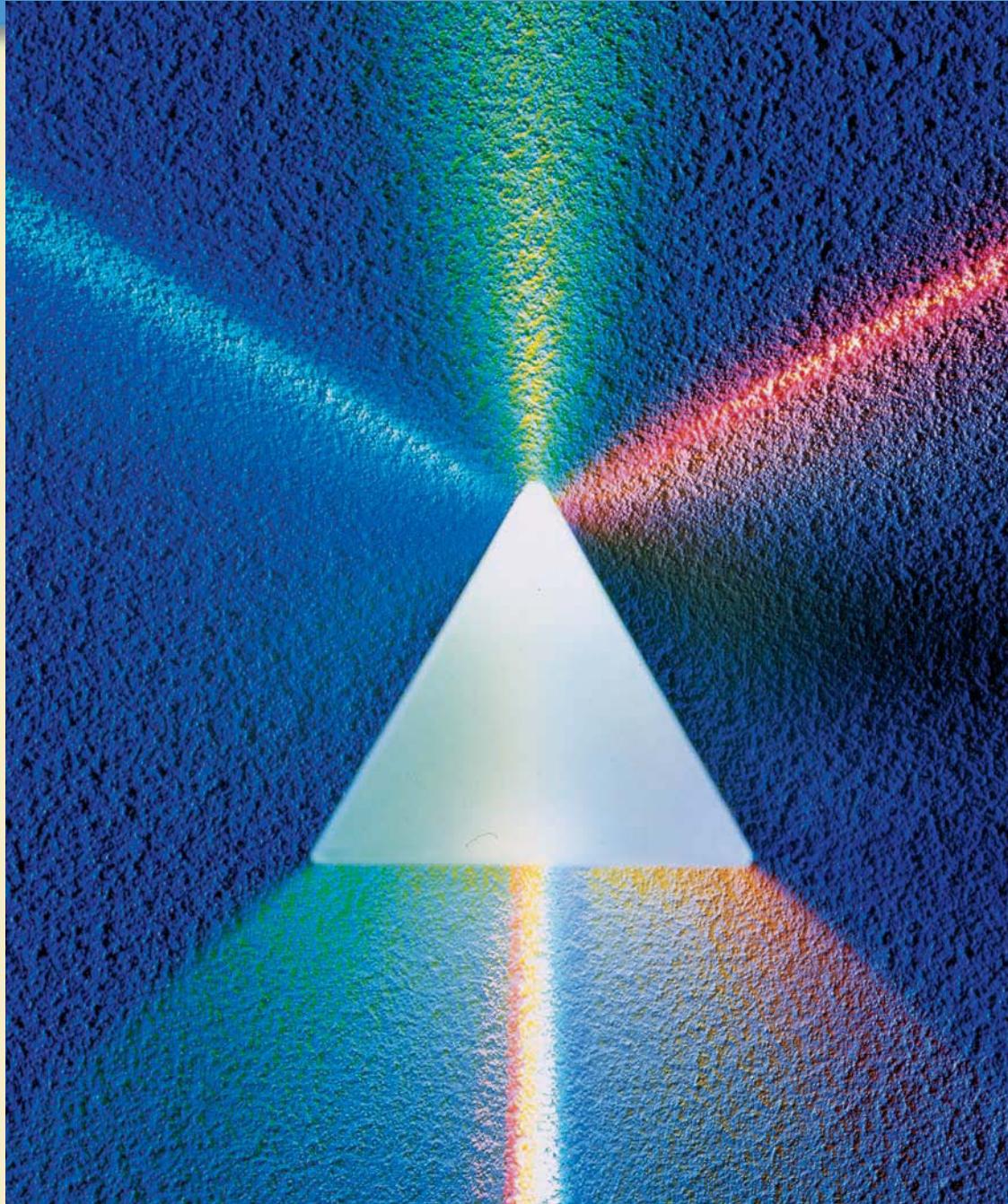


Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [College.hmco.com/PIC/Zumdahl17e](http://College.hmco.com/PIC/Zumdahl17e).

# 7 Atomic Structure and Periodicity

## Contents

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- 7.2 The Nature of Matter
  - The Photoelectric Effect
- 7.3 The Atomic Spectrum of Hydrogen
- 7.4 The Bohr Model
- 7.5 The Quantum Mechanical Model of the Atom
  - The Physical Meaning of a Wave Function
- 7.6 Quantum Numbers
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- 7.12 Periodic Trends in Atomic Properties
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  - Electron Affinity
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  - Information Contained in the Periodic Table
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Light refracted through a prism.

**I**

In the past 200 years, a great deal of experimental evidence has accumulated to support the atomic model. This theory has proved to be both extremely useful and physically reasonable. When atoms were first suggested by the Greek philosophers Democritus and Leucippus about 400 b.c., the concept was based mostly on intuition. In fact, for the following 20 centuries, no convincing experimental evidence was available to support the existence of atoms. The first real scientific data were gathered by Lavoisier and others from quantitative measurements of chemical reactions. The results of these stoichiometric experiments led John Dalton to propose the first systematic atomic theory. Dalton's theory, although crude, has stood the test of time extremely well.

Once we came to "believe in" atoms, it was logical to ask: What is the nature of an atom? Does an atom have parts, and if so, what are they? In Chapter 2 we considered some of the experiments most important for shedding light on the nature of the atom. Now we will see how the atomic theory has evolved to its present state.

One of the most striking things about the chemistry of the elements is the periodic repetition of properties. There are several groups of elements that show great similarities in chemical behavior. As we saw in Chapter 2, these similarities led to the development of the periodic table of the elements. In this chapter we will see that the modern theory of atomic structure accounts for periodicity in terms of the electron arrangements in atoms.

However, before we examine atomic structure, we must consider the revolution that took place in physics in the first 30 years of the twentieth century. During that time, experiments were carried out, the results of which could not be explained by the theories of classical physics developed by Isaac Newton and many others who followed him. A radical new theory called *quantum mechanics* was developed to account for the behavior of light and atoms. This "new physics" provides many surprises for humans who are used to the macroscopic world, but it seems to account flawlessly (within the bounds of necessary approximations) for the behavior of matter.

As the first step in our exploration of this revolution in science we will consider the properties of light, more properly called *electromagnetic radiation*.

## 7.1 Electromagnetic Radiation

One of the ways that energy travels through space is by **electromagnetic radiation**. The light from the sun, the energy used to cook food in a microwave oven, the X rays used by dentists, and the radiant heat from a fireplace are all examples of electromagnetic radiation. Although these forms of radiant energy seem quite different, they all exhibit the same type of wavelike behavior and travel at the speed of light in a vacuum.

Waves have three primary characteristics: wavelength, frequency, and speed. **Wavelength** (symbolized by the lowercase Greek letter lambda,  $\lambda$ ) is the *distance between two consecutive peaks or troughs in a wave*, as shown in Fig. 7.1. The **frequency** (symbolized by the lowercase Greek letter nu,  $\nu$ ) is defined as the *number of waves (cycles) per second that pass a given point in space*. Since all types of electromagnetic radiation travel at the speed of light, short-wavelength radiation must have a high frequency. You can see this in Fig. 7.1, where three waves are shown traveling between two points at constant speed. Note that the wave with the shortest wavelength ( $\lambda_3$ ) has the highest frequency and the wave with the longest wavelength ( $\lambda_1$ ) has the lowest frequency. This implies an inverse relationship between wavelength and frequency, that is,  $\lambda \propto 1/\nu$ , or

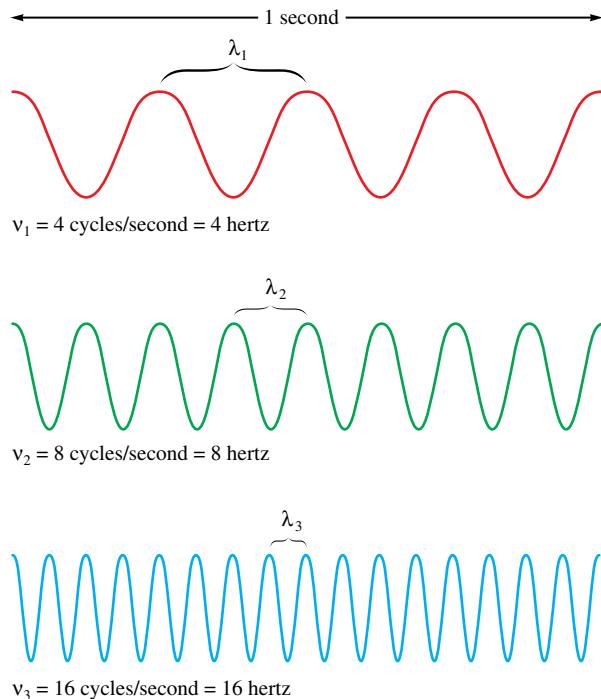
*Wavelength  $\lambda$  and frequency  $\nu$  are inversely related.*

$$c = \text{speed of light} \\ = 2.9979 \times 10^8 \text{ m/s}$$

$$\lambda\nu = c$$



Visualization: Electromagnetic Wave

**FIGURE 7.1**

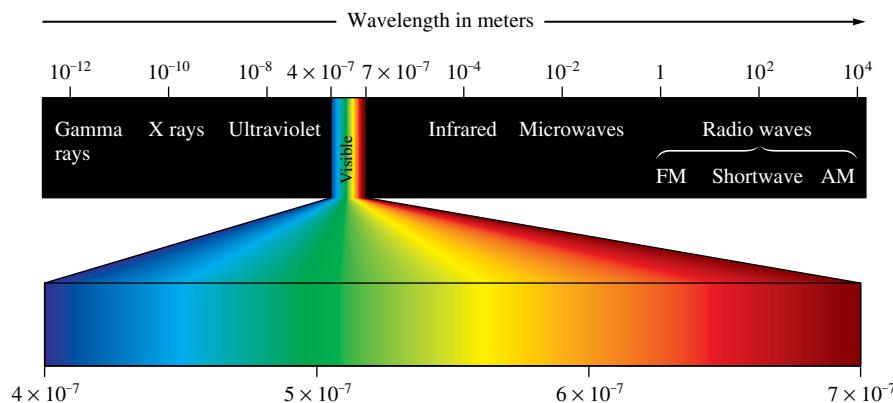
The nature of waves. Note that the radiation with the shortest wavelength has the highest frequency.



Although the waves associated with light are not obvious to the naked eye, ocean waves provide a familiar source of recreation.

where  $\lambda$  is the wavelength in meters,  $\nu$  is the frequency in cycles per second, and  $c$  is the speed of light ( $2.9979 \times 10^8 \text{ m/s}$ ). In the SI system, cycles is understood, and the unit per second becomes  $1/\text{s}$ , or  $\text{s}^{-1}$ , which is called the *hertz* (abbreviated Hz).

Electromagnetic radiation is classified as shown in Fig. 7.2. Radiation provides an important means of energy transfer. For example, the energy from the sun reaches the earth mainly in the form of visible and ultraviolet radiation, whereas the glowing coals of a fireplace transmit heat energy by infrared radiation. In a microwave oven the water molecules in food absorb microwave radiation, which increases their motions. This energy is then transferred to other types of molecules via collisions, causing an increase in the food's temperature. As we proceed in the study of chemistry, we will consider many of the classes of electromagnetic radiation and the ways in which they affect matter.

**FIGURE 7.2**

Classification of electromagnetic radiation. Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).



## CHEMICAL IMPACT

### Flies That Dye

**M**editerranean and Mexican fruit flies are formidable pests that have the potential to seriously damage several important fruit crops. Because of this, there have been several widely publicized sprayings of residential areas in southern California with the pesticide malathion to try to control fruit flies. Now there may be a better way to kill fruit flies—with a blend of two common dyes (red dye no. 28 and yellow dye no. 8) long used to color drugs and cosmetics. One of the most interesting things about this new pesticide is that it

is activated by light. After an insect eats the blend of dyes, the molecules absorb light (through the insect's transparent body), which causes them to generate oxidizing agents that attack the proteins and cell membranes in the bug's body. Death occurs within 12 hours.

The sunlight that turns on the dye's toxicity after the fly ingests it also degrades the dye in the environment, making it relatively safe. It appears likely that in the near future the fruit fly will "dye" with little harm to the environment.

#### Sample Exercise 7.1

### Frequency of Electromagnetic Radiation



When a strontium salt is dissolved in methanol (with a little water) and ignited, it gives a brilliant red flame. The red color is produced by emission of light when electrons, excited by the energy of the burning methanol, fall back to their ground states.

The brilliant red colors seen in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts such as  $\text{Sr}(\text{NO}_3)_2$  and  $\text{SrCO}_3$  are heated. (This can be easily demonstrated in the lab by dissolving one of these salts in methanol that contains a little water and igniting the mixture in an evaporating dish.) Calculate the frequency of red light of wavelength  $6.50 \times 10^2$  nm.

#### Solution

We can convert wavelength to frequency using the equation

$$\lambda\nu = c \quad \text{or} \quad \nu = \frac{c}{\lambda}$$

where  $c = 2.9979 \times 10^8$  m/s. In this case  $\lambda = 6.50 \times 10^2$  nm. Changing the wavelength to meters, we have

$$6.50 \times 10^2 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.50 \times 10^{-7} \text{ m}$$

and

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{6.50 \times 10^{-7} \text{ m}} = 4.61 \times 10^{14} \text{ s}^{-1} = 4.61 \times 10^{14} \text{ Hz}$$

*See Exercises 7.31 and 7.32.*

## 7.2 The Nature of Matter

It is probably fair to say that at the end of the nineteenth century, physicists were feeling rather smug. Theories could explain phenomena as diverse as the motions of the planets and the dispersion of visible light by a prism. Rumor has it that students were being discouraged from pursuing physics as a career because it was felt that all the major problems had been solved, or at least described in terms of the current physical theories.

At the end of the nineteenth century, the idea prevailed that matter and energy were distinct. Matter was thought to consist of particles, whereas energy in the form of light (electromagnetic radiation) was described as a wave. Particles were things that had mass and whose position in space could be specified. Waves were described as massless and delocalized; that is, their position in space could not be specified. It also was assumed that there was no intermingling of matter and light. Everything known before 1900 seemed to fit neatly into this view.



Visualization: Electrified Pickle



When alternating current at 110 volts is applied to a dill pickle, a glowing discharge occurs. The current flowing between the electrodes (forks), which is supported by the  $\text{Na}^+$  and  $\text{Cl}^-$  ions present, apparently causes some sodium atoms to form in an excited state. When these atoms relax to the ground state, they emit visible light at 589 nm, producing the yellow glow reminiscent of sodium vapor lamps.

At the beginning of the twentieth century, however, certain experimental results suggested that this picture was incorrect. The first important advance came in 1900 from the German physicist Max Planck (1858–1947). Studying the radiation profiles emitted by solid bodies heated to incandescence, Planck found that the results could not be explained in terms of the physics of his day, which held that matter could absorb or emit any quantity of energy. Planck could account for these observations only by postulating that energy can be gained or lost only in *whole-number multiples* of the quantity  $h\nu$ , where  $h$  is a constant called **Planck's constant**, determined by experiment to have the value  $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ . That is, the change in energy for a system  $\Delta E$  can be represented by the equation

$$\Delta E = nh\nu$$

where  $n$  is an integer (1, 2, 3, . . .),  $h$  is Planck's constant, and  $\nu$  is the frequency of the electromagnetic radiation absorbed or emitted.

Planck's result was a real surprise. It had always been assumed that the energy of matter was continuous, which meant that the transfer of any quantity of energy was possible. Now it seemed clear that energy is in fact **quantized** and can occur only in discrete units of size  $h\nu$ . Each of these small “packets” of energy is called a *quantum*. A system can transfer energy only in whole quanta. Thus energy seems to have particulate properties.

**Energy can be gained or lost only in integer multiples of  $h\nu$ .**

Planck's constant =  $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ .

### Sample Exercise 7.2

### The Energy of a Photon

The blue color in fireworks is often achieved by heating copper(I) chloride ( $\text{CuCl}$ ) to about  $1200^\circ\text{C}$ . Then the compound emits blue light having a wavelength of 450 nm. What is the increment of energy (the quantum) that is emitted at  $4.50 \times 10^2$  nm by  $\text{CuCl}$ ?

#### Solution

The quantum of energy can be calculated from the equation

$$\Delta E = h\nu$$

The frequency  $\nu$  for this case can be calculated as follows:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{4.50 \times 10^{-7} \text{ m}} = 6.66 \times 10^{14} \text{ s}^{-1}$$

So

$$\Delta E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(6.66 \times 10^{14} \text{ s}^{-1}) = 4.41 \times 10^{-19} \text{ J}$$

A sample of  $\text{CuCl}$  emitting light at 450 nm can lose energy only in increments of  $4.41 \times 10^{-19} \text{ J}$ , the size of the quantum in this case.

**See Exercises 7.33 and 7.34.**

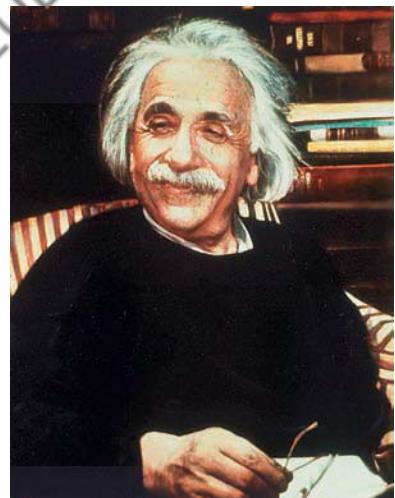
The next important development in the knowledge of atomic structure came when Albert Einstein (see Fig. 7.3) proposed that electromagnetic radiation is itself quantized. Einstein suggested that electromagnetic radiation can be viewed as a stream of “particles” called **photons**. The energy of each photon is given by the expression

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

where  $h$  is Planck's constant,  $\nu$  is the frequency of the radiation, and  $\lambda$  is the wavelength of the radiation.



Visualization: Photoelectric Effect

**FIGURE 7.3**

Albert Einstein (1879–1955) was born in Germany. Nothing in his early development suggested genius; even at the age of 9 he did not speak clearly, and his parents feared that he might be handicapped. When asked what profession Einstein should follow, his school principal replied, "It doesn't matter; he'll never make a success of anything." When he was 10, Einstein entered the Luitpold Gymnasium (high school), which was typical of German schools of that time in being harshly disciplinarian. There he developed a deep suspicion of authority and a skepticism that encouraged him to question and doubt—valuable qualities in a scientist. In 1905, while a patent clerk in Switzerland, Einstein published a paper explaining the photoelectric effect via the quantum theory. For this revolutionary thinking he received a Nobel Prize in 1921. Highly regarded by this time, he worked in Germany until 1933, when Hitler's persecution of the Jews forced him to come to the United States. He worked at the Institute for Advanced Studies in Princeton, New Jersey, until his death in 1955.

Einstein was undoubtedly the greatest physicist of our age. Even if someone else had derived the theory of relativity, his other work would have ensured his ranking as the second greatest physicist of his time. Our concepts of space and time were radically changed by ideas he first proposed when he was 26 years old. From then until the end of his life, he attempted unsuccessfully to find a single unifying theory that would explain all physical events.

## The Photoelectric Effect

Einstein arrived at this conclusion through his analysis of the **photoelectric effect** (for which he later was awarded the Nobel Prize). The photoelectric effect refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes it. The following observations characterize the photoelectric effect.

1. Studies in which the frequency of the light is varied show that no electrons are emitted by a given metal below a specific threshold frequency  $\nu_0$ .
2. For light with frequency lower than the threshold frequency, no electrons are emitted regardless of the intensity of the light.
3. For light with frequency greater than the threshold frequency, the number of electrons emitted increases with the intensity of the light.
4. For light with frequency greater than the threshold frequency, the kinetic energy, of the emitted electrons increases linearly with the frequency of the light.

These observations can be explained by assuming that electromagnetic radiation is quantized (consists of photons), and that the threshold frequency represents the minimum energy required to remove the electron from the metal's surface.

$$\text{Minimum energy required to remove an electron} = E_0 = h\nu_0$$

Because a photon with energy less than  $E_0$  ( $\nu < \nu_0$ ) cannot remove an electron, light with a frequency less than the threshold frequency produces no electrons. On the other hand, for light where  $\nu > \nu_0$ , the energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

$$\text{KE}_{\text{electron}} = \frac{1}{2}mv^2 = h\nu - h\nu_0$$

Mass of      Velocity      Energy of      Energy required  
 electron      of      incident      to remove electron  
 electron      photon      from metal's surface

Because in this picture the intensity of light is a measure of the number of photons present in a given part of the beam, a greater intensity means that more photons are available to release electrons (as long as  $\nu > \nu_0$  for the radiation).

In a related development, Einstein derived the famous equation

$$E = mc^2$$

in his *special theory of relativity* published in 1905. The main significance of this equation is that *energy has mass*. This is more apparent if we rearrange the equation in the following form:

$$m = \frac{E}{c^2}$$

Mass                  Energy  
 ↑                  ←  
 Speed of light



## CHEMICAL IMPACT

### Chemistry That Doesn't Leave You in the Dark

In the animal world, the ability to see at night provides predators with a distinct advantage over their prey. The same advantage can be gained by military forces and law enforcement agencies around the world through the use of recent advances in night vision technology.

All types of night vision equipment are electro-optical devices that amplify existing light. A lens collects light and focuses it on an image intensifier. The image intensifier is based on the photoelectric effect—materials that give off electrons when light is shined on them. Night vision intensifiers use semiconductor-based materials to produce large numbers of electrons for a given input of photons. The emitted electrons are then directed onto a screen covered with compounds that phosphoresce (glow when struck by electrons). While television tubes use various phosphors to produce color pictures, night vision devices use phosphors that appear green, because the human eye can distinguish more shades of green than any other color. The viewing screen shows an image that otherwise would be invisible to the naked eye during nighttime viewing.

Current night vision devices use gallium arsenide (GaAs)-based intensifiers that can amplify input light as much as 50,000 times. These devices are so sensitive they can use starlight to produce an image. It is also now possible to use light (infrared) that cannot be sensed with the human eye to create an image.

This technology, while developed originally for military and law enforcement applications, is now becoming available to the consumer. For example, Cadillac included night vision as an option on its cars for the year 2000. As night-imaging technology improves and costs become less prohibitive, a whole new world is opening up for the technophile—after the sun goes down.



A night vision photo of the midair refueling of a U.S. Air Force plane.

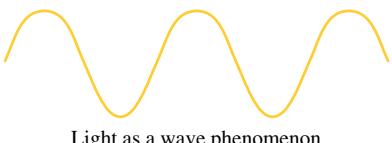
Using this form of the equation, we can calculate the mass associated with a given quantity of energy. For example, we can calculate the *apparent* mass of a photon. For electromagnetic radiation of wavelength  $\lambda$ , the energy of each photon is given by the expression

$$E_{\text{photon}} = \frac{hc}{\lambda}$$

Then the apparent mass of a photon of light with wavelength  $\lambda$  is given by

$$m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{\lambda c}$$

Does a photon really have mass? The answer *appears to be* yes. In 1922 American physicist Arthur Compton (1892–1962) performed experiments involving collisions of X rays and electrons that showed that photons do exhibit the apparent mass calculated from the preceding equation. However, it is clear that photons do not have mass in the classical sense. A photon has mass only in a relativistic sense—it has no rest mass.



Light as a wave phenomenon



Light as a stream of photons

**FIGURE 7.4**

Electromagnetic radiation exhibits wave properties and particulate properties. The energy of each photon of the radiation is related to the wavelength and frequency by the equation  $E_{\text{photon}} = h\nu = hc/\lambda$ .

We can summarize the important conclusions from the work of Planck and Einstein as follows:

Energy is quantized. It can occur only in discrete units called quanta.

Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the **dual nature of light** and is illustrated in Fig. 7.4.

Thus light, which previously was thought to be purely wavelike, was found to have certain characteristics of particulate matter. But is the opposite also true? That is, does matter that is normally assumed to be particulate exhibit wave properties? This question was raised in 1923 by a young French physicist named Louis de Broglie (1892–1987). To see how de Broglie supplied the answer to this question, recall that the relationship between mass and wavelength for electromagnetic radiation is  $m = h/\lambda c$ . For a particle with velocity  $v$ , the corresponding expression is

$$m = \frac{h}{\lambda v}$$

Rearranging to solve for  $\lambda$ , we have

$$\lambda = \frac{h}{mv}$$

This equation, called *de Broglie's equation*, allows us to calculate the wavelength for a particle, as shown in Sample Exercise 7.3.

### Sample Exercise 7.3

### Calculations of Wavelength

Compare the wavelength for an electron (mass =  $9.11 \times 10^{-31}$  kg) traveling at a speed of  $1.0 \times 10^7$  m/s with that for a ball (mass = 0.10 kg) traveling at 35 m/s.

#### Solution

We use the equation  $\lambda = h/mv$ , where

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \quad \text{or} \quad 6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$$

since

$$1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$$

For the electron,

$$\lambda_e = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{s}}{\text{s}}}{(9.11 \times 10^{-31} \text{ kg})(1.0 \times 10^7 \text{ m/s})} = 7.27 \times 10^{-11} \text{ m}$$

For the ball,

$$\lambda_b = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m} \cdot \text{s}}{\text{s}}}{(0.10 \text{ kg})(35 \text{ m/s})} = 1.9 \times 10^{-34} \text{ m}$$

*See Exercises 7.41 through 7.44.*

Notice from Sample Exercise 7.3 that the wavelength associated with the ball is incredibly short. On the other hand, the wavelength of the electron, although still quite small, happens to be on the same order as the spacing between the atoms in a typical crystal. This is important because, as we will see presently, it provides a means for testing de Broglie's equation.



## CHEMICAL IMPACT

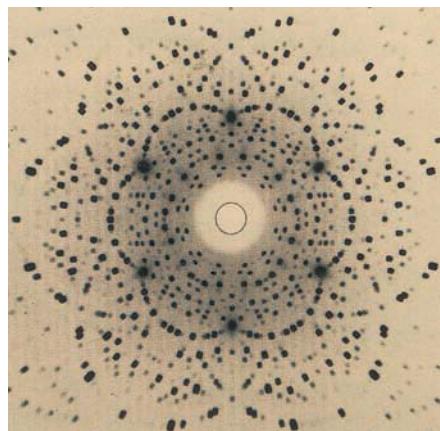
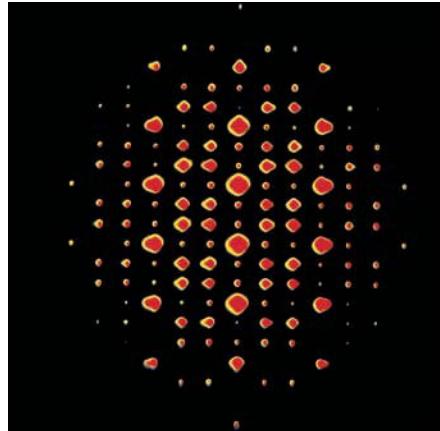
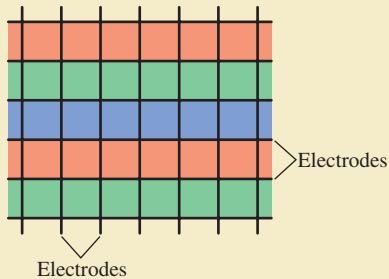
### Thin Is In

**S**ince the beginning of television about 75 years ago, TV sets have been built around cathode ray tubes (CRTs) in which a “gun” fires electrons at a screen containing phosphors (compounds that emit colored light when excited by some energy source). Although CRT televisions produce excellent pictures, big-screen TVs are very thick and very heavy. Several new technologies are now being used that reduce the bulk of color monitors. One such approach involves a plasma flat-panel display. As the name suggests, the major advantage of these screens is that they are very thin and relatively light.

All color monitors work by manipulating millions of pixels, each of which contains red, blue, and green color-producing phosphors. By combining these three fundamental colors with various weightings, all colors of the rainbow can be generated, thereby producing color images on the monitor. The various types of monitors differ in the energy source used to excite the phosphors. Whereas a CRT monitor uses an electron gun as the energy source, a plasma monitor

uses an applied voltage to produce gas-phase ions and electrons, which, when they recombine, emit ultraviolet light. This light, in turn, excites the phosphors.

Plasma monitors have pixel compartments that contain xenon and neon gas. Each pixel consists of three subpixels: one containing a red phosphor, one with a green phosphor, and one with a blue phosphor. Two perpendicular sets of electrodes define a matrix around the subpixels:



**Diffraction** results when light is scattered from a regular array of points or lines. You may have noticed the diffraction of light from the ridges and grooves of a compact disc. The colors result because the various wavelengths of visible light are not all scattered in the same way. The colors are “separated,” giving the same effect as light passing through a prism. Just as a regular arrangement of ridges and grooves produces diffraction, so does a regular array of atoms or ions in a crystal, as shown in the photographs below. For example, when X rays are directed onto a crystal of sodium chloride, with its regular array of  $\text{Na}^+$  and  $\text{Cl}^-$  ions, the scattered radiation produces a **diffraction pattern** of bright spots and dark areas on a photographic plate, as shown in Fig. 7.5(a). This occurs because the scattered light can interfere constructively (the peaks and troughs of the beams are in phase) to produce a bright spot [Fig. 7.5(b)] or destructively (the peaks and troughs are out of phase) to produce a dark area [Fig. 7.5(c)].

A diffraction pattern can only be explained in terms of waves. Thus this phenomenon provides a test for the postulate that particles such as electrons have wavelengths. As we saw in Sample Exercise 7.3, an electron with a velocity of  $10^7 \text{ m/s}$  (easily achieved by acceleration of the electron in an electric field) has a wavelength of about  $10^{-10} \text{ m}$ , which is roughly the distance between the ions in a crystal such as sodium chloride. This is important because diffraction occurs most efficiently when the spacing between the scattering points is about the same as the wavelength of the wave being diffracted. Thus, if electrons really do have an associated wavelength, a crystal should diffract electrons. An experiment to test this idea was carried out in 1927 by C. J. Davisson and

(top) The pattern produced by electron diffraction of a titanium/nickel alloy. (bottom) Pattern produced by X-ray diffraction of a beryl crystal.

One set of the electrodes is above the pixels, and the perpendicular set is below the pixels. When the computer managing the image places a voltage difference across a given subpixel, electrons are removed from the xenon and neon atoms present to form a plasma (cations and electrons). When the cations recombine with the electrons, photons of light are emitted that are absorbed by the phosphor compound, which then emits red, green, or blue light. By controlling the size of the voltage on a given subpixel, a given pixel can produce a variety of colors. When all of the pixels are excited appropriately, a color image is produced.

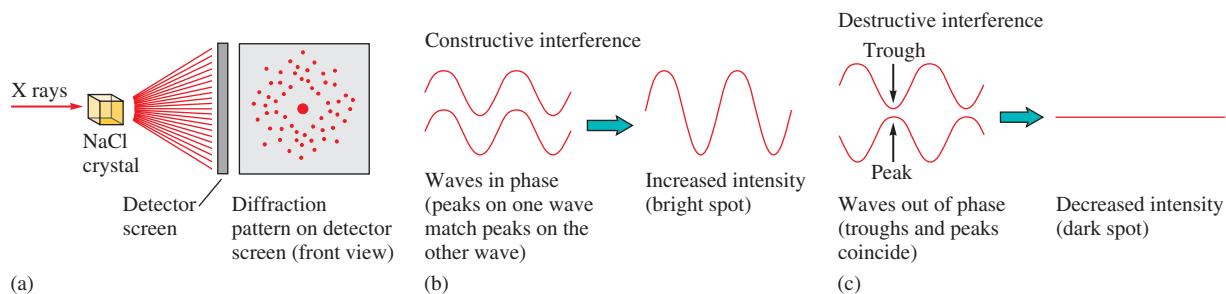
The plasma display makes it possible to have a large, yet relatively thin screen. Since each pixel is energized individually, this display looks bright and clear from almost any angle. The main disadvantage of this technology is its relatively high cost. However, as advances are being made, the price is falling significantly. CRT monitors may soon be of interest only to antique collectors.



A plasma display from Sony.

L. H. Germer at Bell Laboratories. When they directed a beam of electrons at a nickel crystal, they observed a diffraction pattern similar to that seen from the diffraction of X rays. This result verified de Broglie's relationship, at least for electrons. Larger chunks of matter, such as balls, have such small wavelengths (see Sample Exercise 7.3) that they are impossible to verify experimentally. However, we believe that all matter obeys de Broglie's equation.

Now we have come full circle. Electromagnetic radiation, which at the turn of the twentieth century was thought to be a pure waveform, was found to possess particulate properties. Conversely, electrons, which were thought to be particles, were found to have a wavelength associated with them. The significance of these results is that matter and energy are not distinct.



**FIGURE 7.5**

(a) Diffraction occurs when electromagnetic radiation is scattered from a regular array of objects, such as the ions in a crystal of sodium chloride. The large spot in the center is from the main incident beam of X rays. (b) Bright spots in the diffraction pattern result from *constructive interference* of waves. The waves are in phase; that is, their peaks match. (c) Dark areas result from *destructive interference* of waves. The waves are out of phase; the peaks of one wave coincide with the troughs of another wave.

Energy is really a form of matter, and all matter shows the same types of properties. That is, *all matter exhibits both particulate and wave properties*. Large pieces of matter, such as baseballs, exhibit predominantly particulate properties. The associated wavelength is so small that it is not observed. Very small “bits of matter,” such as photons, while showing some particulate properties, exhibit predominantly wave properties. Pieces of matter with intermediate mass, such as electrons, show clearly both the particulate and wave properties of matter.

## 7.3 The Atomic Spectrum of Hydrogen



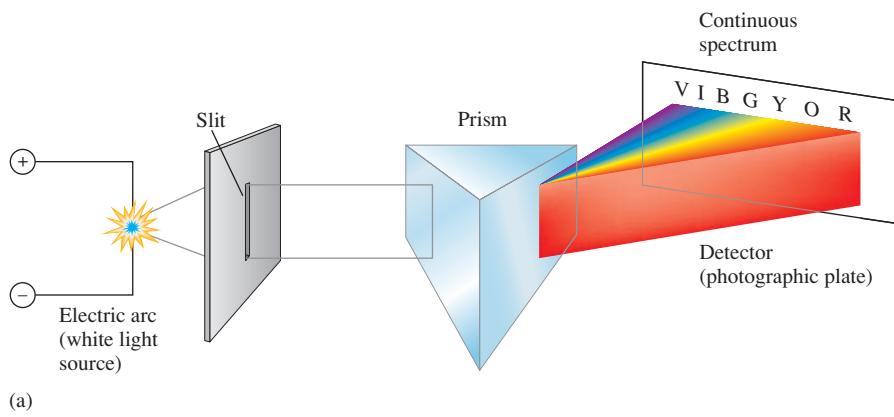
A beautiful rainbow.



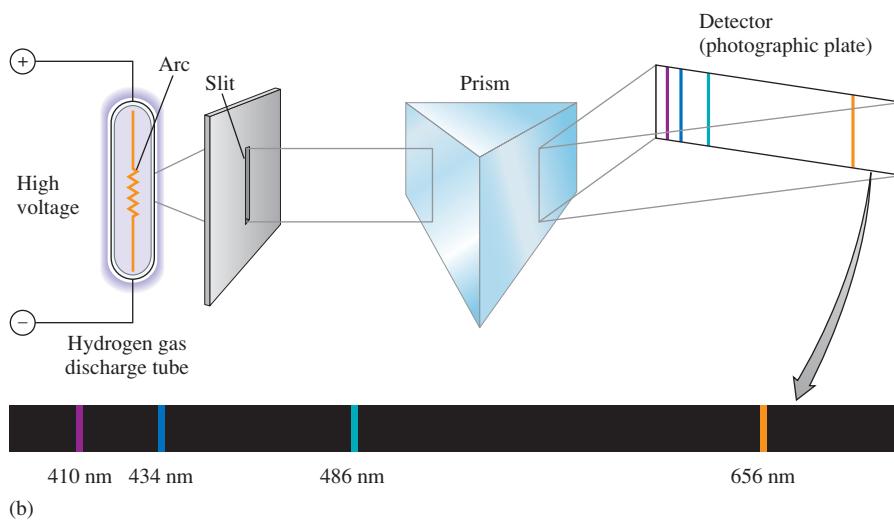
**Visualization: Refraction of White Light**

As we saw in Chapter 2, key information about the atom came from several experiments carried out in the early twentieth century, in particular Thomson’s discovery of the electron and Rutherford’s discovery of the nucleus. Another important experiment was the study of the emission of light by excited hydrogen atoms. When a sample of hydrogen gas receives a high-energy spark, the H<sub>2</sub> molecules absorb energy, and some of the H—H bonds are broken. The resulting hydrogen atoms are *excited*; that is, they contain excess energy, which they release by emitting light of various wavelengths to produce what is called the *emission spectrum* of the hydrogen atom.

To understand the significance of the hydrogen emission spectrum, we must first describe the **continuous spectrum** that results when white light is passed through a prism, as shown in Fig. 7.6(a). This spectrum, like the rainbow produced when sunlight is



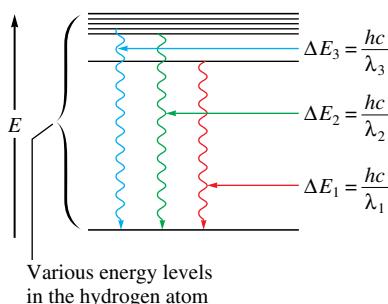
**Visualization: The Line Spectrum of Hydrogen**



**FIGURE 7.6**

(a) A continuous spectrum containing all wavelengths of visible light (indicated by the initial letters of the colors of the rainbow). (b) The hydrogen line spectrum contains only a few discrete wavelengths.

Spectrum adapted by permission from C. W. Keenan, D. C. Kleinfelter, and J. H. Wood, *General College Chemistry*, 6th ed. (New York: Harper & Row, 1980).

**FIGURE 7.7**

A change between two discrete energy levels emits a photon of light.

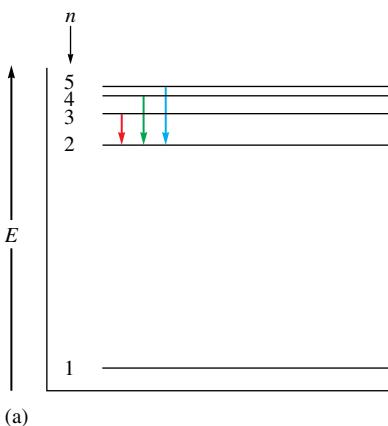
dispersed by raindrops, contains *all* the wavelengths of visible light. In contrast, when the hydrogen emission spectrum in the visible region is passed through a prism, as shown in Fig. 7.6(b), we see only a few lines, each of which corresponds to a discrete wavelength. The hydrogen emission spectrum is called a **line spectrum**.

What is the significance of the line spectrum of hydrogen? It indicates that *only certain energies are allowed for the electron in the hydrogen atom*. In other words, the energy of the electron in the hydrogen atom is *quantized*. This observation ties in perfectly with the postulates of Max Planck discussed in Section 7.2. Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light, as shown in Fig. 7.7. For example, a given change in energy from a high to a lower level would give a wavelength of light that can be calculated from Planck's equation:

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Change in energy      Frequency of light emitted      Wavelength of light emitted

The discrete line spectrum of hydrogen shows that only certain energies are possible; that is, the electron energy levels are quantized. In contrast, if any energy level were allowed, the emission spectrum would be continuous.

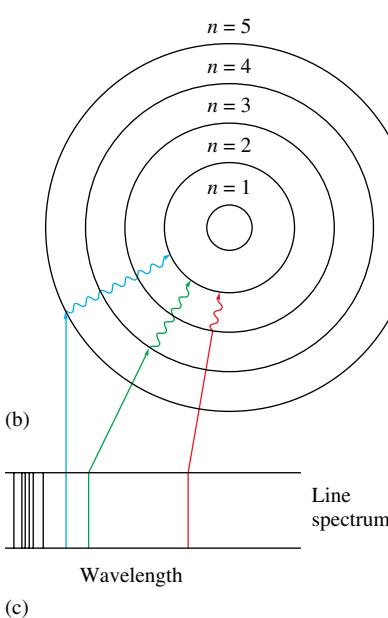


## 7.4 The Bohr Model

In 1913, a Danish physicist named Niels Bohr (1885–1962), aware of the experimental results we have just discussed, developed a **quantum model** for the hydrogen atom. Bohr proposed that the *electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits*. He calculated the radii for these allowed orbits by using the theories of classical physics and by making some new assumptions.

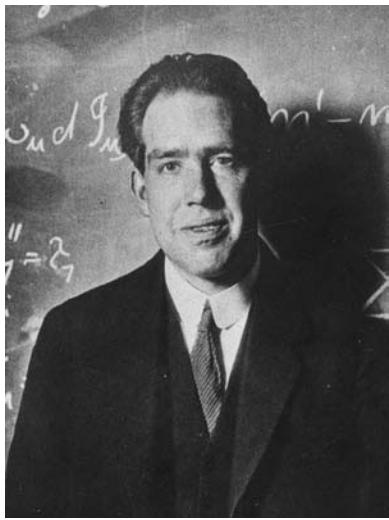
From classical physics Bohr knew that a particle in motion tends to move in a straight line and can be made to travel in a circle only by application of a force toward the center of the circle. Thus Bohr reasoned that the tendency of the revolving electron to fly off the atom must be just balanced by its attraction for the positively charged nucleus. But classical physics also decreed that a charged particle under acceleration should radiate energy. Since an electron revolving around the nucleus constantly changes its direction, it is constantly accelerating. Therefore, the electron should emit light and lose energy—and thus be drawn into the nucleus. This, of course, does not correlate with the existence of stable atoms.

Clearly, an atomic model based solely on the theories of classical physics was untenable. Bohr also knew that the correct model had to account for the experimental spectrum of hydrogen, which showed that only certain electron energies were allowed. The experimental data were absolutely clear on this point. Bohr found that his model would fit the experimental results if he assumed that the angular momentum of the electron (angular momentum equals the product of mass, velocity, and orbital radius) could occur only in certain increments. It was not clear why this should be true, but with this assumption, Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum. The model is represented pictorially in Fig. 7.8.

**FIGURE 7.8**

Electronic transitions in the Bohr model for the hydrogen atom. (a) An energy-level diagram for electronic transitions. (b) An orbit-transition diagram, which accounts for the experimental spectrum. (Note that the orbits shown are schematic. They are not drawn to scale.) (c) The resulting line spectrum on a photographic plate. Note that the lines in the visible region of the spectrum correspond to transitions from higher levels to the  $n = 2$  level.

The J in Equation (7.1) stands for joules.



Niels Hendrik David Bohr (1885–1962) as a boy lived in the shadow of his younger brother Harald, who played on the 1908 Danish Olympic Soccer Team and later became a distinguished mathematician. In school, Bohr received his poorest marks in composition and struggled with writing during his entire life. In fact, he wrote so poorly that he was forced to dictate his Ph.D. thesis to his mother. Nevertheless, Bohr was a brilliant physicist. After receiving his Ph.D. in Denmark, he constructed a quantum model for the hydrogen atom by the time he was 27. Even though his model later proved to be incorrect, Bohr remained a central figure in the drive to understand the atom. He was awarded the Nobel Prize in physics in 1922.

Although we will not show the derivation here, the most important equation to come from Bohr's model is the expression for the *energy levels available to the electron in the hydrogen atom*:

$$E = -2.178 \times 10^{-18} \text{ J} \left( \frac{Z^2}{n^2} \right) \quad (7.1)$$

in which  $n$  is an integer (the larger the value of  $n$ , the larger is the orbit radius) and  $Z$  is the nuclear charge. Using Equation (7.1), Bohr was able to calculate hydrogen atom energy levels that exactly matched the values obtained by experiment.

The negative sign in Equation (7.1) simply means that the energy of the electron bound to the nucleus is lower than it would be if the electron were at an infinite distance ( $n = \infty$ ) from the nucleus, where there is no interaction and the energy is zero:

$$E = -2.178 \times 10^{-18} \text{ J} \left( \frac{Z^2}{\infty} \right) = 0$$

The energy of the electron in any orbit is negative relative to this reference state.

Equation (7.1) can be used to calculate the change in energy of an electron when the electron changes orbits. For example, suppose an electron in level  $n = 6$  of an excited hydrogen atom falls back to level  $n = 1$  as the hydrogen atom returns to its lowest possible energy state, its **ground state**. We use Equation (7.1) with  $Z = 1$ , since the hydrogen nucleus contains a single proton. The energies corresponding to the two states are as follows:

$$\text{For } n = 6: \quad E_6 = -2.178 \times 10^{-18} \text{ J} \left( \frac{1^2}{6^2} \right) = -6.050 \times 10^{-20} \text{ J}$$

$$\text{For } n = 1: \quad E_1 = -2.178 \times 10^{-18} \text{ J} \left( \frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

Note that for  $n = 1$  the electron has a more negative energy than it does for  $n = 6$ , which means that the electron is more tightly bound in the smallest allowed orbit.

The change in energy  $\Delta E$  when the electron falls from  $n = 6$  to  $n = 1$  is

$$\begin{aligned} \Delta E &= \text{energy of final state} - \text{energy of initial state} \\ &= E_1 - E_6 = (-2.178 \times 10^{-18} \text{ J}) - (-6.050 \times 10^{-20} \text{ J}) \\ &= -2.117 \times 10^{-18} \text{ J} \end{aligned}$$

The negative sign for the *change* in energy indicates that the atom has *lost* energy and is now in a more stable state. The energy is carried away from the atom by the production (emission) of a photon.

The wavelength of the emitted photon can be calculated from the equation

$$\Delta E = h \left( \frac{c}{\lambda} \right) \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

where  $\Delta E$  represents the change in energy of the atom, which equals the energy of the emitted photon. We have

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{2.117 \times 10^{-18} \text{ J}} = 9.383 \times 10^{-8} \text{ m}$$

Note that for this calculation the absolute value of  $\Delta E$  is used (we have not included the negative sign). In this case we indicate the direction of energy flow by saying that a photon

of wavelength  $9.383 \times 10^{-8}$  m has been *emitted* from the hydrogen atom. Simply plugging the negative value of  $\Delta E$  into the equation would produce a negative value for  $\lambda$ , which is physically meaningless.\*

### Sample Exercise 7.4

## Energy Quantization in Hydrogen

Calculate the energy required to excite the hydrogen electron from level  $n = 1$  to level  $n = 2$ . Also calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach this excited state.\*

### Solution

Using Equation (7.1) with  $Z = 1$ , we have

$$E_1 = -2.178 \times 10^{-18} \text{ J} \left( \frac{1^2}{1^2} \right) = -2.178 \times 10^{-18} \text{ J}$$

$$E_2 = -2.178 \times 10^{-18} \text{ J} \left( \frac{1^2}{2^2} \right) = -5.445 \times 10^{-19} \text{ J}$$

$$\Delta E = E_2 - E_1 = (-5.445 \times 10^{-19} \text{ J}) - (-2.178 \times 10^{-18} \text{ J}) = 1.633 \times 10^{-18} \text{ J}$$

The positive value for  $\Delta E$  indicates that the system has gained energy. The wavelength of light that must be *absorbed* to produce this change is

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{1.633 \times 10^{-18} \text{ J}} \\ = 1.216 \times 10^{-7} \text{ m}$$

### See Exercises 7.45 and 7.46.

Note from Fig. 7.2 that the light required to produce the transition from the  $n = 1$  to  $n = 2$  level in hydrogen lies in the ultraviolet region.

At this time we must emphasize two important points about the Bohr model:

1. The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
2. As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (corresponding to the electron being at infinite distance from the nucleus). As the electron is brought closer to the nucleus, energy is released from the system.

Using Equation (7.1), we can derive a general equation for the electron moving from one level ( $n_{\text{initial}}$ ) to another level ( $n_{\text{final}}$ ):

$$\begin{aligned} \Delta E &= \text{energy of level } n_{\text{final}} - \text{energy of level } n_{\text{initial}} \\ &= E_{\text{final}} - E_{\text{initial}} \\ &= (-2.178 \times 10^{-18} \text{ J}) \left( \frac{1^2}{n_{\text{final}}^2} \right) - (-2.178 \times 10^{-18} \text{ J}) \left( \frac{1^2}{n_{\text{initial}}^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \end{aligned} \quad (7.2)$$

Equation (7.2) can be used to calculate the energy change between *any* two energy levels in a hydrogen atom, as shown in Sample Exercise 7.5.

\*After this exercise we will no longer show cancellation marks. However, the same process for canceling units applies throughout this text.



## CHEMICAL IMPACT

### Fireworks

The art of using mixtures of chemicals to produce explosives is an ancient one. Black powder—a mixture of potassium nitrate, charcoal, and sulfur—was being used in China well before 1000 A.D. and has been used subsequently through the centuries in military explosives, in construction blasting, and for fireworks. The DuPont Company, now a major chemical manufacturer, started out as a manufacturer of black powder. In fact, the founder, Eleuthère duPont, learned the manufacturing technique from none other than Lavoisier.

Before the nineteenth century, fireworks were confined mainly to rockets and loud bangs. Orange and yellow colors came from the presence of charcoal and iron filings. However, with the great advances in chemistry in the nineteenth century, new compounds found their way into fireworks. Salts of copper, strontium, and barium added brilliant colors. Magnesium and aluminum metals gave a dazzling white light. Fireworks, in fact, have changed very little since then.

How do fireworks produce their brilliant colors and loud bangs? Actually, only a handful of different chemicals are responsible for most of the spectacular effects. To produce the noise and flashes, an oxidizer (an oxidizing agent) and a fuel (a reducing agent) are used. A common mixture involves potassium perchlorate ( $KClO_4$ ) as the oxidizer and aluminum and sulfur as the fuel. The perchlorate oxidizes the fuel in a very exothermic reaction, which produces a brilliant flash, due to the aluminum, and a loud report from the rapidly expanding gases produced. For a color effect, an element with a colored emission spectrum is included. Recall that the electrons in atoms can be raised to higher-energy orbitals when the atoms absorb energy. The excited atoms can then release this excess energy by emitting light of specific wavelengths, often in the visible region. In fireworks, the energy to excite the electrons comes from the reaction between the oxidizer and fuel.

Yellow colors in fireworks are due to the 589-nm emission of sodium ions. Red colors come from strontium salts emitting at 606 nm and from 636 to 688 nm. This red color is familiar from highway safety flares. Barium salts give a green color in fireworks, due to a series of emission lines

between 505 and 535 nm. A really good blue color, however, is hard to obtain. Copper salts give a blue color, emitting in the 420- to 460-nm region. But difficulties occur because the oxidizing agent, potassium chlorate ( $KClO_3$ ), reacts with copper salts to form copper chlorate, a highly explosive compound that is dangerous to store. (The use of  $KClO_3$  in fireworks has been largely abandoned because of its explosive hazards.) Paris green, a copper salt containing arsenic, was once used extensively but is now considered to be too toxic.

In recent years the colors produced by fireworks have become more intense because of the formation of metal chlorides during the burning process. These gaseous metal chloride molecules produce colors much more brilliant than do the metal atoms by themselves. For example, strontium chloride produces a much brighter red than do strontium atoms.



Fireworks in Washington, D.C.

Thus, chlorine-donating compounds are now included in many fireworks shells.

A typical aerial shell is shown in the diagram. The shell is launched from a mortar (a steel cylinder) using black powder as the propellant. Time-delayed fuses are used to fire the shell in stages. A list of chemicals commonly used in fireworks is given in the table.

Although you might think that the chemistry of fireworks is simple, the achievement of the vivid white flashes and the brilliant colors requires complex combinations of chemicals. For example, because the white flashes produce high flame temperatures, the colors tend to wash out. Thus oxidizers such as  $\text{KClO}_4$  are commonly used with fuels that produce relatively low flame temperatures. An added difficulty, however, is that perchlorates are very sensitive to accidental ignition and are therefore quite hazardous. Another problem arises from the use of sodium salts. Because sodium produces an extremely bright yellow emission, sodium salts cannot be used when other colors are desired. Carbon-based fuels also give a yellow flame that masks other colors, and this limits the use of organic compounds as fuels. You can see that the manufacture of fireworks that produce the desired effects and are also safe to handle requires careful selection of chemicals. And, of course, there is still the dream of a deep blue flame.

Chemicals Commonly Used in the Manufacture of Fireworks		
Oxidizers	Fuels	Special Effects
Potassium nitrate	Aluminum	Red flame: strontium nitrate, strontium carbonate
Potassium chlorate	Magnesium	Green flame: barium nitrate, barium chlorate
Potassium perchlorate	Titanium	Blue flame: copper carbonate, copper sulfate, copper oxide
Ammonium perchlorate	Charcoal	Yellow flame: sodium oxalate, cryolite ( $\text{Na}_3\text{AlF}_6$ )
Barium nitrate	Sulfur	White flame: magnesium, aluminum
Barium chloride	Antimony sulfide	Gold sparks: iron filings, charcoal
Strontium nitrate	Dextrin	White sparks: aluminum, magnesium, aluminum-magnesium alloy, titanium
	Red gum	Whistle effect: potassium benzoate or sodium salicylate
	Polyvinyl chloride	White smoke: mixture of potassium nitrate and sulfur
		Colored smoke: mixture of potassium chlorate, sulfur, and organic dye

**Sample Exercise 7.5****Electron Energies**

Calculate the energy required to remove the electron from a hydrogen atom in its ground state.

**Solution**

Removing the electron from a hydrogen atom in its ground state corresponds to taking the electron from  $n_{\text{initial}} = 1$  to  $n_{\text{final}} = \infty$ . Thus

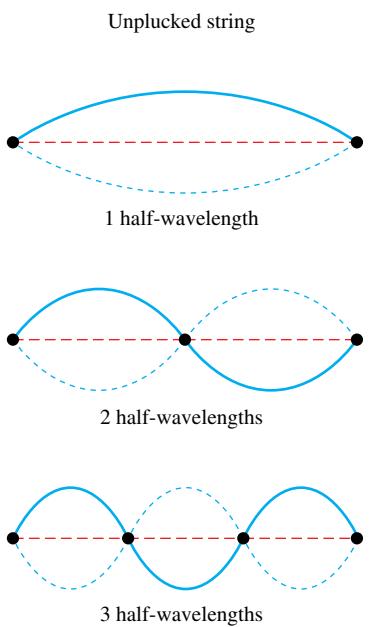
$$\begin{aligned}\Delta E &= -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{\infty} - \frac{1}{1^2} \right) \\ &= -2.178 \times 10^{-18} \text{ J}(0 - 1) = 2.178 \times 10^{-18} \text{ J}\end{aligned}$$

The energy required to remove the electron from a hydrogen atom in its ground state is  $2.178 \times 10^{-18} \text{ J}$ .

**See Exercises 7.51 and 7.52.**

**Visualization: Flame Tests**

Although Bohr's model fits the energy levels for hydrogen, it is a fundamentally incorrect model for the hydrogen atom.



**FIGURE 7.9**

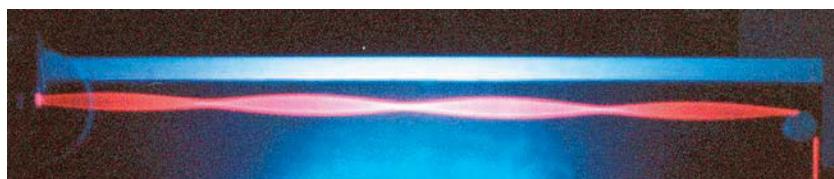
The standing waves caused by the vibration of a guitar string fastened at both ends. Each dot represents a node (a point of zero displacement).

At first Bohr's model appeared to be very promising. The energy levels calculated by Bohr closely agreed with the values obtained from the hydrogen emission spectrum. However, when Bohr's model was applied to atoms other than hydrogen, it did not work at all. Although some attempts were made to adapt the model using elliptical orbits, it was concluded that Bohr's model is fundamentally incorrect. The model is, however, very important historically, because it showed that the observed quantization of energy in atoms could be explained by making rather simple assumptions. Bohr's model paved the way for later theories. It is important to realize, however, that the current theory of atomic structure is in no way derived from the Bohr model. Electrons do *not* move around the nucleus in circular orbits, as we shall see later in this chapter.

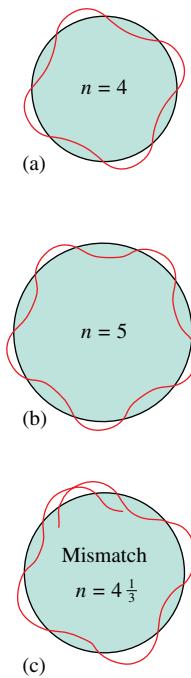
## 7.5 The Quantum Mechanical Model of the Atom

By the mid-1920s it had become apparent that the Bohr model could not be made to work. A totally new approach was needed. Three physicists were at the forefront of this effort: Werner Heisenberg (1901–1976), Louis de Broglie (1892–1987), and Erwin Schrödinger (1887–1961). The approach they developed became known as *wave mechanics* or, more commonly, *quantum mechanics*. As we have already seen, de Broglie originated the idea that the electron, previously considered to be a particle, also shows wave properties. Pursuing this line of reasoning, Schrödinger, an Austrian physicist, decided to attack the problem of atomic structure by giving emphasis to the wave properties of the electron. To Schrödinger and de Broglie, the electron bound to the nucleus seemed similar to a **standing wave**, and they began research on a wave mechanical description of the atom.

The most familiar example of standing waves occurs in association with musical instruments such as guitars or violins, where a string attached at both ends vibrates to produce a musical tone. The waves are described as “standing” because they are stationary;



Wave-generating apparatus.

**FIGURE 7.10**

The hydrogen electron visualized as a standing wave around the nucleus. The circumference of a particular circular orbit would have to correspond to a whole number of wavelengths, as shown in (a) and (b), or else destructive interference occurs, as shown in (c). This is consistent with the fact that only certain electron energies are allowed; the atom is quantized. (Although this idea encouraged scientists to use a wave theory, it does not mean that the electron really travels in circular orbits.)

the waves do not travel along the length of the string. The motions of the string can be explained as a combination of simple waves of the type shown in Fig. 7.9. The dots in this figure indicate the nodes, or points of zero lateral (sideways) displacement, for a given wave. Note that there are limitations on the allowed wavelengths of the standing wave. Each end of the string is fixed, so there is always a node at each end. This means that there must be a whole number of *half* wavelengths in any of the allowed motions of the string (see Fig. 7.9). Standing waves can be illustrated using the wave generator shown in the photo below.

A similar situation results when the electron in the hydrogen atom is imagined to be a standing wave. As shown in Fig. 7.10, only certain circular orbits have a circumference into which a whole number of wavelengths of the standing electron wave will “fit.” All other orbits would produce destructive interference of the standing electron wave and are not allowed. This seemed like a possible explanation for the observed quantization of the hydrogen atom, so Schrödinger worked out a model for the hydrogen atom in which the electron was assumed to behave as a standing wave.

It is important to recognize that Schrödinger could not be sure that this idea would work. The test had to be whether or not the model would correctly fit the experimental data on hydrogen and other atoms. The physical principles for describing standing waves were well known in 1925 when Schrödinger decided to treat the electron in this way. His mathematical treatment is too complicated to be detailed here. However, the form of Schrödinger’s equation is

$$\hat{H}\psi = E\psi$$

where  $\psi$ , called the **wave function**, is a function of the coordinates ( $x$ ,  $y$ , and  $z$ ) of the electron’s position in three-dimensional space and  $\hat{H}$  represents a set of mathematical instructions called an *operator*. In this case, the operator contains mathematical terms that produce the total energy of the atom when they are applied to the wave function.  $E$  represents the total energy of the atom (the sum of the potential energy due to the attraction between the proton and electron and the kinetic energy of the moving electron). When this equation is analyzed, many solutions are found. Each solution consists of a wave function  $\psi$  that is characterized by a particular value of  $E$ . A specific wave function is often called an **orbital**.

To illustrate the most important ideas of the **quantum (wave) mechanical model** of the atom, we will first concentrate on the wave function corresponding to the lowest energy for the hydrogen atom. This wave function is called the  $1s$  orbital. The first point of interest is to explore the meaning of the word *orbital*. As we will see, this is not a trivial matter. One thing is clear: An orbital is *not* a Bohr orbit. The electron in the hydrogen  $1s$  orbital is not moving around the nucleus in a circular orbit. How, then, is the electron moving? The answer is quite surprising: *We do not know*. The wave function gives us no information about the detailed pathway of the electron. This is somewhat disturbing. When we solve problems involving the motions of particles in the macroscopic world, we are able to predict their pathways. For example, when two billiard balls with known velocities collide, we can predict their motions after the collision. However, we cannot predict the electron’s motion from the  $1s$  orbital function. Does this mean that the theory is wrong? Not necessarily: We have already learned that an electron does not behave much like a billiard ball, so we must examine the situation closely before we discard the theory.

To help us understand the nature of an orbital, we need to consider a principle discovered by Werner Heisenberg, one of the primary developers of quantum mechanics. Heisenberg’s mathematical analysis led him to a surprising conclusion: *There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time*. This is a statement of the **Heisenberg uncertainty principle**. Stated mathematically, the uncertainty principle is

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

where  $\Delta x$  is the uncertainty in a particle's position,  $\Delta(mv)$  is the uncertainty in a particle's momentum, and  $h$  is Planck's constant. Thus the minimum uncertainty in the product  $\Delta \cdot \Delta(mv)$  is  $h/4\pi$ . What this equation really says is that the more accurately we know a particle's position, the less accurately we can know its momentum, and vice versa. This limitation is so small for large particles such as baseballs or billiard balls that it is unnoticed. However, for a small particle such as the electron, the limitation becomes quite important. Applied to the electron, the uncertainty principle implies that we cannot know the exact motion of the electron as it moves around the nucleus. It is therefore not appropriate to assume that the electron is moving around the nucleus in a well-defined orbit, as in the Bohr model.

### The Physical Meaning of a Wave Function

Given the limitations indicated by the uncertainty principle, what then is the physical meaning of a wave function for an electron? That is, what is an atomic orbital? Although the wave function itself has no easily visualized meaning, the square of the function does have a definite physical significance. *The square of the function indicates the probability of finding an electron near a particular point in space.* For example, suppose we have two positions in space, one defined by the coordinates  $x_1$ ,  $y_1$ , and  $z_1$  and the other by the coordinates  $x_2$ ,  $y_2$ , and  $z_2$ . The relative probability of finding the electron at positions 1 and 2 is given by substituting the values of  $x$ ,  $y$ , and  $z$  for the two positions into the wave function, squaring the function value, and computing the following ratio:

$$\frac{[\psi(x_1, y_1, z_1)]^2}{[\psi(x_2, y_2, z_2)]^2} = \frac{N_1}{N_2}$$

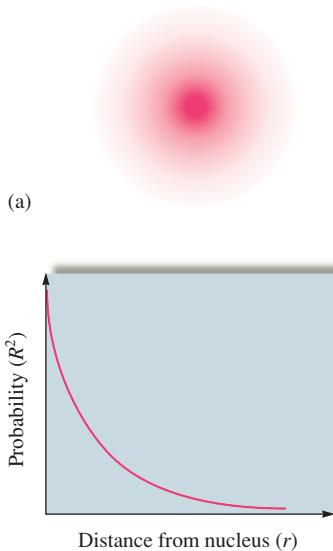
The quotient  $N_1/N_2$  is the ratio of the probabilities of finding the electron at positions 1 and 2. For example, if the value of the ratio  $N_1/N_2$  is 100, the electron is 100 times more likely to be found at position 1 than at position 2. The model gives no information concerning when the electron will be at either position or how it moves between the positions. This vagueness is consistent with the concept of the Heisenberg uncertainty principle.

The square of the wave function is most conveniently represented as a **probability distribution**, in which the intensity of color is used to indicate the probability value near a given point in space. The probability distribution for the hydrogen 1s wave function (orbital) is shown in Fig. 7.11(a). The best way to think about this diagram is as a three-dimensional time exposure with the electron as a tiny moving light. The more times the electron visits a particular point, the darker the negative becomes. Thus the darkness of a point indicates the probability of finding an electron at that position. This diagram is also known as an *electron density map*; *electron density* and *electron probability* mean the same thing. When a chemist uses the term *atomic orbital*, he or she is probably picturing an electron density map of this type.

Another way of representing the electron probability distribution for the 1s wave function is to calculate the probability at points along a line drawn outward in any direction from the nucleus. The result is shown in Fig. 7.11(b). Note that the probability of finding the electron at a particular position is greatest close to the nucleus and drops off rapidly as the distance from the nucleus increases. We are also interested in knowing the *total* probability of finding the electron in the hydrogen atom at a particular *distance* from the nucleus. Imagine that the space around the hydrogen nucleus is made up of a series of thin spherical shells (rather like layers in an onion), as shown in Fig. 7.12(a). When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, the plot in Fig. 7.12(b) is obtained. This graph is called the **radial probability distribution**.

The maximum in the curve occurs because of two opposing effects. The probability of finding an electron at a particular position is greatest near the nucleus, but the volume

Probability is the likelihood, or odds, that something will occur.

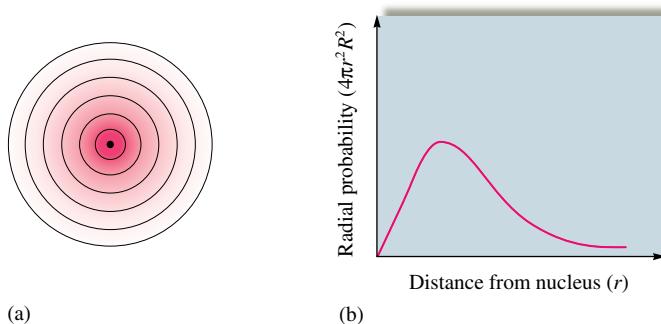


**FIGURE 7.11**

(a) The probability distribution for the hydrogen 1s orbital in three-dimensional space. (b) The probability of finding the electron at points along a line drawn from the nucleus outward in any direction for the hydrogen 1s orbital.

**FIGURE 7.12**

(a) Cross section of the hydrogen 1s orbital probability distribution divided into successive thin spherical shells. (b) The radial probability distribution. A plot of the total probability of finding the electron in each thin spherical shell as a function of distance from the nucleus.



$1 \text{ \AA} = 10^{-10} \text{ m}$ ; the angstrom is most often used as the unit for atomic radius because of its convenient size. Another convenient unit is the picometer:

$$1 \text{ pm} = 10^{-12} \text{ m}$$



Visualization: 1s Orbital

of the spherical shell increases with distance from the nucleus. Therefore, as we move away from the nucleus, the probability of finding the electron at a given position decreases, but we are summing more positions. Thus the total probability increases to a certain radius and then decreases as the electron probability at each position becomes very small. For the hydrogen 1s orbital, the maximum radial probability (the distance at which the electron is most likely to be found) occurs at a distance of  $5.29 \times 10^{-2} \text{ nm}$  or  $0.529 \text{ \AA}$  from the nucleus. Interestingly, this is exactly the radius of the innermost orbit in the Bohr model. Note that in Bohr's model the electron is assumed to have a circular path and so is *always* found at this distance. In the quantum mechanical model, the specific electron motions are unknown, and this is the *most probable* distance at which the electron is found.

One more characteristic of the hydrogen 1s orbital that we must consider is its size. As we can see from Fig. 7.11, the size of this orbital cannot be defined precisely, since the probability never becomes zero (although it drops to an extremely small value at large values of  $r$ ). So, in fact, the hydrogen 1s orbital has no distinct size. However, it is useful to have a definition of relative orbital size. *The definition most often used by chemists to describe the size of the hydrogen 1s orbital is the radius of the sphere that encloses 90% of the total electron probability.* That is, 90% of the time the electron is inside this sphere.

So far we have described only the lowest-energy wave function in the hydrogen atom, the 1s orbital. Hydrogen has many other orbitals, which we will describe in the next section. However, before we proceed, we should summarize what we have said about the meaning of an atomic orbital. An orbital is difficult to define precisely at an introductory level. Technically, an orbital is a wave function. However, it is usually most helpful to picture an orbital as a three-dimensional electron density map. That is, an electron "in" a particular atomic orbital is assumed to exhibit the electron probability indicated by the orbital map.

## 7.6 Quantum Numbers

When we solve the Schrödinger equation for the hydrogen atom, we find many wave functions (orbitals) that satisfy it. Each of these orbitals is characterized by a series of numbers called **quantum numbers**, which describe various properties of the orbital:

The **principal quantum number** ( $n$ ) has integral values: 1, 2, 3, . . . . The principal quantum number is related to the size and energy of the orbital. As  $n$  increases, the orbital becomes larger and the electron spends more time farther from the nucleus. An increase in  $n$  also means higher energy, because the electron is less tightly bound to the nucleus, and the energy is less negative.

The **angular momentum quantum number** ( $\ell$ ) has integral values from 0 to  $n - 1$  for each value of  $n$ . This quantum number is related to the shape of atomic orbitals. The value of  $\ell$  for a particular orbital is commonly assigned a letter:  $\ell = 0$  is called s;

**TABLE 7.1 The Angular Momentum Quantum Numbers and Corresponding Letters Used to Designate Atomic Orbitals**

<b>Value of <math>\ell</math></b>	0	1	2	3	4
<b>Letter Used</b>	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>

**Number of Orbitals per Subshell***s* = 1*p* = 3*d* = 5*f* = 7*g* = 9**TABLE 7.2 Quantum Numbers for the First Four Levels of Orbitals in the Hydrogen Atom**

<b><i>n</i></b>	<b><math>\ell</math></b>	<b>Orbital Designation</b>	<b><math>m_\ell</math></b>	<b>Number of Orbitals</b>
1	0	1 <i>s</i>	0	1
	0	2 <i>s</i>	0	1
	1	2 <i>p</i>	-1, 0, +1	3
	0	3 <i>s</i>	0	1
	1	3 <i>p</i>	-1, 0, 1	3
	2	3 <i>d</i>	-2, -1, 0, 1, 2	5
4	0	4 <i>s</i>	0	1
	1	4 <i>p</i>	-1, 0, 1	3
	2	4 <i>d</i>	-2, -1, 0, 1, 2	5
	3	4 <i>f</i>	-3, -2, -1, 0, 1, 2, 3	7

$\ell = 1$  is called *p*;  $\ell = 2$  is called *d*;  $\ell = 3$  is called *f*. This system arises from early spectral studies and is summarized in Table 7.1.

The **magnetic quantum number** ( $m_\ell$ ) has integral values between  $\ell$  and  $-\ell$ , including zero. The value of  $m_\ell$  is related to the orientation of the orbital in space relative to the other orbitals in the atom.

The first four levels of orbitals in the hydrogen atom are listed with their quantum numbers in Table 7.2. Note that each set of orbitals with a given value of  $\ell$  (sometimes called a **subshell**) is designated by giving the value of  $n$  and the letter for  $\ell$ . Thus an orbital where  $n = 2$  and  $\ell = 1$  is symbolized as  $2p$ . There are three  $2p$  orbitals, which have different orientations in space. We will describe these orbitals in the next section.

$$\begin{aligned} n &= 1, 2, 3, \dots \\ \ell &= 0, 1, \dots (n-1) \\ m_\ell &= -\ell, \dots 0, \dots +\ell \end{aligned}$$

**Sample Exercise 7.6****Electron Subshells**

For principal quantum level  $n = 5$ , determine the number of allowed subshells (different values of  $\ell$ ), and give the designation of each.

**Solution**

For  $n = 5$ , the allowed values of  $\ell$  run from 0 to 4 ( $n - 1 = 5 - 1$ ). Thus the subshells and their designations are

$$\begin{array}{ccccc} \ell = 0 & \ell = 1 & \ell = 2 & \ell = 3 & \ell = 4 \\ 5s & 5p & 5d & 5f & 5g \end{array}$$

*See Exercises 7.57 through 7.59.*

## 7.7 Orbital Shapes and Energies

We have seen that the meaning of an orbital is represented most clearly by a probability distribution. Each orbital in the hydrogen atom has a unique probability distribution. We also saw that another means of representing an orbital is by the surface that surrounds 90% of the total electron probability. These two types of representations for the hydrogen 1s, 2s, and 3s orbitals are shown in Fig. 7.13. Note the characteristic spherical shape of each of the s orbitals. Note also that the 2s and 3s orbitals contain areas of high probability separated by areas of zero probability. These latter areas are called **nodal surfaces**, or simply **nodes**. The number of nodes increases as  $n$  increases. For s orbitals, the number of nodes is given by  $n - 1$ . For our purposes, however, we will think of s orbitals only in terms of their overall spherical shape, which becomes larger as the value of  $n$  increases.

The two types of representations for the 2p orbitals (there are no 1p orbitals) are shown in Fig. 7.14. Note that the p orbitals are not spherical like s orbitals but have two *lobes* separated by a node at the nucleus. The p orbitals are labeled according to the axis of the xyz coordinate system along which the lobes lie. For example, the 2p orbital with lobes centered along the x axis is called the  $2p_x$  orbital.

At this point it is useful to remember that mathematical functions have signs. For example, a simple sine wave (see Fig. 7.1) oscillates from positive to negative and repeats this pattern. Atomic orbital functions also have signs. The functions for s orbitals are positive everywhere in three-dimensional space. That is, when the s orbital function is evaluated at any point in space, it results in a positive number. In contrast, the p orbital functions have different signs in different regions of space. For example, the  $p_z$  orbital has a positive sign in all the regions of space in which z is positive and has a negative sign when z is negative. This behavior is indicated in Fig. 7.14(b) by the positive and negative signs inside their boundary surfaces. It is important to understand that these are mathematical signs, not charges. Just as a sine wave has alternating positive and negative phases, so too p orbitals have positive and negative phases. The phases of the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals are indicated in Fig. 7.14(b).

As you might expect from our discussion of the s orbitals, the 3p orbitals have a more complex probability distribution than that of the 2p orbitals (see Fig. 7.15), but they can still be represented by the same boundary surface shapes. The surfaces just grow larger as the value of  $n$  increases.

There are no d orbitals that correspond to principal quantum levels  $n = 1$  and  $n = 2$ . The d orbitals ( $\ell = 2$ ) first occur in level  $n = 3$ . The five 3d orbitals have the shapes shown in Fig. 7.16. The d orbitals have two different fundamental shapes. Four of the orbitals ( $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ , and  $d_{x^2-y^2}$ ) have four lobes centered in the plane indicated in the orbital label. Note that  $d_{xy}$  and  $d_{x^2-y^2}$  are both centered in the xy plane; however, the lobes of  $d_{x^2-y^2}$  lie *along* the x and y axes, while the lobes of  $d_{xy}$  lie *between* the axes. The fifth orbital,  $d_{z^2}$ , has a unique shape with two lobes along the z axis and a belt centered in the xy plane. The d orbitals for levels  $n > 3$  look like the 3d orbitals but have larger lobes.

The f orbitals first occur in level  $n = 4$ , and as might be expected, they have shapes even more complex than those of the d orbitals. Figure 7.17 shows representations of the 4f orbitals ( $\ell = 3$ ) along with their designations. These orbitals are not involved in the bonding in any of the compounds we will consider in this text. Their shapes and labels are simply included for completeness.

So far we have talked about the shapes of the hydrogen atomic orbitals but not about their energies. For the hydrogen atom, the energy of a particular orbital is determined by its value of  $n$ . Thus *all* orbitals with the same value of  $n$  have the *same energy*—they are said to be **degenerate**. This is shown in Fig. 7.18, where the energies for the orbitals in the first three quantum levels for hydrogen are shown.



Visualization: Orbital Energies

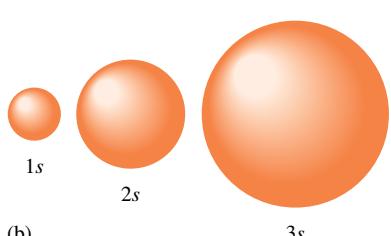
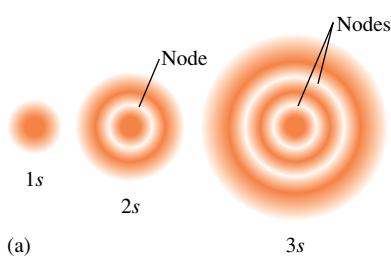


Visualization:  $2p_x$ ,  $2p_y$ ,  $2p_z$  Orbitals

$n$  value  
↓  
 $2p_x \leftarrow$  orientation in space  
↑  
 $\ell$  value

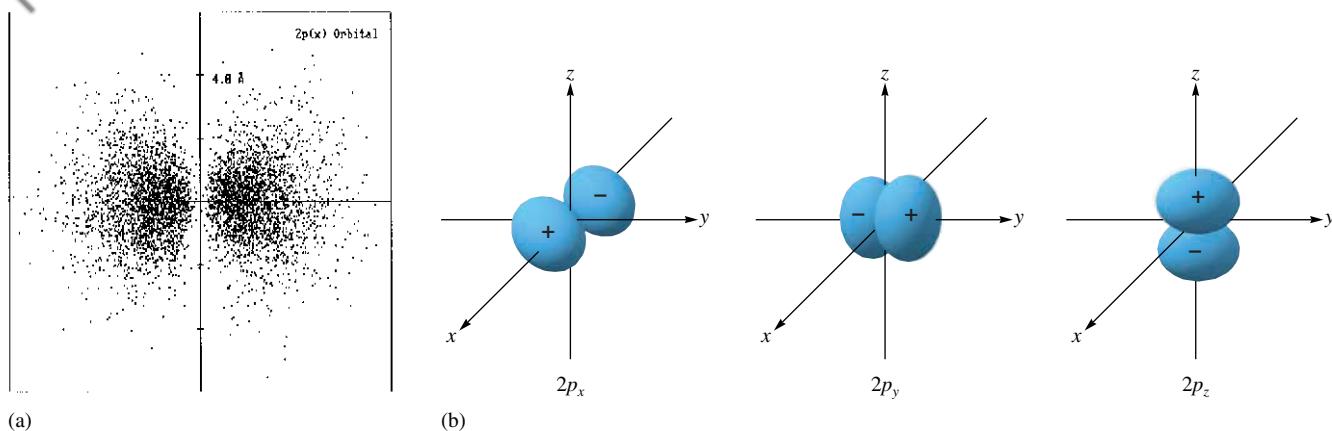


Visualization:  
 $3d_{x^2-y^2}$ ,  $3d_{xy}$ ,  $3d_{xz}$ ,  $3d_{yz}$ ,  $3d_{z^2}$  Orbitals



**FIGURE 7.13**

Two representations of the hydrogen 1s, 2s, and 3s orbitals. (a) The electron probability distribution. (b) The surface that contains 90% of the total electron probability (the size of the orbital, by definition).

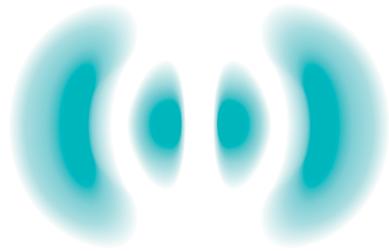
**FIGURE 7.14**

Representation of the 2p orbitals. (a) The electron probability distribution for a 2p orbital. (Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC 2402; reprinted with permission.) (b) The boundary surface representations of all three 2p orbitals. Note that the signs inside the surface indicate the phases (signs) of the orbital in that region of space.

Hydrogen's single electron can occupy any of its atomic orbitals. However, in the lowest energy state, the *ground state*, the electron resides in the 1s orbital. If energy is put into the atom, the electron can be transferred to a higher-energy orbital, producing an *excited state*.

### A Summary of the Hydrogen Atom

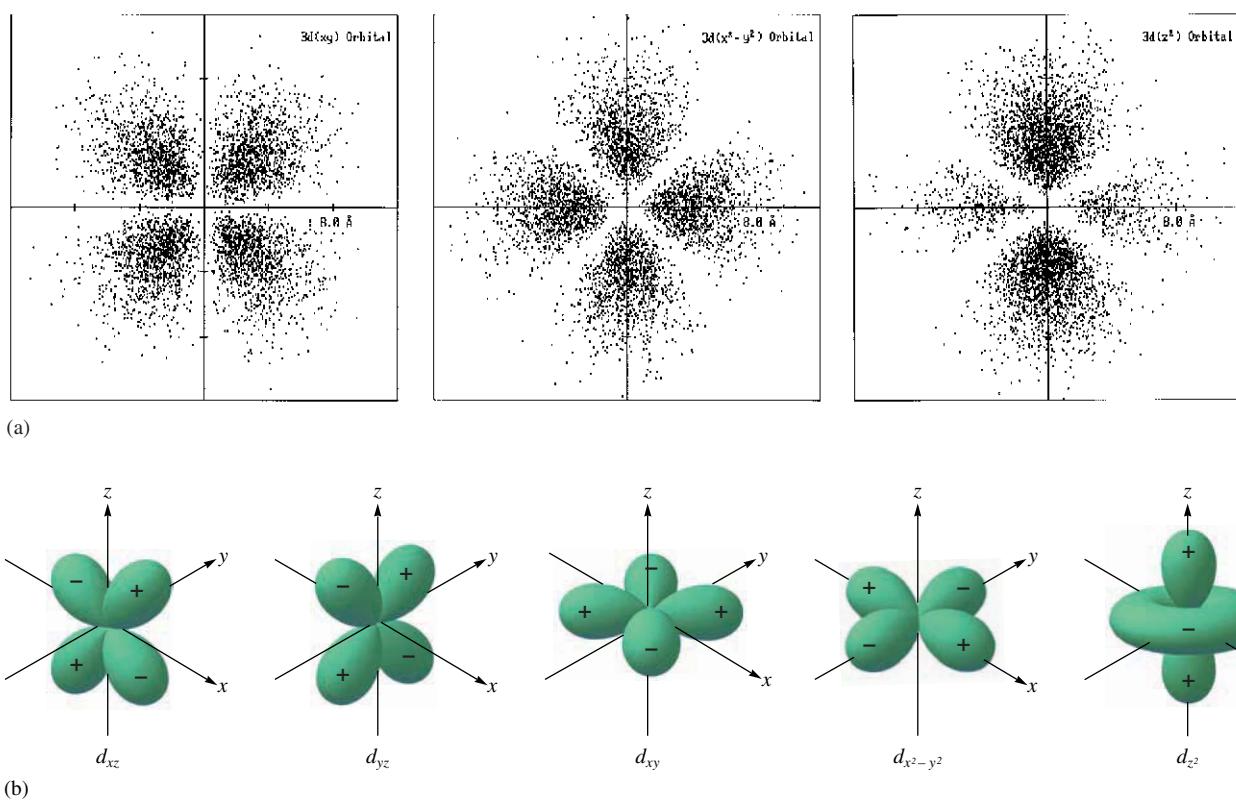
- In the quantum (wave) mechanical model, the electron is viewed as a standing wave. This representation leads to a series of wave functions (orbitals) that describe the possible energies and spatial distributions available to the electron.
- In agreement with the Heisenberg uncertainty principle, the model cannot specify the detailed electron motions. Instead, the square of the wave function represents the probability distribution of the electron in that orbital. This allows us to picture orbitals in terms of probability distributions, or electron density maps.
- The size of an orbital is arbitrarily defined as the surface that contains 90% of the total electron probability.
- The hydrogen atom has many types of orbitals. In the ground state, the single electron resides in the 1s orbital. The electron can be excited to higher-energy orbitals if energy is put into the atom.

**FIGURE 7.15**

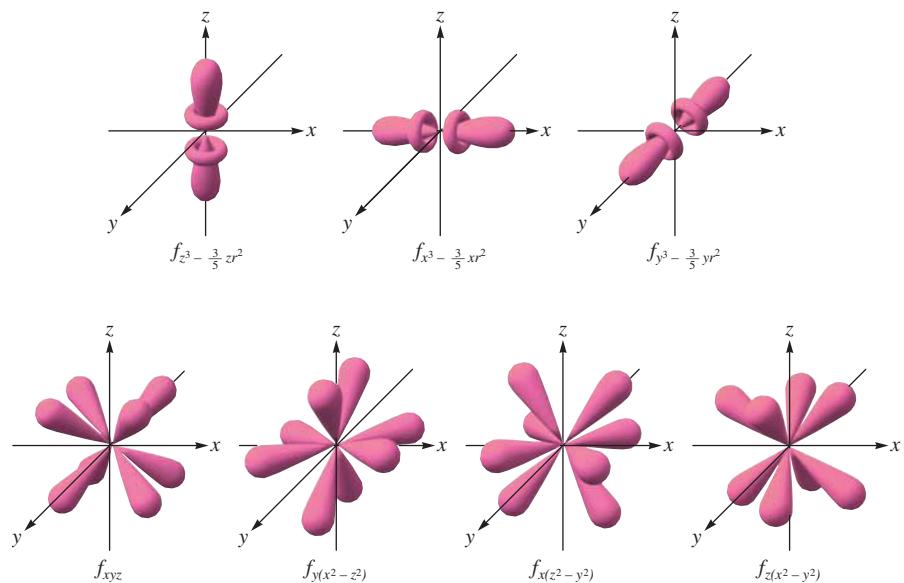
A cross section of the electron probability distribution for a 3p orbital.

## 7.8 Electron Spin and the Pauli Principle

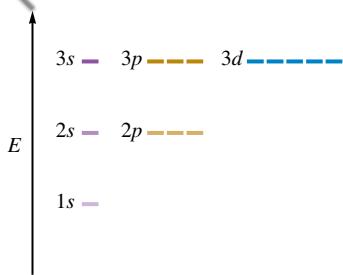
The concept of **electron spin** was developed by Samuel Goudsmit and George Uhlenbeck while they were graduate students at the University of Leyden in the Netherlands. They found that a fourth quantum number (in addition to  $n$ ,  $\ell$ , and  $m_\ell$ ) was necessary to account for the details of the emission spectra of atoms. The spectral data indicate that the electron has a magnetic moment with two possible orientations when the atom is placed in an external magnetic field. Since they knew from classical physics that a spinning charge produces a magnetic moment, it seemed reasonable to assume that the electron could have two spin states, thus producing the two oppositely directed magnetic moments

**FIGURE 7.16**

Representation of the 3d orbitals. (a) Electron density plots of selected 3d orbitals. (Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC 2402; reprinted with permission.) (b) The boundary surfaces of all five 3d orbitals, with the signs (phases) indicated.

**FIGURE 7.17**

Representation of the 4f orbitals in terms of their boundary surfaces.

**FIGURE 7.18**

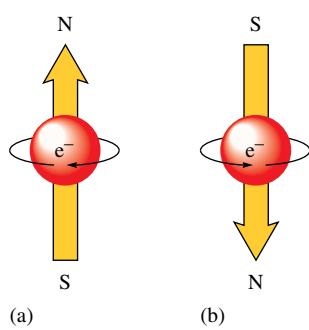
Orbital energy levels for the hydrogen atom.

(see Fig. 7.19). The new quantum number adopted to describe this phenomenon, called the **electron spin quantum number** ( $m_s$ ), can have only one of two values,  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . We can interpret this to mean that the electron can spin in one of two opposite directions, although other interpretations also have been suggested.

For our purposes, the main significance of electron spin is connected with the postulate of Austrian physicist Wolfgang Pauli (1900–1958): *In a given atom no two electrons can have the same set of four quantum numbers ( $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$ )*. This is called the **Pauli exclusion principle**. Since electrons in the same orbital have the same values of  $n$ ,  $\ell$ , and  $m_\ell$ , this postulate says that they must have different values of  $m_s$ . Then, since only two values of  $m_s$  are allowed, *an orbital can hold only two electrons, and they must have opposite spins*. This principle will have important consequences as we use the atomic model to account for the electron arrangements of the atoms in the periodic table.

$$m_s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Each orbital can hold a maximum of two electrons.

**FIGURE 7.19**

A picture of the spinning electron. Spinning in one direction, the electron produces the magnetic field oriented as shown in (a). Spinning in the opposite direction, it gives a magnetic field of the opposite orientation, as shown in (b).

## 7.9 Polyelectronic Atoms

The quantum mechanical model gives a description of the hydrogen atom that agrees very well with experimental data. However, the model would not be very useful if it did not account for the properties of all the other atoms as well.

To see how the model applies to **polyelectronic atoms**, that is, atoms with more than one electron, let's consider helium, which has two protons in its nucleus and two electrons:



Three energy contributions must be considered in the description of the helium atom: (1) the kinetic energy of the electrons as they move around the nucleus, (2) the potential energy of attraction between the nucleus and the electrons, and (3) the potential energy of repulsion between the two electrons.

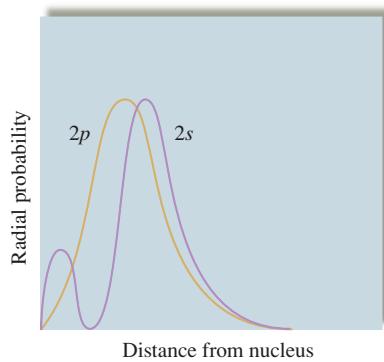
Although the helium atom can be readily described in terms of the quantum mechanical model, the Schrödinger equation that results cannot be solved exactly. The difficulty arises in dealing with the repulsions between the electrons. Since the electron pathways are unknown, the electron repulsions cannot be calculated exactly. This is called the *electron correlation problem*.

The electron correlation problem occurs with all polyelectronic atoms. To treat these systems using the quantum mechanical model, we must make approximations. Most commonly, the approximation used is to treat each electron as if it were moving in a *field of charge that is the net result of the nuclear attraction and the average repulsions of all the other electrons*.

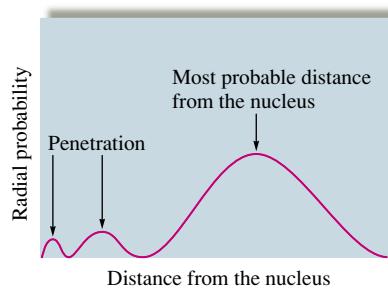
For example, consider the sodium atom, which has 11 electrons:



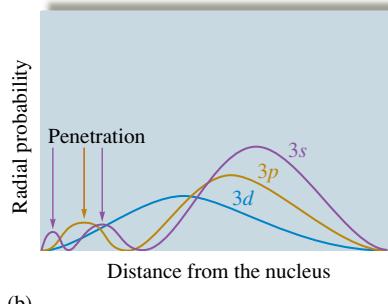
Now let's single out the outermost electron and consider the forces this electron feels. The electron clearly is attracted to the highly charged nucleus. However, the electron also feels the repulsions caused by the other 10 electrons. The net effect is that the electron is not

**FIGURE 7.20**

A comparison of the radial probability distributions of the 2s and 2p orbitals.



(a)



(b)

**FIGURE 7.21**

(a) The radial probability distribution for an electron in a 3s orbital. Although a 3s electron is mostly found far from the nucleus, there is a small but significant probability (shown by the arrows) of its being found close to the nucleus. The 3s electron penetrates the shield of inner electrons. (b) The radial probability distribution for the 3s, 3p, and 3d orbitals. The arrows indicate that the s orbital (red arrow) allows greater electron penetration than the p orbital (yellow arrow) does; the d orbital allows minimal electron penetration.

bound nearly as tightly to the nucleus as it would be if the other electrons were not present. We say that the electron is *screened* or *shielded* from the nuclear charge by the repulsions of the other electrons.

This picture of polyelectronic atoms leads to *hydrogenlike orbitals* for these atoms. They have the same general shapes as the orbitals for hydrogen, but their sizes and energies are different. The differences occur because of the interplay between nuclear attraction and the electron repulsions.

One especially important difference between polyelectronic atoms and the hydrogen atom is that for hydrogen all the orbitals in a given principal quantum level have the same energy (they are said to be *degenerate*). This is not the case for polyelectronic atoms, where we find that for a given principal quantum level the orbitals vary in energy as follows:

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

In other words, when electrons are placed in a particular quantum level, they “prefer” the orbitals in the order *s*, *p*, *d*, and then *f*. Why does this happen? Although the concept of orbital energies is a complicated matter, we can qualitatively understand why the 2s orbital has a lower energy than the 2p orbital in a polyelectronic atom by looking at the probability profiles of these orbitals (see Fig. 7.20). Notice that the 2p orbital has its maximum probability closer to the nucleus than for the 2s. This might lead us to predict that the 2p would be preferable (lower energy) to the 2s orbital. However, notice the small hump of electron density that occurs in the 2s profile very near the nucleus. This means that although an electron in the 2s orbital spends most of its time a little farther from the nucleus than does an electron in the 2p orbital, it spends a small but very significant amount of time very near the nucleus. We say that the 2s electron *penetrates* to the nucleus more than one in the 2p orbital. This *penetration effect* causes an electron in a 2s orbital to be attracted to the nucleus more strongly than an electron in a 2p orbital. That is, the 2s orbital is lower in energy than the 2p orbitals in a polyelectronic atom.

The same thing happens in the other principal quantum levels as well. Figure 7.21 shows the radial probability profiles for the 3s, 3p, and 3d orbitals. Note again the hump in the 3s profile very near the nucleus. The innermost hump for the 3p is farther out, which causes the energy of the 3s orbital to be lower than that of the 3p. Notice that the 3d orbital has its maximum probability closer to the nucleus than either the 3s or 3p does, but its absence of probability near the nucleus causes it to be highest in energy of the three orbitals. The relative energies of the orbitals for  $n = 3$  are

$$E_{3s} < E_{3p} < E_{3d}$$

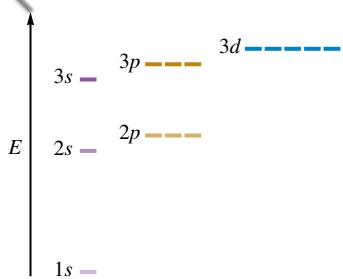
In general, the more effectively an orbital allows its electron to penetrate the shielding electrons to be close to the nuclear charge, the lower is the energy of that orbital.

A summary diagram of the orders of the orbital energies for polyelectronic atoms is represented in Fig. 7.22. We will use these orbitals in Section 7.11 to show how the electrons are arranged in polyelectronic atoms.

## 7.10 The History of the Periodic Table

The modern periodic table contains a tremendous amount of useful information. In this section we will discuss the origin of this valuable tool; later we will see how the quantum mechanical model for the atom explains the periodicity of chemical properties. Certainly the greatest triumph of the quantum mechanical model is its ability to account for the arrangement of the elements in the periodic table.

The periodic table was originally constructed to represent the patterns observed in the chemical properties of the elements. As chemistry progressed during the eighteenth and nineteenth centuries, it became evident that the earth is composed of a great many

**FIGURE 7.22**

The orders of the energies of the orbitals in the first three levels of polyelectronic atoms.

elements with very different properties. Things are much more complicated than the simple model of earth, air, fire, and water suggested by the ancients. At first, the array of elements and properties was bewildering. Gradually, however, patterns were noticed.

The first chemist to recognize patterns was Johann Dobereiner (1780–1849), who found several groups of three elements that have similar properties, for example, chlorine, bromine, and iodine. However, as Dobereiner attempted to expand this model of *triads* (as he called them) to the rest of the known elements, it became clear that it was severely limited.

The next notable attempt was made by the English chemist John Newlands, who in 1864 suggested that elements should be arranged in *octaves*, based on the idea that certain properties seemed to repeat for every eighth element in a way similar to the musical scale, which repeats for every eighth tone. Even though this model managed to group several elements with similar properties, it was not generally successful.

The present form of the periodic table was conceived independently by two chemists: the German Julius Lothar Meyer (1830–1895) and Dmitri Ivanovich Mendeleev (1834–1907), a Russian (Fig. 7.23). Usually Mendeleev is given most of the credit, because it was he who emphasized how useful the table could be in predicting the existence and properties of still unknown elements. For example, in 1872 when Mendeleev first published his table (see Fig. 7.24), the elements gallium, scandium, and germanium were unknown. Mendeleev correctly predicted the existence and properties of these elements from gaps in his periodic table. The data for germanium (which Mendeleev called “*ekasilicon*”) are shown in Table 7.3. Note the excellent agreement between the actual values and Mendeleev’s predictions, which were based on the properties of other members in the group of elements similar to germanium.

Using his table, Mendeleev also was able to correct several values for atomic masses. For example, the original atomic mass of 76 for indium was based on the assumption that indium oxide had the formula  $\text{InO}$ . This atomic mass placed indium, which has metallic properties, among the nonmetals. Mendeleev assumed the atomic mass was probably incorrect and proposed that the formula of indium oxide was really  $\text{In}_2\text{O}_3$ . Based on this correct formula, indium has an atomic mass of approximately 113, placing the element among the metals. Mendeleev also corrected the atomic masses of beryllium and uranium.

Because of its obvious usefulness, Mendeleev’s periodic table was almost universally adopted, and it remains one of the most valuable tools at the chemist’s disposal. For example, it is still used to predict the properties of elements recently discovered, as shown in Table 7.4.

A current version of the periodic table is shown inside the front cover of this book. The only fundamental difference between this table and that of Mendeleev is that it lists the elements in order by atomic number rather than by atomic mass. The reason for this will become clear later in this chapter as we explore the electron arrangements of the atom. Another recent format of the table is discussed in the following section.

**FIGURE 7.23**

Dmitri Ivanovich Mendeleev (1834–1907), born in Siberia as the youngest of 17 children, taught chemistry at the University of St. Petersburg. In 1860 Mendeleev heard the Italian chemist Cannizzaro lecture on a reliable method for determining the correct atomic masses of the elements. This important development paved the way for Mendeleev’s own brilliant contribution to chemistry—the periodic table. In 1861 Mendeleev returned to St. Petersburg, where he wrote a book on organic chemistry. Later Mendeleev also wrote a book on inorganic chemistry, and he was struck by the fact that the systematic approach characterizing organic chemistry was lacking in inorganic chemistry. In attempting to systematize inorganic chemistry, he eventually arranged the elements in the form of the periodic table.

Mendeleev was a versatile genius who was interested in many fields of science. He worked on many problems associated with Russia’s natural resources, such as coal, salt, and various metals. Being particularly interested in the petroleum industry, he visited the United States in 1876 to study the Pennsylvania oil fields. His interests also included meteorology and hot-air balloons. In 1887 he made an ascent in a balloon to study a total eclipse of the sun.

REIHEN	GRUPPE I.	GRUPPE II.	GRUPPE III.	GRUPPE IV.	GRUPPE V.	GRUPPE VI.	GRUPPE VII.	GRUPPE VIII.
	— R <sup>2</sup> O	— RO	— R <sup>2</sup> O <sub>3</sub>	RH <sub>4</sub> R <sub>2</sub> O <sub>2</sub>	RH <sub>3</sub> R <sub>2</sub> O <sub>5</sub>	RH <sub>2</sub> R <sub>2</sub> O <sub>3</sub>	RH R <sub>2</sub> O <sub>7</sub>	— R <sub>2</sub> O <sub>4</sub>
I	H=1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	

**FIGURE 7.24**

Mendeleev's early periodic table, published in 1872. Note the spaces left for missing elements with atomic masses 44, 68, 72, and 100.

(From *Annalen der Chemie und Pharmacie*, VIII, Supplementary Volume for 1872, page 511.)

**TABLE 7.3 Comparison of the Properties of Germanium as Predicted by Mendeleev and as Actually Observed**

Properties of Germanium	Predicted in 1871	Observed in 1886
Atomic weight	72	72.3
Density	5.5 g/cm <sup>3</sup>	5.47 g/cm <sup>3</sup>
Specific heat	0.31 J/(°C · g)	0.32 J/(°C · g)
Melting point	Very high	960°C
Oxide formula	RO <sub>2</sub>	GeO <sub>2</sub>
Oxide density	4.7 g/cm <sup>3</sup>	4.70 g/cm <sup>3</sup>
Chloride formula	RCl <sub>4</sub>	GeCl <sub>4</sub>
bp of chloride	100°C	86°C

**TABLE 7.4 Predicted Properties of Elements 113 and 114**

Property	Element 113	Element 114
Chemically like	Thallium	Lead
Atomic mass	297	298
Density	16 g/mL	14 g/mL
Melting point	430°C	70°C
Boiling point	1100°C	150°C

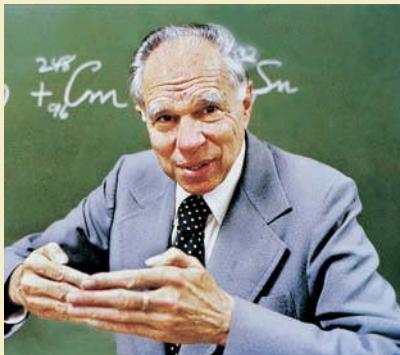


## CHEMICAL IMPACT

### The Growing Periodic Table

The periodic table of the elements has undergone significant changes since Mendeleev published his first version in 1869. In particular, in the past 60 years we have added 20 new elements beyond uranium. These so-called transuranium elements all have been synthesized using particle accelerators.

Edwin M. McMillan and Phillip H. Abelson succeeded in synthesizing the first transuranium element, neptunium (element 93), at the University of California, Berkeley, in 1940. In 1941, Glenn T. Seaborg synthesized and identified element 94 (plutonium), and over the next several years, researchers under his direction at UC Berkeley discovered nine other transuranium elements. In 1945 Seaborg suggested that the elements heavier than element 89 (actinium) were misplaced as transition metals and should be relocated on the periodic table in a series below the transition metals



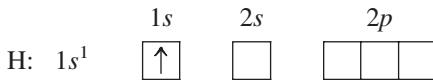
Dr. Glenn Seaborg.

(the actinide series). Seaborg was awarded a Nobel Prize in chemistry in 1951 for his contributions.

## 7.11 The Aufbau Principle and the Periodic Table

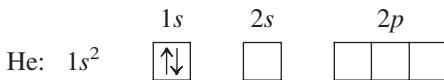
We can use the quantum mechanical model of the atom to show how the electron arrangements in the hydrogenlike atomic orbitals of the various atoms account for the organization of the periodic table. Our main assumption here is that all atoms have the same type of orbitals as have been described for the hydrogen atom. As protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogenlike orbitals. This is called the **aufbau principle**.

Hydrogen has one electron, which occupies the 1s orbital in its ground state. The configuration for hydrogen is written as  $1s^1$ , which can be represented by the following *orbital diagram*:

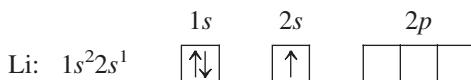


The arrow represents an electron spinning in a particular direction.

The next element, *helium*, has two electrons. Since two electrons with opposite spins can occupy an orbital, according to the Pauli exclusion principle, the electrons for helium are in the 1s orbital with opposite spins, producing a  $1s^2$  configuration:



*Lithium* has three electrons, two of which can go into the 1s orbital before the orbital is filled. Since the 1s orbital is the only orbital for  $n = 1$ , the third electron will occupy the lowest-energy orbital with  $n = 2$ , or the 2s orbital, giving a  $1s^22s^1$  configuration:



In recent years, three major research facilities have taken the lead in synthesizing new elements. Along with UC Berkeley, Nuclear Research in Dubna, Russia, and GSI in Darmstadt, Germany, were responsible for synthesizing elements 104–112 by the end of 1996.

As it turned out, naming the new elements has caused more controversy than anything else connected with their discovery. Traditionally, the discoverer of an element is allowed to name it. However, because there is some dispute among the researchers at Berkeley, Darmstadt, and Dubna about who really discovered the various elements, competing names were submitted. After years of controversy, the International Union of Pure and Applied Chemistry (IUPAC) finally settled on the names listed in the accompanying table.

The name for element 106 in honor of Glenn Seaborg caused special controversy because an element had never before been named for a living person (Dr. Seaborg died in 1999). However, because of Seaborg's commanding stature

in the scientific community, the name seaborgium was adopted.

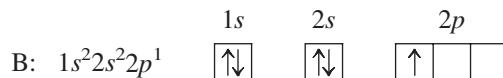
Names for the elements beyond 111 have not been decided, and these elements are represented on many periodic tables with three letters that symbolize their atomic numbers. More traditional names will no doubt be assigned in due time (hopefully with a minimum of controversy).

Atomic Number	Name	Symbol
104	Rutherfordium	Rf
105	Dubium	Db
106	Seaborgium	Sg
107	Bohrium	Bh
108	Hassium	Hs
109	Meitnerium	Mt
110	Darmstadtium	Ds
111	Roentgenium	Rg

The next element, *beryllium*, has four electrons, which occupy the 1s and 2s orbitals:



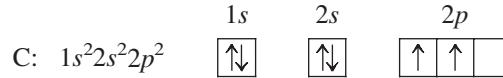
*Boron* has five electrons, four of which occupy the 1s and 2s orbitals. The fifth electron goes into the second type of orbital with  $n = 2$ , the 2p orbitals:



Since all the 2p orbitals have the same energy (are degenerate), it does not matter which 2p orbital the electron occupies.

*Carbon* is the next element and has six electrons. Two electrons occupy the 1s orbital, two occupy the 2s orbital, and two occupy 2p orbitals. Since there are three 2p orbitals with the same energy, the mutually repulsive electrons will occupy *separate* 2p orbitals. This behavior is summarized by **Hund's rule** (named for the German physicist F. H. Hund), which states that *the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerate orbitals*. By convention, the unpaired electrons are represented as having parallel spins (with spin "up").

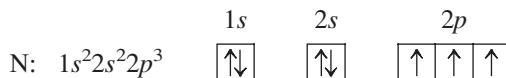
The configuration for carbon could be written  $1s^2 2s^2 2p^1 2p^1$  to indicate that the electrons occupy separate 2p orbitals. However, the configuration is usually given as  $1s^2 2s^2 2p^2$ , and it is understood that the electrons are in different 2p orbitals. The orbital diagram for carbon is



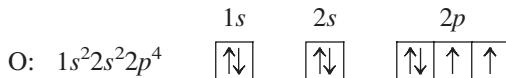
Note that the unpaired electrons in the 2p orbitals are shown with parallel spins.

For an atom with unfilled subshells, the lowest energy is achieved by electrons occupying separate orbitals with parallel spins, as far as allowed by the Pauli exclusion principle.

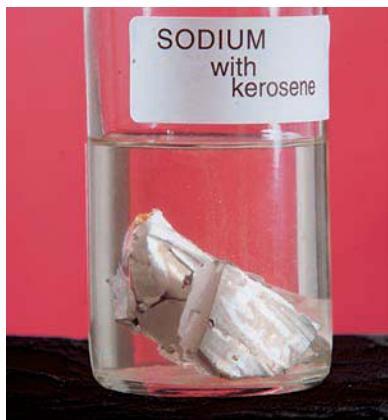
The configuration for *nitrogen*, which has seven electrons, is  $1s^22s^22p^3$ . The three electrons in the  $2p$  orbitals occupy separate orbitals with parallel spins:



The configuration for *oxygen*, which has eight electrons, is  $1s^22s^22p^4$ . One of the  $2p$  orbitals is now occupied by a pair of electrons with opposite spins, as required by the Pauli exclusion principle:



[Ne] is shorthand for  $1s^22s^22p^6$ .

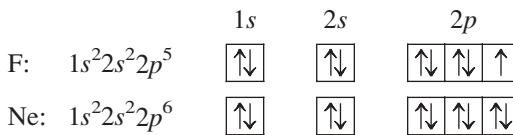


Sodium metal is so reactive that it is stored under kerosene to protect it from the oxygen in the air.



A vial containing potassium metal. The sealed vial contains an inert gas to protect the potassium from reacting with oxygen.

The orbital diagrams and electron configurations for *fluorine* (nine electrons) and *neon* (ten electrons) are as follows:



With neon, the orbitals with  $n = 1$  and  $n = 2$  are now completely filled.

For *sodium*, the first ten electrons occupy the  $1s$ ,  $2s$ , and  $2p$  orbitals, and the eleventh electron must occupy the first orbital with  $n = 3$ , the  $3s$  orbital. The electron configuration for sodium is  $1s^22s^22p^63s^1$ . To avoid writing the inner-level electrons, this configuration is often abbreviated as [Ne] $3s^1$ , where [Ne] represents the electron configuration of neon,  $1s^22s^22p^6$ .

The next element, *magnesium*, has the configuration  $1s^22s^22p^63s^2$ , or [Ne] $3s^2$ . Then the next six elements, *aluminum* through *argon*, have configurations obtained by filling the  $3p$  orbitals one electron at a time. Figure 7.25 summarizes the electron configurations of the first 18 elements by giving the number of electrons in the type of orbital occupied last.

At this point it is useful to introduce the concept of **valence electrons**, *the electrons in the outermost principal quantum level of an atom*. The valence electrons of the nitrogen atom, for example, are the  $2s$  and  $2p$  electrons. For the sodium atom, the valence electron is the electron in the  $3s$  orbital, and so on. Valence electrons are the most important electrons to chemists because they are involved in bonding, as we will see in the next two chapters. The inner electrons are known as **core electrons**.

Note in Fig. 7.25 that a very important pattern is developing: *The elements in the same group (vertical column of the periodic table) have the same valence electron configuration*. Remember that Mendeleev originally placed the elements in groups based on similarities in chemical properties. Now we understand the reason behind these

H $1s^1$							He $1s^2$
Li $2s^1$	Be $2s^2$		B $2p^1$	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$
Na $3s^1$	Mg $3s^2$		Al $3p^1$	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$

**FIGURE 7.25**

The electron configurations in the type of orbital occupied last for the first 18 elements.

groupings. Elements with the same valence electron configuration show similar chemical behavior.

The element after argon is *potassium*. Since the  $3p$  orbitals are fully occupied in argon, we might expect the next electron to go into a  $3d$  orbital (recall that for  $n = 3$  the orbitals are  $3s$ ,  $3p$ , and  $3d$ ). However, the chemistry of potassium is clearly very similar to that of lithium and sodium, indicating that the last electron in potassium occupies the  $4s$  orbital instead of one of the  $3d$  orbitals, a conclusion confirmed by many types of experiments. The electron configuration of potassium is



The next element is *calcium*:



The next element, *scandium*, begins a series of 10 elements (scandium through zinc) called the **transition metals**, whose configurations are obtained by adding electrons to the five  $3d$  orbitals. The configuration of scandium is



That of *titanium* is



And that of *vanadium* is

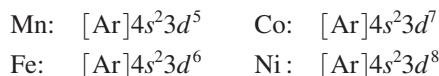


*Chromium* is the next element. The expected configuration is  $[\text{Ar}]4s^2 3d^4$ . However, the observed configuration is



The explanation for this configuration of chromium is beyond the scope of this book. In fact, chemists are still disagreeing over the exact cause of this anomaly. Note, however, that the observed configuration has both the  $4s$  and  $3d$  orbitals half-filled. This is a good way to remember the correct configuration.

The next four elements, *manganese* through *nickel*, have the expected configurations:



The configuration for *copper* is expected to be  $[\text{Ar}]4s^2 3d^9$ . However, the observed configuration is



In this case, a half-filled  $4s$  orbital and a filled set of  $3d$  orbitals characterize the actual configuration.

*Zinc* has the expected configuration:



The configurations of the transition metals are shown in Fig. 7.26. After that, the next six elements, *gallium* through *krypton*, have configurations that correspond to filling the  $4p$  orbitals (see Fig. 7.26).

The entire periodic table is represented in Fig. 7.27 in terms of which orbitals are being filled. The valence electron configurations are given in Fig. 7.28. From these two figures, note the following additional points:

1. The  $(n + 1)s$  orbitals always fill before the  $nd$  orbitals. For example, the  $5s$  orbitals fill in rubidium and strontium before the  $4d$  orbitals fill in the second row of transition



Calcium metal.



Chromium is often used to plate bumpers and hood ornaments, such as this statue of Mercury found on a 1929 Buick.

The  $(n + 1)s$  orbital fills before the  $nd$  orbitals.

## 306 Chapter Seven Atomic Structure and Periodicity

K 4s <sup>1</sup>	Ca 4s <sup>2</sup>	Sc 3d <sup>1</sup>	Ti 3d <sup>2</sup>	V 3d <sup>3</sup>	Cr 4s <sup>1</sup> 3d <sup>5</sup>	Mn 3d <sup>5</sup>	Fe 3d <sup>6</sup>	Co 3d <sup>7</sup>	Ni 3d <sup>8</sup>	Cu 4s <sup>1</sup> 3d <sup>10</sup>	Zn 3d <sup>10</sup>	Ga 4p <sup>1</sup>	Ge 4p <sup>2</sup>	As 4p <sup>3</sup>	Se 4p <sup>4</sup>	Br 4p <sup>5</sup>	Kr 4p <sup>6</sup>

**FIGURE 7.26**

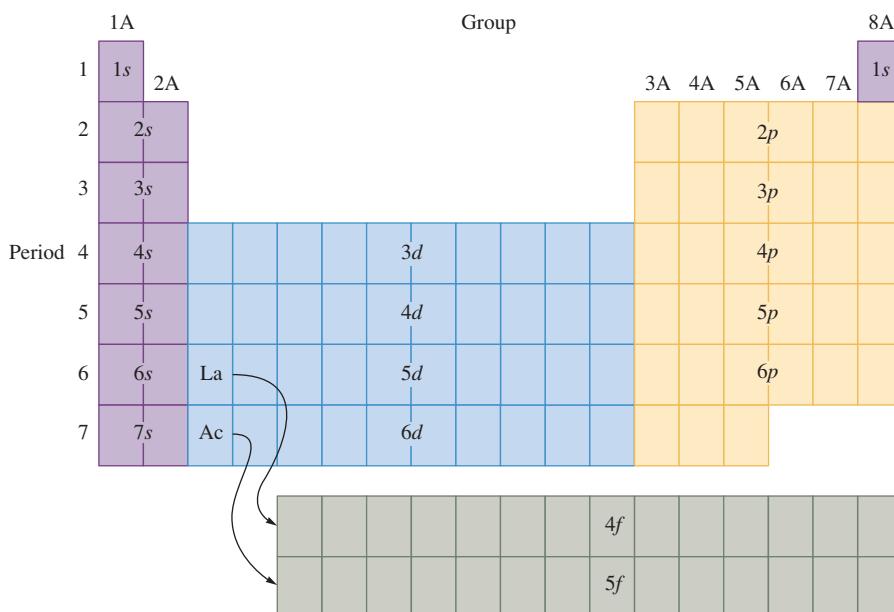
Electron configurations for potassium through krypton. The transition metals (scandium through zinc) have the general configuration [Ar]4s<sup>2</sup>3d<sup>n</sup>, except for chromium and copper.

metals (yttrium through cadmium). This early filling of the *s* orbitals can be explained by the penetration effect. For example, the 4s orbital allows for so much more penetration to the vicinity of the nucleus that it becomes lower in energy than the 3d orbital. Thus the 4s fills before the 3d. The same things can be said about the 5s and 4d, the 6s and 5d, and the 7s and 6d orbitals.

- After lanthanum, which has the configuration [Xe]6s<sup>2</sup>5d<sup>1</sup>, a group of 14 elements called the **lanthanide series**, or the **lanthanides**, occurs. This series of elements corresponds to the filling of the seven 4f orbitals. Note that sometimes an electron occupies a 5d orbital instead of a 4f orbital. This occurs because the energies of the 4f and 5d orbitals are very similar.
- After actinium, which has the configuration [Rn]7s<sup>2</sup>6d<sup>1</sup>, a group of 14 elements called the **actinide series**, or the **actinides**, occurs. This series corresponds to the filling of the seven 5f orbitals. Note that sometimes one or two electrons occupy the 6d orbitals instead of the 5f orbitals, because these orbitals have very similar energies.

Lanthanides are elements in which the 4f orbitals are being filled.

Actinides are elements in which the 5f orbitals are being filled.

**FIGURE 7.27**

The orbitals being filled for elements in various parts of the periodic table. Note that in going along a horizontal row (a period), the  $(n + 1)$ s orbital fills before the  $nd$  orbital. The group labels indicate the number of valence electrons ( $ns$  plus  $np$  electrons) for the elements in each group.

The group label tells the total number of valence electrons for that group.

- The group labels for Groups 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A indicate the *total number* of valence electrons for the atoms in these groups. For example, all the elements in Group 5A have the configuration  $ns^2np^3$ . (The *d* electrons fill one period late and are usually not counted as valence electrons.) The meaning of the group labels for the transition metals is not as clear as for the Group A elements, and these will not be used in this text.
- The groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A are often called the **main-group, or representative, elements**. Every member of these groups has the same valence electron configuration.

The International Union of Pure and Applied Chemistry (IUPAC), a body of scientists organized to standardize scientific conventions, has recommended a new form for the periodic table, which the American Chemical Society has adopted (see the blue numbers in Fig. 7.28). In this new version the group number indicates the number of *s*, *p*, and *d* electrons added since the last noble gas. We will not use the new format in this book, but you

Representative Elements		d-Transition Elements										Representative Elements					Noble Gases																		
1	1A $ns^1$											13	14	15	16	17	18 8A $ns^2np^6$																		
1	H $1s^1$											5	6	7	8	9	He $1s^2$																		
2	Li $2s^1$											B $2s^2p^1$	C $2s^2p^2$	N $2s^2p^3$	O $2s^2p^4$	F $2s^2p^5$	Ne $2s^2p^6$																		
3	Na $3s^1$											Al $3s^23p^1$	Si $3s^23p^2$	P $3s^23p^3$	S $3s^23p^4$	Cl $3s^23p^5$	Ar $3s^23p^6$																		
4	K $4s^1$	20	Sc $4s^2$	21	Ti $4s^23d^1$	22	V $4s^23d^2$	23	Cr $4s^23d^3$	24	Mn $4s^23d^5$	25	Fe $4s^23d^6$	26	Co $4s^23d^7$	27	Ni $4s^23d^8$	28	Cu $4s^13d^{10}$	29	Zn $4s^23d^{10}$	30	Ga $4s^24p^1$	31	Ge $4s^24p^2$	32	As $4s^24p^3$	33	Se $4s^24p^4$	34	Br $4s^24p^5$	35	Kr $4s^24p^6$		
5	Rb $5s^1$	38	Y $5s^2$	39	Zr $5s^24d^1$	40	Nb $5s^24d^2$	41	Mo $5s^24d^4$	42	Tc $5s^24d^5$	43	Ru $5s^24d^6$	44	Rh $5s^24d^7$	45	Pd $5s^24d^8$	46	Ag $4d^{10}$	47	Cd $5s^24d^{10}$	48	In $5s^25p^1$	49	Sn $5s^25p^2$	50	Sb $5s^25p^3$	51	Te $5s^25p^4$	52	I $5s^25p^5$	53	Xe $5s^25p^6$		
6	Cs $6s^1$	56	Ba $6s^2$	55	La* $6s^25d^1$	57	Hf $4f^{14}6s^25d^2$	72	Ta $6s^25d^3$	73	W $6s^25d^4$	74	Re $6s^25d^5$	75	Os $6s^25d^6$	76	Ir $6s^25d^7$	77	Pt $6s^15d^9$	78	Au $6s^15d^{10}$	79	Hg $6s^25d^{10}$	80	Tl $6s^26p^1$	81	Pb $6s^26p^2$	82	Bi $6s^26p^3$	83	Po $6s^26p^4$	84	At $6s^26p^5$	85	Rn $6s^26p^6$
7	Fr $7s^1$	88	Ac** $7s^2$	89	Rf $7s^26d^1$	104	Db $7s^26d^2$	105	Sg $7s^26d^3$	106	Bh $7s^26d^4$	107	Hs $7s^26d^5$	108	Mt $7s^26d^6$	109	Ds $7s^26d^7$	110	Rg $7s^16d^{10}$	111	Uub $7s^26d^{10}$	112	Uut $7s^26d^{10}7p^1$	113	Uuq $7s^26d^{10}7p^2$	114	Uup $7s^26d^{10}7p^3$	115							
<i>f</i> -Transition Elements																																			
*Lanthanides		58	Ce $6s^24f^15d^1$	59	Pr $6s^24f^15d^0$	60	Nd $6s^24f^45d^0$	61	Pm $6s^24f^55d^0$	62	Sm $6s^24f^65d^0$	63	Eu $6s^24f^75d^1$	64	Gd $6s^24f^75d^0$	65	Tb $6s^24f^95d^0$	66	Dy $6s^24f^{10}5d^0$	67	Ho $6s^24f^{11}5d^0$	68	Er $6s^24f^{12}5d^0$	69	Tm $6s^24f^{13}5d^0$	70	Yb $6s^24f^{14}5d^0$	71	Lu $6s^24f^{14}5d^1$						
**Actinides		90	Th $7s^{25}f^06d^2$	91	Pa $7s^{25}f^26d^1$	92	U $7s^{25}f^36d^1$	93	Np $7s^{25}f^46d^1$	94	Pu $7s^{25}f^66d^0$	95	Am $7s^{25}f^76d^0$	96	Cm $7s^{25}f^76d^1$	97	Bk $7s^{25}f^96d^0$	98	Cf $7s^{25}f^{10}6d^0$	99	Es $7s^{25}f^{11}6d^0$	100	Fm $7s^{25}f^{12}6d^0$	101	Md $7s^{25}f^{13}6d^0$	102	No $7s^{25}f^{14}6d^0$	103	Lr $7s^{25}f^{14}6d^1$						

**FIGURE 7.28**

The periodic table with atomic symbols, atomic numbers, and partial electron configurations.

should be aware that the familiar periodic table may be soon replaced by this or a similar format.

The results considered in this section are very important. We have seen that the quantum mechanical model can be used to explain the arrangement of the elements in the periodic table. This model allows us to understand that the similar chemistry exhibited by the members of a given group arises from the fact that they all have the same valence electron configuration. Only the principal quantum number of the valence orbitals changes in going down a particular group.

It is important to be able to give the electron configuration for each of the main-group elements. This is most easily done by using the periodic table. If you understand how the table is organized, it is not necessary to memorize the order in which the orbitals fill. Review Figs. 7.27 and 7.28 to make sure that you understand the correspondence between the orbitals and the periods and groups.

Predicting the configurations of the transition metals ( $3d$ ,  $4d$ , and  $5d$  elements), the lanthanides ( $4f$  elements), and the actinides ( $5f$  elements) is somewhat more difficult because there are many exceptions of the type encountered in the first-row transition metals (the  $3d$  elements). You should memorize the configurations of chromium and copper, the two exceptions in the first-row transition metals, since these elements are often encountered.

**When an electron configuration is given in this text, the orbitals are listed in the order in which they fill.**

Cr: [Ar] $4s^13d^5$   
Cu: [Ar] $4s^13d^{10}$

### Sample Exercise 7.7

## Electron Configurations

Give the electron configurations for sulfur (S), cadmium (Cd), hafnium (Hf), and radium (Ra) using the periodic table inside the front cover of this book.

### Solution

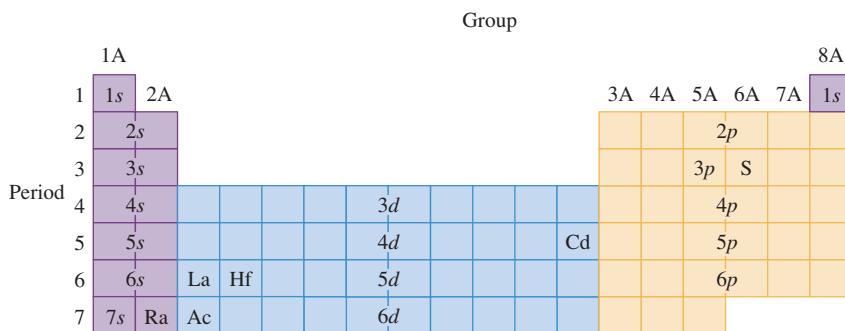
*Sulfur* is element 16 and resides in Period 3, where the  $3p$  orbitals are being filled (see Fig. 7.29). Since sulfur is the fourth among the “ $3p$  elements,” it must have four  $3p$  electrons. Its configuration is

$$\text{S: } 1s^22s^22p^63s^23p^4 \quad \text{or} \quad [\text{Ne}]3s^23p^4$$

*Cadmium* is element 48 and is located in Period 5 at the end of the  $4d$  transition metals, as shown in Fig. 7.29. It is the tenth element in the series and thus has 10 electrons in the  $4d$  orbitals, in addition to the 2 electrons in the  $5s$  orbital. The configuration is

$$\text{Cd: } 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10} \quad \text{or} \quad [\text{Kr}]5s^24d^{10}$$

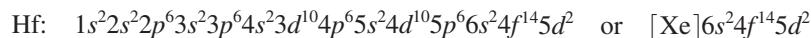
*Hafnium* is element 72 and is found in Period 6, as shown in Fig. 7.29. Note that it occurs just after the lanthanide series. Thus the  $4f$  orbitals are already filled. Hafnium is



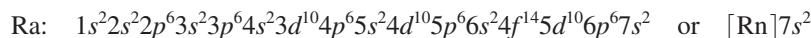
**FIGURE 7.29**

The positions of the elements considered in Sample Exercise 7.7.

the second member of the  $5d$  transition series and has two  $5d$  electrons. The configuration is



Radium is element 88 and is in Period 7 (and Group 2A), as shown in Fig. 7.29. Thus radium has two electrons in the  $7s$  orbital, and the configuration is



*See Exercises 7.69 through 7.72.*

## 7.12 Periodic Trends in Atomic Properties



Visualization: Periodic Table Trends

Ionization energy results in the formation of a positive ion.

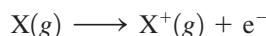


Setting the aluminum cap on the Washington Monument in 1884. At that time, aluminum was regarded as a precious metal.

We have developed a fairly complete picture of polyelectronic atoms. Although the model is rather crude because the nuclear attractions and electron repulsions are simply lumped together, it is very successful in accounting for the periodic table of elements. We will next use the model to account for the observed trends in several important atomic properties: ionization energy, electron affinity, and atomic size.

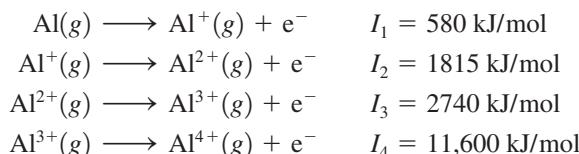
### Ionization Energy

*Ionization energy* is the energy required to remove an electron from a gaseous atom or ion:



where the atom or ion is assumed to be in its ground state.

To introduce some of the characteristics of ionization energy, we will consider the energy required to remove several electrons in succession from aluminum in the gaseous state. The ionization energies are



Several important points can be illustrated from these results. In a stepwise ionization process, it is always the highest-energy electron (the one bound least tightly) that is removed first. The **first ionization energy**  $I_1$  is the energy required to remove the highest-energy electron of an atom. The first electron removed from the aluminum atom comes from the  $3p$  orbital (Al has the electron configuration  $[\text{Ne}]3s^2 3p^1$ ). The second electron comes from the  $3s$  orbital (since  $\text{Al}^+$  has the configuration  $[\text{Ne}]3s^2$ ). Note that the value of  $I_1$  is considerably smaller than the value of  $I_2$ , the **second ionization energy**.

This makes sense for several reasons. The primary factor is simply charge. Note that the first electron is removed from a neutral atom (Al), whereas the second electron is removed from a  $1+$  ion ( $\text{Al}^+$ ). The increase in positive charge binds the electrons more firmly, and the ionization energy increases. The same trend shows up in the third ( $I_3$ ) and fourth ( $I_4$ ) ionization energies, where the electron is removed from the  $\text{Al}^{2+}$  and  $\text{Al}^{3+}$  ions, respectively.

The increase in successive ionization energies for an atom also can be interpreted using our simple model for polyelectronic atoms. The increase in ionization energy from  $I_1$  to  $I_2$  makes sense because the first electron is removed from a  $3p$  orbital that is higher in energy than the  $3s$  orbital from which the second electron is removed. The largest jump in ionization energy by far occurs in going from the third ionization energy ( $I_3$ ) to the fourth ( $I_4$ ). This is so because  $I_4$  corresponds to removing a core electron ( $\text{Al}^{3+}$  has the configuration  $1s^2 2s^2 2p^6$ ), and core electrons are bound much more tightly than valence electrons.

**TABLE 7.5 Successive Ionization Energies in Kilojoules per Mole for the Elements in Period 3**

Element	$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$	$I_7$
Na	495	4560					
Mg	735	1445	7730		Core electrons*		
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

\*Note the large jump in ionization energy in going from removal of valence electrons to removal of core electrons.

General increase →

**TABLE 7.6 First Ionization Energies for the Alkali Metals and Noble Gases**

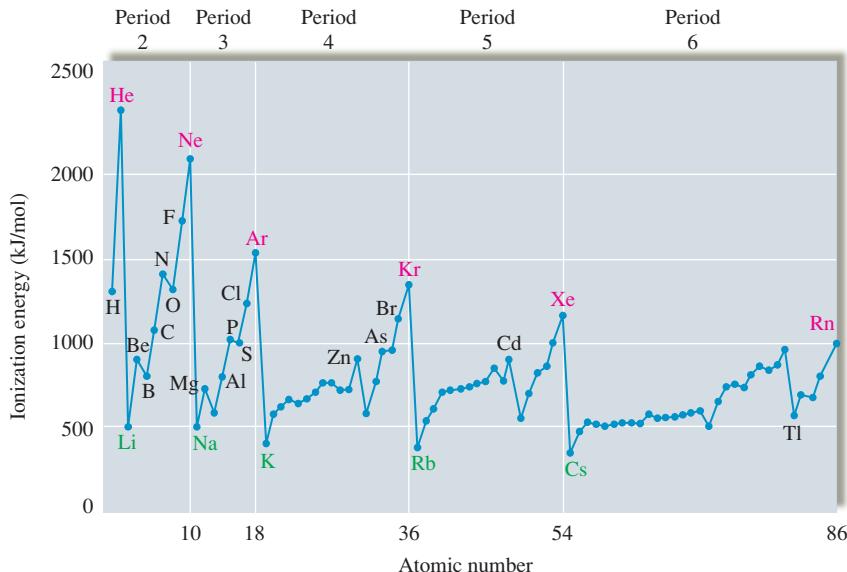
Atom	$I_1$ (kJ/mol)
<b>Group 1A</b>	
Li	520
Na	495
K	419
Rb	409
Cs	382
<b>Group 8A</b>	
He	2377
Ne	2088
Ar	1527
Kr	1356
Xe	1176
Rn	1042

First ionization energy increases across a period and decreases down a group.

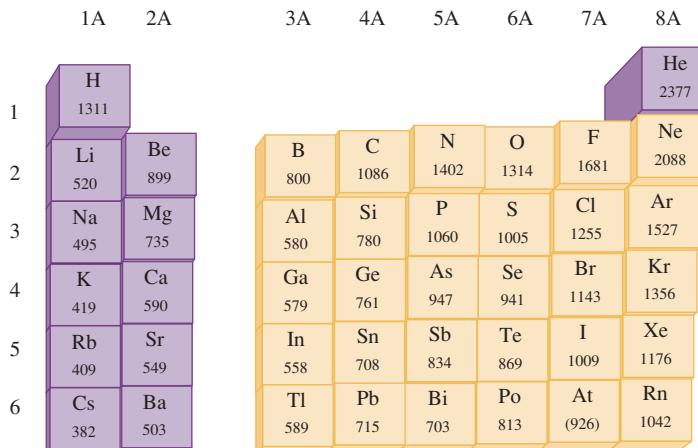
Table 7.5 gives the values of ionization energies for all the Period 3 elements. Note the large jump in energy in each case in going from removal of valence electrons to removal of core electrons.

The values of the first ionization energies for the elements in the first six periods of the periodic table are graphed in Fig. 7.30. Note that in general as we go *across a period from left to right, the first ionization energy increases*. This is consistent with the idea that electrons added in the same principal quantum level do not completely shield the increasing nuclear charge caused by the added protons. Thus electrons in the same principal quantum level are generally more strongly bound as we move to the right on the periodic table, and there is a general increase in ionization energy values as electrons are added to a given principal quantum level.

On the other hand, *first ionization energy decreases in going down a group*. This can be seen most clearly by focusing on the Group 1A elements (the alkali metals) and the Group 8A elements (the noble gases), as shown in Table 7.6. The main reason for the decrease in ionization energy in going down a group is that the electrons being removed are, on average, farther from the nucleus. As  $n$  increases, the size of the orbital increases, and the electron is easier to remove.

**FIGURE 7.30**

The values of first ionization energy for the elements in the first six periods. In general, ionization energy decreases in going down a group. For example, note the decrease in values for Group 1A and Group 8A. In general, ionization energy increases in going left to right across a period. For example, note the sharp increase going across Period 2 from lithium through neon.

**FIGURE 7.31**

Trends in ionization energies (kJ/mol) for the representative elements.

In Fig. 7.30 we see that there are some discontinuities in ionization energy in going across a period. For example, for Period 2, discontinuities occur in going from beryllium to boron and from nitrogen to oxygen. These exceptions to the normal trend can be explained in terms of electron repulsions. The decrease in ionization energy in going from beryllium to boron reflects the fact that the electrons in the filled 2s orbital provide some shielding for electrons in the 2p orbital from the nuclear charge. The decrease in ionization energy in going from nitrogen to oxygen reflects the extra electron repulsions in the doubly occupied oxygen 2p orbital.

The ionization energies for the representative elements are summarized in Fig. 7.31.

### Sample Exercise 7.8

### Trends in Ionization Energies

The first ionization energy for phosphorus is 1060 kJ/mol, and that for sulfur is 1005 kJ/mol. Why?

#### *Solution*

Phosphorus and sulfur are neighboring elements in Period 3 of the periodic table and have the following valence electron configurations: Phosphorus is  $3s^23p^3$ , and sulfur is  $3s^23p^4$ .

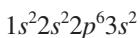
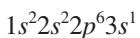
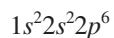
Ordinarily, the first ionization energy increases as we go across a period, so we might expect sulfur to have a greater ionization energy than phosphorus. However, in this case the fourth p electron in sulfur must be placed in an already occupied orbital. The electron-electron repulsions that result cause this electron to be more easily removed than might be expected.

*See Exercises 7.93 and 7.94.*

### Sample Exercise 7.9

### Ionization Energies

Consider atoms with the following electron configurations:



Which atom has the largest first ionization energy, and which one has the smallest second ionization energy? Explain your choices.

**Solution**

The atom with the largest value of  $I_1$  is the one with the configuration  $1s^22s^22p^6$  (this is the neon atom), because this element is found at the right end of Period 2. Since the  $2p$  electrons do not shield each other very effectively,  $I_1$  will be relatively large. The other configurations given include  $3s$  electrons. These electrons are effectively shielded by the core electrons and are farther from the nucleus than the  $2p$  electrons in neon. Thus  $I_1$  for these atoms will be smaller than for neon.

The atom with the smallest value of  $I_2$  is the one with the configuration  $1s^22s^22p^63s^2$  (the magnesium atom). For magnesium, both  $I_1$  and  $I_2$  involve valence electrons. For the atom with the configuration  $1s^22s^22p^63s^1$  (sodium), the second electron lost (corresponding to  $I_2$ ) is a core electron (from a  $2p$  orbital).

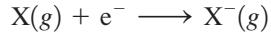
*See Exercises 7.121 and 7.123.*

**Electron Affinity**

Electron affinity is associated with the production of a negative ion.

The sign convention for electron affinity values follows the convention for energy changes used in Chapter 6.

**Electron affinity** is the energy change associated with the addition of an electron to a gaseous atom:



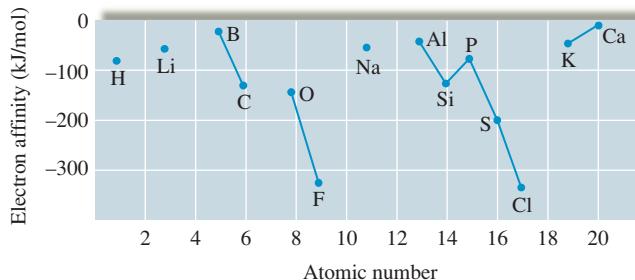
Because two different conventions have been used, there is a good deal of confusion in the chemical literature about the signs for electron affinity values. Electron affinity has been defined in many textbooks as the energy *released* when an electron is added to a gaseous atom. This convention requires that a positive sign be attached to an exothermic addition of an electron to an atom, which opposes normal thermodynamic conventions. Therefore, in this book we define electron affinity as a *change* in energy, which means that if the addition of the electron is exothermic, the corresponding value for electron affinity will carry a negative sign.

Figure 7.32 shows the electron affinity values for the atoms among the first 20 elements that form stable, isolated negative ions—that is, the atoms that undergo the addition of an electron as shown above. As expected, all these elements have negative (exothermic) electron affinities. Note that the *more negative* the energy, the greater the quantity of energy released. Although electron affinities generally become more negative from left to right across a period, there are several exceptions to this rule in each period. The dependence of electron affinity on atomic number can be explained by considering the changes in electron repulsions as a function of electron configurations. For example, the fact that the nitrogen atom does not form a stable, isolated  $N^-(g)$  ion, whereas carbon forms  $C^-(g)$ , reflects the difference in the electron configurations of these atoms. An electron added to nitrogen ( $1s^22s^22p^3$ ) to form the  $N^-(g)$  ion ( $1s^22s^22p^4$ ) would have to occupy a  $2p$  orbital that already contains one electron. The extra repulsion between the electrons in this doubly occupied orbital causes  $N^-(g)$  to be unstable. When an electron is added to carbon ( $1s^22s^22p^2$ ) to form the  $C^-(g)$  ion ( $1s^22s^22p^3$ ), no such extra repulsions occur.

In contrast to the nitrogen atom, the oxygen atom can add one electron to form the stable  $O^-(g)$  ion. Presumably oxygen's greater nuclear charge compared with that of nitrogen

**FIGURE 7.32**

The electron affinity values for atoms among the first 20 elements that form stable, isolated  $X^-$  ions. The lines shown connect adjacent elements. The absence of a line indicates missing elements (He, Be, N, Ne, Mg, and Ar) whose atoms do not add an electron exothermically and thus do not form stable, isolated  $X^-$  ions.



**TABLE 7.7** Electron Affinities of the Halogens

<b>Atom</b>	<b>Electron Affinity (kJ/mol)</b>
F	-327.8
Cl	-348.7
Br	-324.5
I	-295.2

is sufficient to overcome the repulsion associated with putting a second electron into an already occupied  $2p$  orbital. However, it should be noted that a second electron *cannot* be added to an oxygen atom [ $\text{O}^-(g) + \text{e}^- \not\rightarrow \text{O}^{2-}(g)$ ] to form an isolated oxide ion. This outcome seems strange in view of the many stable oxide compounds ( $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ , and so on) that are known. As we will discuss in detail in Chapter 8, the  $\text{O}^{2-}$  ion is stabilized in ionic compounds by the large attractions that occur among the positive ions and the oxide ions.

When we go down a group, electron affinity should become more positive (less energy released), since the electron is added at increasing distances from the nucleus. Although this is generally the case, the changes in electron affinity in going down most groups are relatively small, and numerous exceptions occur. This behavior is demonstrated by the electron affinities of the Group 7A elements (the halogens) shown in Table 7.7. Note that the range of values is quite small compared with the changes that typically occur across a period. Also note that although chlorine, bromine, and iodine show the expected trend, the energy released when an electron is added to fluorine is smaller than might be expected. This smaller energy release has been attributed to the small size of the  $2p$  orbitals. Because the electrons must be very close together in these orbitals, there are unusually large electron–electron repulsions. In the other halogens with their larger orbitals, the repulsions are not as severe.

## Atomic Radius

Just as the size of an orbital cannot be specified exactly, neither can the size of an atom. We must make some arbitrary choices to obtain values for **atomic radii**. These values can be obtained by measuring the distances between atoms in chemical compounds. For example, in the bromine molecule, the distance between the two nuclei is known to be 228 pm. The bromine atomic radius is assumed to be half this distance, or 114 pm, as shown in Fig. 7.33. These radii are often called *covalent atomic radii* because of the way they are determined (from the distances between atoms in covalent bonds).

For nonmetallic atoms that do not form diatomic molecules, the atomic radii are estimated from their various covalent compounds. The radii for metal atoms (called *metallic radii*) are obtained from half the distance between metal atoms in solid metal crystals.

The values of the atomic radii for the representative elements are shown in Fig. 7.34. Note that these values are significantly smaller than might be expected from the 90% electron density volumes of isolated atoms, because when atoms form bonds, their electron “clouds” interpenetrate. However, these values form a self-consistent data set that can be used to discuss the trends in atomic radii.

Note from Fig. 7.34 that the atomic radii decrease in going from left to right across a period. This decrease can be explained in terms of the increasing effective nuclear charge (decreasing shielding) in going from left to right. This means that the valence electrons are drawn closer to the nucleus, decreasing the size of the atom.

Atomic radius increases down a group, because of the increases in the orbital sizes in successive principal quantum levels.



## Visualization: Determining the Atomic Radius of a Nonmetal (Chlorine)



## Visualization: Determining the Atomic Radius of a Nonmetal (Carbon)

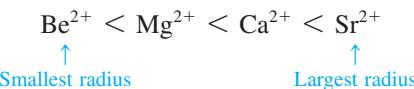
### *Sample Exercise 7.10*

## Trends in Radii

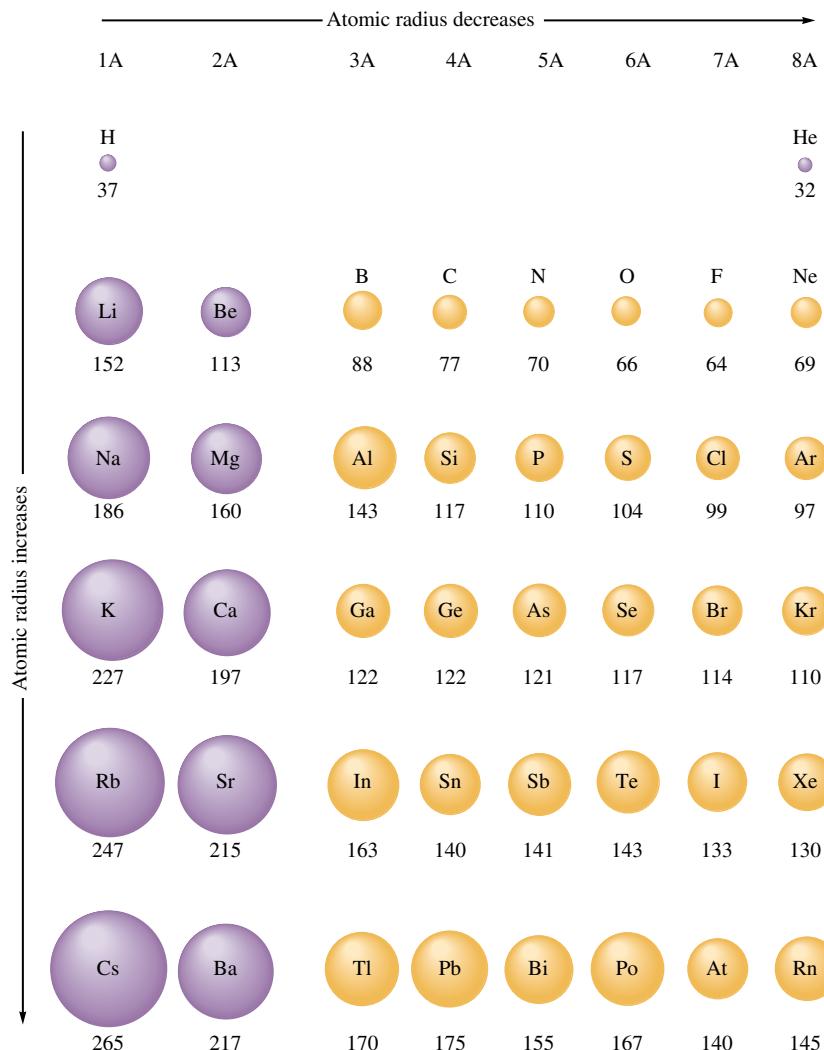
Predict the trend in radius for the following ions:  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$ .

### *Solution*

All these ions are formed by removing two electrons from an atom of a Group 2A element. In going from beryllium to strontium, we are going down the group, so the sizes increase.



*See Exercises 7.85, 7.86, and 7.89.*

**FIGURE 7.34**

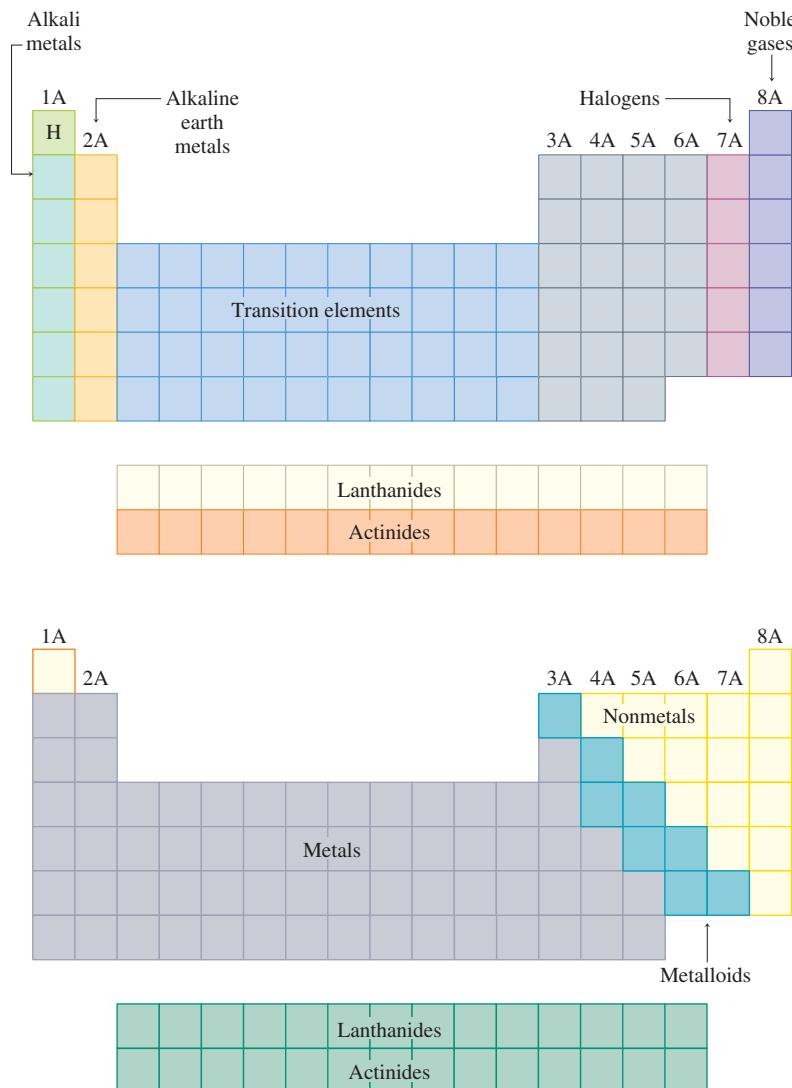
Atomic radii (in picometers) for selected atoms. Note that atomic radius decreases going across a period and increases going down a group. The values for the noble gases are estimated, because data from bonded atoms are lacking.

## 7.13 The Properties of a Group: The Alkali Metals

We have seen that the periodic table originated as a way to portray the systematic properties of the elements. Mendeleev was primarily responsible for first showing its usefulness in correlating and predicting the elemental properties. In this section we will summarize much of the information available from the table. We also will illustrate the usefulness of the table by discussing the properties of a representative group, the alkali metals.

### Information Contained in the Periodic Table

1. The essence of the periodic table is that the groups of representative elements exhibit similar chemical properties that change in a regular way. The quantum mechanical model of the atom has allowed us to understand the basis for the similarity of properties in a group—that each group member has the same valence electron configuration. *It is the number and type of valence electrons that primarily determine an atom's chemistry.*
2. One of the most valuable types of information available from the periodic table is the electron configuration of any representative element. If you understand the organization



**FIGURE 7.35**  
Special names for groups in the periodic table.

Metals and nonmetals were first discussed in Chapter 2.

of the table, you will not need to memorize electron configurations for these elements. Although the predicted electron configurations for transition metals are sometimes incorrect, this is not a serious problem. You should, however, memorize the configurations of two exceptions, chromium and copper, since these  $3d$  transition elements are found in many important compounds.

- As we mentioned in Chapter 2, certain groups in the periodic table have special names. These are summarized in Fig. 7.35. Groups are often referred to by these names, so you should learn them.
- The most basic division of the elements in the periodic table is into metals and nonmetals. The most important chemical property of a metal atom is the tendency to give up one or more electrons to form a positive ion; metals tend to have low ionization energies. The metallic elements are found on the left side of the table, as shown in Fig. 7.35. The most chemically reactive metals are found on the lower left-hand portion of the table, where the ionization energies are smallest. The most distinctive chemical property of a nonmetal atom is the ability to gain one or more electrons to form an anion when reacting with a metal. Thus nonmetals are elements

with large ionization energies and the most negative electron affinities. The nonmetals are found on the right side of the table, with the most reactive ones in the upper right-hand corner, except for the noble gas elements, which are quite unreactive. The division into metals and nonmetals shown in Fig. 7.35 is only approximate. Many elements along the division line exhibit both metallic and nonmetallic properties under certain circumstances. These elements are often called **metalloids**, or sometimes **semimetals**.

### The Alkali Metals

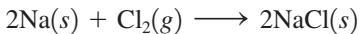
The metals of Group 1A, the alkali metals, illustrate very well the relationships among the properties of the elements in a group. Lithium, sodium, potassium, rubidium, cesium, and francium are the most chemically reactive of the metals. We will not discuss francium here because it occurs in nature in only very small quantities. Although hydrogen is found in Group 1A of the periodic table, it behaves as a nonmetal, in contrast to the other members of that group. The fundamental reason for hydrogen's nonmetallic character is its very small size (see Fig. 7.34). The electron in the small 1s orbital is bound tightly to the nucleus.

Some important properties of the first five alkali metals are shown in Table 7.8. The data in Table 7.8 show that in going down the group, the first ionization energy decreases and the atomic radius increases. This agrees with the general trends discussed in Section 7.12.

The overall increase in density in going down Group 1A is typical of all groups. This occurs because atomic mass generally increases more rapidly than atomic size. Thus there is more mass per unit volume for each succeeding element.

The smooth decrease in melting point and boiling point in going down Group 1A is not typical; in most other groups more complicated behavior occurs. Note that the melting point of cesium is only 29°C. Cesium can be melted readily using only the heat from your hand. This is very unusual—metals typically have rather high melting points. For example, tungsten melts at 3410°C. The only other metals with low melting points are mercury (mp –38°C) and gallium (mp 30°C).

The chemical property most characteristic of a metal is the ability to lose its valence electrons. The Group 1A elements are very reactive. They have low ionization energies and react with nonmetals to form ionic solids. A typical example involves the reaction of sodium with chlorine to form sodium chloride:



where sodium chloride contains  $\text{Na}^+$  and  $\text{Cl}^-$  ions. This is an oxidation–reduction reaction in which chlorine oxidizes sodium. In the reactions between metals and nonmetals,

Hydrogen will be discussed further in Chapter 19.

Other groups will be discussed in Chapters 19 and 20.

Oxidation–reduction reactions were discussed in Chapter 4.

**TABLE 7.8 Properties of Five Alkali Metals**

Element	Valence Electron Configuration	Density at 25°C (g/cm³)	mp (°C)	bp (°C)	First Ionization Energy (kJ/mol)	Atomic (covalent) Radius (pm)	Ionic ( $\text{M}^+$ ) Radius (pm)
Li	$2s^1$	0.53	180	1330	520	152	60
Na	$3s^1$	0.97	98	892	495	186	95
K	$4s^1$	0.86	64	760	419	227	133
Rb	$5s^1$	1.53	39	668	409	247	148
Cs	$6s^1$	1.87	29	690	382	265	169



## CHEMICAL IMPACT

### Potassium—Too Much of a Good Thing Can Kill You

**P**otassium is widely recognized as an essential element. In fact, our daily requirement for potassium is more than twice that for sodium. Because most foods contain potassium, serious deficiency of this element in humans is rare. However, potassium deficiency can be caused by kidney malfunction or by the use of certain diuretics. Potassium deficiency leads to muscle weakness, irregular heartbeat, and depression.

Potassium is found in the fluids of the body as the  $K^+$  ion, and its presence is essential to the operation of our nervous system. The passage of impulses along the nerves requires the flow of  $K^+$  (and  $Na^+$ ) through channels in the membranes of the nerve cells. Failure of this ion flow prevents nerve transmissions and results in death. For example, the black mamba snake kills its victims by injecting a venom that blocks the potassium channels in the nerve cells.

Although a steady intake of potassium is essential to preserve life, ironically, too much potassium can be lethal. In fact, the deadly ingredient in the drug mixture used for executing criminals is potassium chloride. Injection of a large amount of a potassium chloride solution produces an excess of  $K^+$  ion in



The black mamba snake's venom kills by blocking the potassium channels in the nerve cells of victims.

the fluids surrounding the cells and prevents the essential flow of  $K^+$  out the cells to allow nerve impulses to occur. This causes the heart to stop beating. Unlike other forms of execution, death by lethal injection of potassium chloride does not harm the organs of the body. Thus condemned criminals who are executed in this manner could potentially donate their organs for transplants. However, this idea is very controversial.



Potassium reacts violently with water.

it is typical for the nonmetal to behave as the oxidizing agent and the metal to behave as the reducing agent, as shown by the following reactions:



For reactions of the types just shown, the relative reducing powers of the alkali metals can be predicted from the first ionization energies listed in Table 7.8. Since it is much easier to remove an electron from a cesium atom than from a lithium atom, cesium should be the better reducing agent. The expected trend in reducing ability is



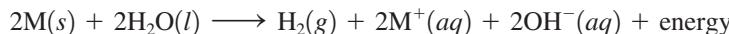
This order is observed experimentally for direct reactions between the solid alkali metals and nonmetals. However, this is not the order for reducing ability found when the alkali

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**TABLE 7.9 Hydration Energies for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  Ions**

Ion	Hydration Energy (kJ/mol)
$\text{Li}^+$	-510
$\text{Na}^+$	-402
$\text{K}^+$	-314

metals react in aqueous solution. For example, the reduction of water by an alkali metal is very vigorous and exothermic:



The order of reducing abilities observed for this reaction for the first three group members is



In the gas phase potassium loses an electron more easily than sodium, and sodium more easily than lithium. Thus it is surprising that lithium is the best reducing agent toward water.

This reversal occurs because the formation of the  $\text{M}^+$  ions in aqueous solution is strongly influenced by the hydration of these ions by the polar water molecules. The *hydration energy* of an ion represents the change in energy that occurs when water molecules attach to the  $\text{M}^+$  ion. The hydration energies for the  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ions (shown in Table 7.9) indicate that the process is exothermic in each case. However, nearly twice as much energy is released by the hydration of the  $\text{Li}^+$  ion as for the  $\text{K}^+$  ion. This difference is caused by size effects; the  $\text{Li}^+$  ion is much smaller than the  $\text{K}^+$  ion, and thus its *charge density* (charge per unit volume) is also much greater. This means that the polar water molecules are more strongly attracted to the small  $\text{Li}^+$  ion. Because the  $\text{Li}^+$  ion is so strongly hydrated, its formation from the lithium atom occurs more readily than the formation of the  $\text{K}^+$  ion from the potassium atom. Although a potassium atom in the gas phase loses its valence electron more readily than a lithium atom in the gas phase, the opposite is true in aqueous solution. This anomaly is an example of the importance of the polarity of the water molecule in aqueous reactions.

There is one more surprise involving the highly exothermic reactions of the alkali metals with water. Experiments show that in water lithium is the best reducing agent, so we might expect that lithium should react the most violently with water. However, this is not true. Sodium and potassium react much more vigorously. Why is this so? The answer lies in the relatively high melting point of lithium. When sodium and potassium react with water, the heat evolved causes them to melt, giving a larger area of contact with water. Lithium, on the other hand, does not melt under these conditions and reacts more slowly. This illustrates the important principle (which we will discuss in detail in Chapter 12) that the energy change for a reaction and the rate at which it occurs are not necessarily related.

In this section we have seen that the trends in atomic properties summarized by the periodic table can be a great help in understanding the chemical behavior of the elements. This fact will be emphasized over and over as we proceed in our study of chemistry.

## Key Terms

### Section 7.1

electromagnetic radiation  
wavelength  
frequency

### Section 7.2

Planck's constant  
quantization  
photon  
photoelectric effect  
 $E = mc^2$   
dual nature of light  
diffraction  
diffraction pattern

### Section 7.3

continuous spectrum  
line spectrum

## For Review

### Electromagnetic radiation

- Characterized by its wavelength ( $\lambda$ ), frequency ( $\nu$ ), and speed ( $c = 2.9979 \times 10^8 \text{ m/s}$ )
- $$\lambda\nu = c$$
- Can be viewed as a stream of “particles” called photons, each with energy  $h\nu$ , where  $h$  is Planck's constant ( $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ )

### Photoelectric effect

- When light strikes a metal surface, electrons are emitted
- Analysis of the kinetic energy and numbers of the emitted electrons led Einstein to suggest that electromagnetic radiation can be viewed as a stream of photons

### Hydrogen spectrum

- The emission spectrum of hydrogen shows discrete wavelengths
- Indicates that hydrogen has discrete energy levels

**Section 7.4**

quantum model  
ground state

**Section 7.5**

standing wave  
wave function  
orbital

quantum (wave) mechanical model  
Heisenberg uncertainty principle  
probability distribution  
radial probability distribution

**Section 7.6**

quantum numbers  
principal quantum number ( $n$ )  
angular momentum quantum number ( $\ell$ )  
magnetic quantum number ( $m_\ell$ )  
subshell

**Section 7.7**

nodal surface  
node  
degenerate orbital

**Section 7.8**

electron spin  
electron spin quantum number  
Pauli exclusion principle

**Section 7.9**

polyelectronic atoms

**Section 7.11**

aufbau principle  
Hund's rule  
valence electrons  
core electrons  
transition metals  
lanthanide series  
actinide series  
main-group elements (representative elements)

**Section 7.12**

first ionization energy  
second ionization energy  
electron affinity  
atomic radii

**Section 7.13**

metalloids (semimetals)

**Bohr model of the hydrogen atom**

- Using the data from the hydrogen spectrum and assuming angular momentum to be quantized, Bohr devised a model in which the electron traveled in circular orbits
- Although an important pioneering effort, this model proved to be entirely incorrect

**Wave (quantum) mechanical model**

- An electron is described as a standing wave
- The square of the wave function (often called an orbital) gives a probability distribution for the electron position
- The exact position of the electron is never known, which is consistent with the Heisenberg uncertainty principle: it is impossible to know accurately both the position and the momentum of a particle simultaneously
- Probability maps are used to define orbital shapes
- Orbitals are characterized by the quantum numbers  $n$ ,  $\ell$ , and  $m_\ell$

**Electron spin**

- Described by the spin quantum number  $m_s$  which can have values of  $\pm\frac{1}{2}$
- Pauli exclusion principle: no two electrons in a given atom can have the same set of quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$ , and  $m_s$
- Only two electrons with opposite spins can occupy a given orbital

**Periodic table**

- By populating the orbitals from the wave mechanical model (the aufbau principle), the form of the periodic table can be explained
- According to the wave mechanical model, atoms in a given group have the same valence (outer) electron configuration
- The trends in properties such as ionization energies and atomic radii can be explained in terms of the concepts of nuclear attraction, electron repulsions, shielding, and penetration

**REVIEW QUESTIONS**

- Four types of electromagnetic radiation (EMR) are ultraviolet, microwaves, gamma rays, and visible. All of these types of EMR can be characterized by wavelength, frequency, photon energy, and speed of travel. Define these terms and rank the four types of electromagnetic radiation in order of increasing wavelength, frequency, photon energy, and speed.
- Characterize the Bohr model of the atom. In the Bohr model, what do we mean when we say something is quantized? How does the Bohr model of the hydrogen atom explain the hydrogen emission spectrum? Why is the Bohr model fundamentally incorrect?
- What experimental evidence supports the quantum theory of light? Explain the wave-particle duality of all matter. For what size particles must one consider both the wave and the particle properties?
- List the most important ideas of the quantum mechanical model of the atom. Include in your discussion the terms or names *wave function*, *orbital*, *Heisenberg uncertainty principle*, *de Broglie*, *Schrödinger*, and *probability distribution*.
- What are quantum numbers? What information do we get from the quantum numbers  $n$ ,  $\ell$ , and  $m_\ell$ ? We define a spin quantum number ( $m_s$ ), but do we know that an electron literally spins?
- How do  $2p$  orbitals differ from each other? How do  $2p$  and  $3p$  orbitals differ from each other? What is a nodal surface in an atomic orbital? What is wrong with  $1p$ ,  $1d$ ,  $2d$ ,  $1f$ ,  $2f$ , and  $3f$  orbitals? Explain what we mean when we say that a  $4s$  electron is more penetrating than a  $3d$  electron.

7. Four blocks of elements in a periodic table refer to various atomic orbitals being filled. What are the four blocks and the corresponding orbitals? How do you get the energy ordering of the atomic orbitals from the periodic table? What is the aufbau principle? Hund's rule? The Pauli exclusion principle? There are two common exceptions to the ground-state electron configuration for elements 1–36 as predicted by the periodic table. What are they?
8. What is the difference between core electrons and valence electrons? Why do we emphasize the valence electrons in an atom when discussing atomic properties? What is the relationship between valence electrons and elements in the same group of the periodic table?
9. Using the element phosphorus as an example, write the equation for a process in which the energy change will correspond to the ionization energy and to the electron affinity.

Explain why the first ionization energy tends to increase as one proceeds from left to right across a period. Why is the first ionization energy of aluminum lower than that of magnesium, and the first ionization energy of sulfur lower than that of phosphorus?

Why do the successive ionization energies of an atom always increase? Note the successive ionization energies for silicon given in Table 7.5. Would you expect to see any large jumps between successive ionization energies of silicon as you removed all the electrons, one by one, beyond those shown in the table?

10. The radius trend and the ionization energy trend are exact opposites. Does this make sense? Define electron affinity. Electron affinity values are both exothermic (negative) and endothermic (positive). However, ionization energy values are always endothermic (positive). Explain.

## Active Learning Questions

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

1. What does it mean for something to have wavelike properties? Particulate properties? Electromagnetic radiation can be discussed in terms of both particles and waves. Explain the experimental verification for each of these views.
2. Defend and criticize Bohr's model. Why was it reasonable that such a model was proposed, and what evidence was there that it "works"? Why do we no longer "believe" in it?
3. The first four ionization energies for the elements *X* and *Y* are shown below. The units are not kJ/mol.

	<i>X</i>	<i>Y</i>
First	170	200
Second	350	400
Third	1800	3500
Fourth	2500	5000

Identify the elements *X* and *Y*. There may be more than one correct answer, so explain completely.

4. Compare the first ionization energy of helium to its second ionization energy, remembering that both electrons come from the 1s orbital. Explain the difference without using actual numbers from the text.
5. Which has the larger second ionization energy, lithium or beryllium? Why?
6. Explain why a graph of ionization energy versus atomic number (across a row) is not linear. Where are the exceptions? Why are there exceptions?
7. Without referring to your text, predict the trend of second ionization energies for the elements sodium through argon. Compare your answer with Table 7.5. Explain any differences.
8. Account for the fact that the line that separates the metals from the nonmetals on the periodic table is diagonal downward to the right instead of horizontal or vertical.
9. Explain *electron* from a quantum mechanical perspective, including a discussion of atomic radii, probabilities, and orbitals.
10. Choose the best response for the following. The ionization energy for the chlorine atom is equal in magnitude to the electron affinity for
  - a. the Cl atom.
  - b. the  $\text{Cl}^-$  ion.
  - c. the  $\text{Cl}^+$  ion.
  - d. the F atom.
  - e. none of these.

Explain each choice. Justify your choice, and for the choices you did not select, explain what is incorrect about them.

11. Consider the following statement: "The ionization energy for the potassium atom is negative, because when K loses an electron to become  $K^+$ , it achieves a noble gas electron configuration." Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect information and explain.
12. In going across a row of the periodic table, electrons are added and ionization energy generally increases. In going down a column of the periodic table, electrons are also being added but ionization energy decreases. Explain.
13. How does probability fit into the description of the atom?
14. What is meant by an *orbital*?

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

## Questions

15. What type of relationship (direct or inverse) exists between wavelength, frequency, and photon energy? What does a photon energy unit of a Joule equal?
16. Explain the photoelectric effect.
17. How does the wavelength of a fast-pitched baseball compare to the wavelength of an electron traveling at 1/10 the speed of light? What is the significance of this comparison? See Sample Exercise 7.3.
18. The Bohr model only works for one electron species. Why do we discuss it in this text (what's good about it)?
19. Describe the significance of the radial probability distribution shown in Fig. 7.12(b).
20. The periodic table consists of four blocks of elements which correspond to *s*, *p*, *d*, and *f* orbitals being filled. After *f* orbitals come *g* and *h* orbitals. In theory, if a *g* block and an *h* block of elements existed, how long would the rows of *g* and *h* elements be in this theoretical periodic table?
21. Many times the claim is made that subshells half-filled with electrons are particularly stable. Can you suggest a possible physical basis for this claim?
22. Diagonal relationships in the periodic table exist as well as the vertical relationships. For example, Be and Al are similar in some of their properties, as are B and Si. Rationalize why these diagonal relationships hold for properties such as size, ionization energy, and electron affinity.
23. Elements with very large ionization energies also tend to have highly exothermic electron affinities. Explain. Which group of elements would you expect to be an exception to this statement?
24. The changes in electron affinity as one goes down a group in the periodic table are not nearly as large as the variations in ionization energies. Why?
25. Why is it much harder to explain the line spectra of polyelectronic atoms and ions than it is to explain the line spectra of hydrogen and hydrogenlike ions?
26. Scientists use emission spectra to confirm the presence of an element in materials of unknown composition. Why is this possible?

27. Does the minimization of electron–electron repulsions correlate with Hund's rule?
28. In the hydrogen atom, what is the physical significance of the state for which  $n = \infty$  and  $E = 0$ ?
29. The work function is the energy required to remove an electron from an atom on the surface of a metal. How does this definition differ from that for ionization energy?
30. Many more anhydrous lithium salts are hygroscopic (readily absorb water) than are those of the other alkali metals. Explain.

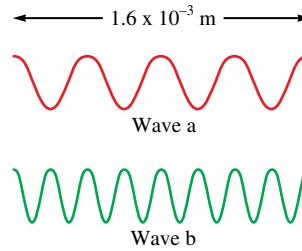
## Exercises

In this section similar exercises are paired.

### Light and Matter

31. Photosynthesis uses 660-nm light to convert  $CO_2$  and  $H_2O$  into glucose and  $O_2$ . Calculate the frequency of this light.
32. An FM radio station broadcasts at 99.5 MHz. Calculate the wavelength of the corresponding radio waves.
33. Microwave radiation has a wavelength on the order of 1.0 cm. Calculate the frequency and the energy of a single photon of this radiation. Calculate the energy of an Avogadro's number of photons (called an *einstein*) of this radiation.
34. A photon of ultraviolet (UV) light possesses enough energy to mutate a strand of human DNA. What is the energy of a single UV photon and a mole of UV photons having a wavelength of 25 nm?

35. Consider the following waves representing electromagnetic radiation:



Which wave has the longer wavelength? Calculate the wavelength. Which wave has the higher frequency and larger photon energy? Calculate these values. Which wave has the faster velocity? What type of electromagnetic radiation are illustrated?

36. One type of electromagnetic radiation has a frequency of 107.1 MHz, another type has a wavelength of  $2.12 \times 10^{-10} \text{ m}$ , and another type of electromagnetic radiation has photons with energy equal to  $3.97 \times 10^{-19} \text{ J/photon}$ . Identify each type of electromagnetic radiation and place them in order of increasing photon energy and increasing frequency.
37. Carbon absorbs energy at a wavelength of 150. nm. The total amount of energy emitted by a carbon sample is  $1.98 \times 10^5 \text{ J}$ . Calculate the number of carbon atoms present in the sample, assuming that each atom emits one photon.

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- 38.** A carbon–oxygen double bond in a certain organic molecule absorbs radiation that has a frequency of  $6.0 \times 10^{13} \text{ s}^{-1}$ .
- What is the wavelength of this radiation?
  - To what region of the spectrum does this radiation belong?
  - What is the energy of this radiation per photon? Per mole of photons?
  - A carbon–oxygen bond in a different molecule absorbs radiation with frequency equal to  $5.4 \times 10^{13} \text{ s}^{-1}$ . Is this radiation more or less energetic?
- 39.** The work function of an element is the energy required to remove an electron from the surface of the solid element. The work function for lithium is 279.7 kJ/mol (that is, it takes 279.7 kJ of energy to remove one mole of electrons from one mole of Li atoms on the surface of Li metal). What is the maximum wavelength of light that can remove an electron from an atom on the surface of lithium metal?
- 40.** It takes 208.4 kJ of energy to remove 1 mole of electrons from an atom on the surface of rubidium metal. How much energy does it take to remove a single electron from an atom on the surface of solid rubidium? What is the maximum wavelength of light capable of doing this?
- 41.** Calculate the de Broglie wavelength for each of the following.
- an electron with a velocity 10% of the speed of light
  - a tennis ball (55 g) served at 35 m/s ( $\sim 80 \text{ mi/h}$ )
- 42.** Neutron diffraction is used in determining the structures of molecules.
- Calculate the de Broglie wavelength of a neutron moving at 1.00% of the speed of light.
  - Calculate the velocity of a neutron with a wavelength of 75 pm ( $1 \text{ pm} = 10^{-12} \text{ m}$ ).
- 43.** A particle has a velocity that is 90% of the speed of light. If the wavelength of the particle is  $1.5 \times 10^{-15} \text{ m}$ , calculate the mass of the particle.
- 44.** Calculate the velocities of electrons with de Broglie wavelengths of  $1.0 \times 10^2 \text{ nm}$  and  $1.0 \text{ nm}$ , respectively.
- Hydrogen Atom: The Bohr Model**
- 45.** Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
- $n = 3 \rightarrow n = 2$
  - $n = 4 \rightarrow n = 2$
  - $n = 2 \rightarrow n = 1$
- 46.** Calculate the wavelength of light emitted when each of the following transitions occur in the hydrogen atom. What type of electromagnetic radiation is emitted in each transition?
- $n = 4 \rightarrow n = 3$
  - $n = 5 \rightarrow n = 4$
  - $n = 5 \rightarrow n = 3$
- 47.** Using vertical lines, indicate the transitions from Exercise 45 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).
- 48.** Using vertical lines, indicate the transitions from Exercise 46 on an energy-level diagram for the hydrogen atom (see Fig. 7.8).
- 49.** Does a photon of visible light ( $\lambda \approx 400$  to  $700 \text{ nm}$ ) have sufficient energy to excite an electron in a hydrogen atom from the  $n = 1$  to the  $n = 5$  energy state? from the  $n = 2$  to the  $n = 6$  energy state?
- 50.** An electron is excited from the  $n = 1$  ground state to the  $n = 3$  state in a hydrogen atom. Which of the following statements are true? Correct the false statements to make them true.
- It takes more energy to ionize (completely remove) the electron from  $n = 3$  than from the ground state.
  - The electron is farther from the nucleus on average in the  $n = 3$  state than in the  $n = 1$  state.
  - The wavelength of light emitted if the electron drops from  $n = 3$  to  $n = 2$  will be shorter than the wavelength of light emitted if the electron falls from  $n = 3$  to  $n = 1$ .
  - The wavelength of light emitted when the electron returns to the ground state from  $n = 3$  will be the same as the wavelength of light absorbed to go from  $n = 1$  to  $n = 3$ .
  - For  $n = 3$ , the electron is in the first excited state.
- 51.** Calculate the maximum wavelength of light capable of removing an electron for a hydrogen atom from the energy state characterized by  $n = 1$  by  $n = 2$ .
- 52.** Consider an electron for a hydrogen atom in an excited state. The maximum wavelength of electromagnetic radiation that can completely remove (ionize) the electron from the H atom is 1460 nm. What is the initial excited state for the electron ( $n = ?$ )?
- 53.** An excited hydrogen atom with an electron in the  $n = 5$  state emits light having a frequency of  $6.90 \times 10^{14} \text{ s}^{-1}$ . Determine the principal quantum level for the final state in this electronic transition.
- 54.** An excited hydrogen atom emits light with a wavelength of 397.2 nm to reach the energy level for which  $n = 2$ . In which principal quantum level did the electron begin?

### Quantum Mechanics, Quantum Numbers, and Orbitals

- 55.** Using the Heisenberg uncertainty principle, calculate  $\Delta x$  for each of the following.
- an electron with  $\Delta v = 0.100 \text{ m/s}$
  - a baseball (mass = 145 g) with  $\Delta v = 0.100 \text{ m/s}$
  - How does the answer in part a compare with the size of a hydrogen atom?
  - How does the answer in part b correspond to the size of a baseball?
- 56.** The Heisenberg uncertainty principle can be expressed in the form
- $$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$
- where  $E$  represents energy and  $t$  represents time. Show that the units for this form are the same as the units for the form used in this chapter:
- $$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$
- 57.** What are the possible values for the quantum numbers  $n$ ,  $\ell$ , and  $m_\ell$ ?

- 58.** Which of the following orbital designations are incorrect:  $1s$ ,  $1p$ ,  $7d$ ,  $9s$ ,  $3f$ ,  $4f$ ,  $2d$ ?
- 59.** Which of the following sets of quantum numbers are not allowed in the hydrogen atom? For the sets of quantum numbers that are incorrect, state what is wrong in each set.
- $n = 3$ ,  $\ell = 2$ ,  $m_\ell = 2$
  - $n = 4$ ,  $\ell = 3$ ,  $m_\ell = 4$
  - $n = 0$ ,  $\ell = 0$ ,  $m_\ell = 0$
  - $n = 2$ ,  $\ell = -1$ ,  $m_\ell = 1$
- 60.** Which of the following sets of quantum numbers are not allowed? For each incorrect set, state why it is incorrect.
- $n = 3$ ,  $\ell = 3$ ,  $m_\ell = 0$ ,  $m_s = -\frac{1}{2}$
  - $n = 4$ ,  $\ell = 3$ ,  $m_\ell = 2$ ,  $m_s = -\frac{1}{2}$
  - $n = 4$ ,  $\ell = 1$ ,  $m_\ell = 1$ ,  $m_s = +\frac{1}{2}$
  - $n = 2$ ,  $\ell = 1$ ,  $m_\ell = -1$ ,  $m_s = -1$
  - $n = 5$ ,  $\ell = -4$ ,  $m_\ell = 2$ ,  $m_s = +\frac{1}{2}$
  - $n = 3$ ,  $\ell = 1$ ,  $m_\ell = 2$ ,  $m_s = -\frac{1}{2}$
- 61.** What is the physical significance of the value of  $\psi^2$  at a particular point in an atomic orbital?
- 62.** In defining the sizes of orbitals, why must we use an arbitrary value, such as 90% of the probability of finding an electron in that region?
- Polyelectronic Atoms**
- 63.** How many orbitals in an atom can have the designation  $5p$ ,  $3d_z$ ,  $4d$ ,  $n = 5$ ,  $n = 4$ ?
- 64.** How many electrons in an atom can have the designation  $1p$ ,  $6d_{x^2-y^2}$ ,  $4f$ ,  $7p_y$ ,  $2s$ ,  $n = 3$ ?
- 65.** Give the maximum number of electrons in an atom that can have these quantum numbers:
- $n = 4$
  - $n = 5$ ,  $m_\ell = +1$
  - $n = 5$ ,  $m_s = +\frac{1}{2}$
  - $n = 3$ ,  $\ell = 2$
  - $n = 2$ ,  $\ell = 1$
- 66.** Give the maximum number of electrons in an atom that can have these quantum numbers:
- $n = 0$ ,  $\ell = 0$ ,  $m_\ell = 0$
  - $n = 2$ ,  $\ell = 1$ ,  $m_\ell = -1$ ,  $m_s = -\frac{1}{2}$
  - $n = 3$ ,  $m_s = +\frac{1}{2}$
  - $n = 2$ ,  $\ell = 2$
  - $n = 1$ ,  $\ell = 0$ ,  $m_\ell = 0$
- 67.** Draw atomic orbital diagrams representing the ground-state electron configuration for each of the following elements.
- Na
  - Co
  - Kr
- How many unpaired electrons are present in each element?
- 68.** For elements 1–36, there are two exceptions to the filling order as predicted from the periodic table. Draw the atomic orbital diagrams for the two exceptions and indicate how many unpaired electrons are present.
- 69.** The elements Si, Ga, As, Ge, Al, Cd, S, and Se are all used in the manufacture of various semiconductor devices. Write the expected electron configuration for these atoms.
- 70.** The elements Cu, O, La, Y, Ba, Tl, and Bi are all found in high-temperature ceramic superconductors. Write the expected electron configuration for these atoms.
- 71.** Write the expected electron configurations for each of the following atoms: Sc, Fe, P, Cs, Eu, Pt, Xe, Br.
- 72.** Write the expected electron configurations for each of the following atoms: Cl, Sb, Sr, W, Pb, Cf.
- 73.** Write the expected ground-state electron configuration for the following.
- the element with one unpaired  $5p$  electron that forms a covalent with compound fluorine
  - the (as yet undiscovered) alkaline earth metal after radium
  - the noble gas with electrons occupying  $4f$  orbitals
  - the first-row transition metal with the most unpaired electrons
- 74.** Using only the periodic table inside the front cover of the text, write the expected ground-state electron configurations for
- the third element in Group 5A.
  - element number 116.
  - an element with three unpaired  $5d$  electrons.
  - the halogen with electrons in the  $6p$  atomic orbitals.
- 75.** In the ground state of mercury, Hg,
- how many electrons occupy atomic orbitals with  $n = 3$ ?
  - how many electrons occupy  $d$  atomic orbitals?
  - how many electrons occupy  $p_z$  atomic orbitals?
  - how many electrons have spin “up” ( $m_s = +\frac{1}{2}$ )?
- 76.** In the ground state of element 115, Uup,
- how many electrons have  $n = 5$  as one of their quantum numbers?
  - how many electrons have  $\ell = 3$  as one of their quantum numbers?
  - how many electrons have  $m_\ell = 1$  as one of their quantum numbers?
  - how many electrons have  $m_s = -\frac{1}{2}$  as one of their quantum numbers?
- 77.** Give a possible set of values of the four quantum numbers for all the electrons in a boron atom and a nitrogen atom if each is in the ground state.
- 78.** Give a possible set of values of the four quantum numbers for the  $4s$  and  $3d$  electrons in titanium.
- 79.** A certain oxygen atom has the electron configuration  $1s^2 2s^2 2p_x^2 2p_y^2$ . How many unpaired electrons are present? Is this an excited state of oxygen? In going from this state to the ground state would energy be released or absorbed?
- 80.** Which of the following electron configurations correspond to an excited state? Identify the atoms and write the ground-state electron configuration where appropriate.
- $1s^2 2s^2 3p^1$
  - $1s^2 2s^2 2p^6$
  - $1s^2 2s^2 2p^4 3s^1$
  - $[Ar]4s^3 3d^5 4p^1$
- How many unpaired electrons are present in each of these species?

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- 81.** Which of elements 1–36 have two unpaired electrons in the ground state?
- 82.** Which of elements 1–36 have one unpaired electron in the ground state?
- 83.** One bit of evidence that the quantum mechanical model is “correct” lies in the magnetic properties of matter. Atoms with unpaired electrons are attracted by magnetic fields and thus are said to exhibit *paramagnetism*. The degree to which this effect is observed is directly related to the number of unpaired electrons present in the atom. Consider the ground-state electron configurations for Li, N, Ni, Te, Ba, and Hg. Which of these atoms would be expected to be paramagnetic, and how many unpaired electrons are present in each paramagnetic atom?
- 84.** How many unpaired electrons are present in each of the following in the ground state: O, O<sup>+</sup>, O<sup>-</sup>, Os, Zr, S, F, Ar?
- The Periodic Table and Periodic Properties**
- 85.** Arrange the following groups of atoms in order of increasing size.
- Te, S, Se
  - K, Br, Ni
  - Ba, Si, F
- 86.** Arrange the following groups of atoms in order of increasing size.
- Rb, Na, Be
  - Sr, Se, Ne
  - Fe, P, O
- 87.** Arrange the atoms in Exercise 85 in order of increasing first ionization energy.
- 88.** Arrange the atoms in Exercise 86 in order of increasing first ionization energy.
- 89.** In each of the following sets, which atom or ion has the smallest radius?
- H, He
  - Cl, In, Se
  - element 120, element 119, element 117
  - Nb, Zn, Si
  - Na<sup>-</sup>, Na, Na<sup>+</sup>
- 90.** In each of the following sets, which atom or ion has the smallest ionization energy?
- Ca, Sr, Ba
  - K, Mn, Ga
  - N, O, F
  - S<sup>2-</sup>, S, S<sup>2+</sup>
  - Cs, Ge, Ar
- 91.** Element 106 has been named seaborgium, Sg, in honor of Glenn Seaborg, discoverer of the first transuranium element.
- Write the expected electron configuration for element 106.
  - What other element would be most like element 106 in its properties?
  - Write the formula for a possible oxide and a possible oxyanion of element 106.
- 92.** Predict some of the properties of element 117 (the symbol is Uus, following conventions proposed by the International Union of Pure and Applied Chemistry, or IUPAC).
- 93.** What will be its electron configuration?
- 94.** What element will it most resemble chemically?
- 95.** What will be the formula of the neutral binary compounds it forms with sodium, magnesium, carbon, and oxygen?
- 96.** What oxyanions would you expect Uus to form?
- 97.** The first ionization energies of As and Se are 0.947 and 0.941 MJ/mol, respectively. Rationalize these values in terms of electron configurations.
- 98.** Rank the elements Be, B, C, N, and O in order of increasing first ionization energy. Explain your reasoning.
- 99.** For each of the following pairs of elements
- (C and N)      (Ar and Br)
- pick the atom with
- more favorable (exothermic) electron affinity.
  - higher ionization energy.
  - larger size.
- 100.** For each of the following pairs of elements
- (Mg and K)      (F and Cl)
- pick the atom with
- more favorable (exothermic) electron affinity.
  - higher ionization energy.
  - larger size.
- 101.** The electron affinities of the elements from aluminum to chlorine are -44, -120, -74, -200.4, and -384.7 kJ/mol, respectively. Rationalize the trend in these values.
- 102.** The electron affinity for sulfur is more exothermic than that for oxygen. How do you account for this?
- 103.** Order each of the following sets from the least exothermic electron affinity to the most exothermic electron affinity.
- F, Cl, Br, I
  - N, O, F
- 104.** Which has the more negative electron affinity, the oxygen atom or the O<sup>-</sup> ion? Explain your answer.
- 105.** Write equations corresponding to the following.
- The fourth ionization energy of Se
  - The electron affinity of S<sup>-</sup>
  - The electron affinity of Fe<sup>3+</sup>
  - The ionization energy of Mg
- 106.** Using data from the text, determine the following values (justify your answer):
- the electron affinity of Mg<sup>2+</sup>
  - the ionization energy of Cl<sup>-</sup>
  - the electron affinity of Cl<sup>+</sup>
  - the ionization energy of Mg<sup>-</sup> (Electron affinity of Mg = 230 kJ/mol)
- Alkali Metals**
- 107.** An ionic compound of potassium and oxygen has the empirical formula KO. Would you expect this compound to be potassium(II) oxide or potassium peroxide? Explain.
- 108.** Give the name and formula of each of the binary compounds formed from the following elements.
- Li and N
  - Na and Br
  - K and S

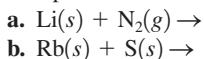
**105.** Cesium was discovered in natural mineral waters in 1860 by R. W. Bunsen and G. R. Kirchhoff using the spectroscope they invented in 1859. The name came from the Latin *caesius* ("sky blue") because of the prominent blue line observed for this element at 455.5 nm. Calculate the frequency and energy of a photon of this light.

**106.** The bright yellow light emitted by a sodium vapor lamp consists of two emission lines at 589.0 and 589.6 nm. What are the frequency and the energy of a photon of light at each of these wavelengths? What are the energies in kJ/mol?

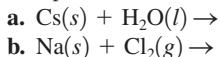
**107.** Does the information on alkali metals in Table 7.8 of the text confirm the general periodic trends in ionization energy and atomic radius? Explain.

**108.** Predict the atomic number of the next alkali metal after francium and give its ground-state electron configuration.

**109.** Complete and balance the equations for the following reactions.

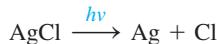


**110.** Complete and balance the equations for the following reactions.



## Additional Exercises

**111.** Photogray lenses incorporate small amounts of silver chloride in the glass of the lens. When light hits the AgCl particles, the following reaction occurs:

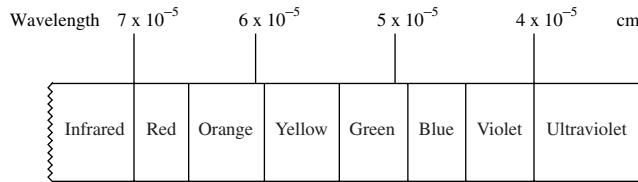


The silver metal that is formed causes the lenses to darken. The enthalpy change for this reaction is  $3.10 \times 10^2$  kJ/mol. Assuming all this energy must be supplied by light, what is the maximum wavelength of light that can cause this reaction?

**112.** A certain microwave oven delivers 750. watts (joule/s) of power to a coffee cup containing 50.0 g of water at 25.0°C. If the wavelength of microwaves in the oven is 9.75 cm, how long does it take, and how many photons must be absorbed, to make the water boil? The specific heat capacity of water is  $4.18 \text{ J}^\circ\text{C} \cdot \text{g}$  and assume only the water absorbs the energy of the microwaves.

**113.** Mars is roughly 60 million km from earth. How long does it take for a radio signal originating from earth to reach Mars?

**114.** Consider the following approximate visible light spectrum:



Barium emits light in the visible region of the spectrum. If each photon of light emitted from barium has an energy of  $3.59 \times 10^{-19}$  J, what color of visible light is emitted?

**115.** One of the visible lines in the hydrogen emission spectrum corresponds to the  $n = 6$  to  $n = 2$  electronic transition. What color light is this transition? See Exercise 114.

**116.** Using Fig. 7.28, list the elements (ignore the lanthanides and actinides) that have ground-state electron configurations that differ from those we would expect from their positions in the periodic table.

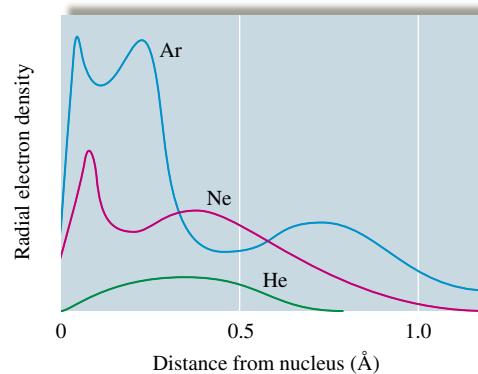
**117.** Are the following statements true for the hydrogen atom only, true for all atoms, or not true for any atoms?

- a. The principal quantum number completely determines the energy of a given electron.
- b. The angular momentum quantum number,  $\ell$ , determines the shapes of the atomic orbitals.
- c. The magnetic quantum number,  $m_\ell$ , determines the direction that the atomic orbitals point in space.

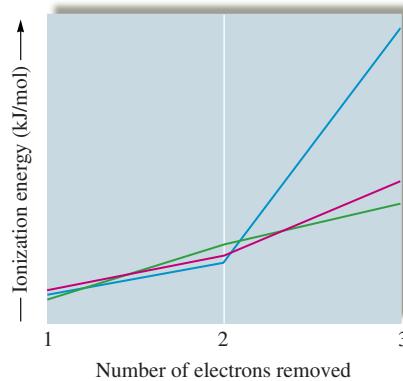
**118.** Although no currently known elements contain electrons in  $g$  orbitals in the ground state, it is possible that these elements will be found or that electrons in excited states of known elements could be in  $g$  orbitals. For  $g$  orbitals, the value of  $\ell$  is 4. What is the lowest value of  $n$  for which  $g$  orbitals could exist? What are the possible values of  $m_\ell$ ? How many electrons could a set of  $g$  orbitals hold?

**119.** Consider the representations of the  $p$  and  $d$  atomic orbitals in Figs. 7.14 and 7.16. What do the + and - signs indicate?

**120.** Total radial probability distributions for the helium, neon, and argon atoms are shown in the following graph. How can one interpret the shapes of these curves in terms of electron configurations, quantum numbers, and nuclear charges?



**121.** The following graph plots the first, second, and third ionization energies for Mg, Al, and Si.



Without referencing the text, which plot corresponds to which element? In one of the plots, there is a huge jump in energy

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between  $I_2$  and  $I_3$ , unlike in the other two plots. Explain this phenomenon.

- 122.** An ion having a 4+ charge and a mass of 49.9 amu has 2 electrons with principal quantum number  $n = 1$ , 8 electrons with  $n = 2$ , and 10 electrons with  $n = 3$ . Supply as many of the properties for the ion as possible from the information given. *Hint:* In forming ions for this species, the 4s electrons are lost before the 3d electrons.

- a. the atomic number
- b. total number of s electrons
- c. total number of p electrons
- d. total number of d electrons
- e. the number of neutrons in the nucleus
- f. the ground-state electron configuration of the neutral atom

- 123.** The successive ionization energies for an unknown element are

$$I_1 = 896 \text{ kJ/mol}$$

$$I_2 = 1752 \text{ kJ/mol}$$

$$I_3 = 14,807 \text{ kJ/mol}$$

$$I_4 = 17,948 \text{ kJ/mol}$$

To which family in the periodic table does the unknown element most likely belong?

- 124.** An unknown element is a nonmetal and has a valence electron configuration of  $ns^2np^4$ .

- a. How many valence electrons does this element have?
- b. What are some possible identities for this element?
- c. What is the formula of the compound this element would form with potassium?
- d. Would this element have a larger or smaller radius than barium?
- e. Would this element have a greater or smaller ionization energy than fluorine?

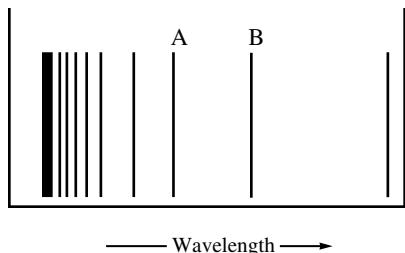
- 125.** Using data from this chapter, calculate the change in energy expected for each of the following processes.

- a.  $\text{Na}(g) + \text{Cl}(g) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)$
- b.  $\text{Mg}(g) + \text{F}(g) \rightarrow \text{Mg}^+(g) + \text{F}^-(g)$
- c.  $\text{Mg}^+(g) + \text{F}(g) \rightarrow \text{Mg}^{2+}(g) + \text{F}^-(g)$
- d.  $\text{Mg}(g) + 2\text{F}(g) \rightarrow \text{Mg}^{2+}(g) + 2\text{F}^-(g)$

### Challenge Problems

- 126.** One of the emission spectral lines for  $\text{Be}^{3+}$  has a wavelength of 253.4 nm for an electronic transition that begins in the state with  $n = 5$ . What is the principal quantum number of the lower-energy state corresponding to this emission? (*Hint:* The Bohr model can be applied to one-electron ions. Don't forget the Z factor:  $Z = \text{nuclear charge} = \text{atomic number}$ .)

- 127.** The figure below represents part of the emission spectrum for a one-electron ion in the gas phase. All the lines result from electronic transitions from excited states to the  $n = 3$  state. (See Exercise 126.)



- a. What electronic transitions correspond to lines A and B?

- b. If the wavelength of line B is 142.5 nm, calculate the wavelength of line A.

- 128.** When the excited electron in a hydrogen atom falls from  $n = 5$  to  $n = 2$ , a photon of blue light is emitted. If an excited electron in  $\text{He}^+$  falls from  $n = 4$ , to which energy level must it fall so that a similar blue light (as with the hydrogen) is emitted? Prove it. (See Exercise 126.)

- 129.** The wave function for the  $2p_z$  orbital in the hydrogen atom is

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left( \frac{Z}{a_0} \right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$$

where  $a_0$  is the value for the radius of the first Bohr orbit in meters ( $5.29 \times 10^{-11}$ ),  $\sigma$  is  $Z(r/a_0)$ ,  $r$  is the value for the distance from the nucleus in meters, and  $\theta$  is an angle. Calculate the value of  $|\psi_{2p_z}|^2$  at  $r = a_0$  for  $\theta = 0$  (z axis) and for  $\theta = 90^\circ$  (xy plane).

- 130.** Answer the following questions assuming that  $m_s$  could have three values rather than two and that the rules for  $n$ ,  $\ell$ , and  $m_\ell$  are the normal ones.

- a. How many electrons would an orbital be able to hold?
- b. How many elements would the first and second periods in the periodic table contain?
- c. How many elements would be contained in the first transition metal series?
- d. How many electrons would the set of  $4f$  orbitals be able to hold?

- 131.** Assume that we are in another universe with different physical laws. Electrons in this universe are described by four quantum numbers with meanings similar to those we use. We will call these quantum numbers  $p$ ,  $q$ ,  $r$ , and  $s$ . The rules for these quantum numbers are as follows:

$$p = 1, 2, 3, 4, 5, \dots$$

$q$  takes on positive odd integer and  $q \leq p$ .

$r$  takes on all even integer values from  $-q$  to  $+q$ . (Zero is considered an even number.)

$$s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

- a. Sketch what the first four periods of the periodic table will look like in this universe.
- b. What are the atomic numbers of the first four elements you would expect to be least reactive?
- c. Give an example, using elements in the first four rows, of ionic compounds with the formulas  $\text{XY}$ ,  $\text{XY}_2$ ,  $\text{X}_2\text{Y}$ ,  $\text{XY}_3$ , and  $\text{X}_2\text{Y}_3$ .
- d. How many electrons can have  $p = 4$ ,  $q = 3$ ?
- e. How many electrons can have  $p = 3$ ,  $q = 0$ ,  $r = 0$ ?
- f. How many electrons can have  $p = 6$ ?

- 132.** Without looking at data in the text, sketch a qualitative graph of the third ionization energy versus atomic number for the elements Na through Ar, and explain your graph.

- 133.** The following numbers are the ratios of second ionization energy to first ionization energy:

Na: 9.2

Mg: 2.0

Al: 3.1

Si: 2.0

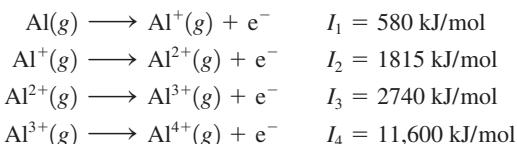
P: 1.8  
S: 2.3  
Cl: 1.8  
Ar: 1.8

Explain these relative numbers.

- 134.** We expect the atomic radius to increase going down a group in the periodic table. Can you suggest why the atomic radius of hafnium breaks this rule? (See data below.)

Atomic Radii, in pm			
Sc	157	Ti	147.7
Y	169.3	Zr	159.3
La	191.5	Hf	147.6

- 135.** Consider the following ionization energies for aluminum:



- a. Account for the trend in the values of the ionization energies.
  - b. Explain the large increase between  $I_3$  and  $I_4$ .
  - c. Which one of the four ions has the greatest electron affinity? Explain.
  - d. List the four aluminum ions given in order of increasing size, and explain your ordering. (*Hint:* Remember that most of the size of an atom or ion is due to its electrons.)
- 136.** While Mendeleev predicted the existence of several undiscovered elements, he did not predict the existence of the noble gases, the lanthanides, or the actinides. Propose reasons why Mendeleev was not able to predict the existence of the noble gases.
- 137.** An atom of a particular element is traveling at 1.00% of the speed of light. The de Broglie wavelength is found to be  $3.31 \times 10^{-3}$  pm. Which element is this? Prove it.

## Integrative Problems

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

- 138.** As the weapons officer aboard the *Starship Chemistry*, it is your duty to configure a photon torpedo to remove an electron from the outer hull of an enemy vessel. You know that the work function (the binding energy of the electron) of the hull of the enemy ship is  $7.52 \times 10^{-19}$  J.
- a. What wavelength does your photon torpedo need to be to eject an electron?
  - b. You find an extra photon torpedo with a wavelength of 259 nm and fire it at the enemy vessel. Does this photon torpedo do any damage to the ship (does it eject an electron)?
  - c. If the hull of the enemy vessel is made of the element with an electron configuration of  $[\text{Ar}]4s^13d^{10}$ , what metal is this?

- 139.** Francium, Fr, is a radioactive element found in some uranium minerals and is formed as a result of the decay of actinium.

- a. What are the electron configurations of francium and its predicted most common ion?
- b. It has been estimated that at any one time, there is only one (1.0) ounce of francium on earth. Assuming this is true, what number of francium atoms exist on earth?
- c. The longest-lived isotope of francium is  $^{223}\text{Fr}$ . What is the total mass in grams of the neutrons in one atom of this isotope?

- 140.** Answer the following questions based on the given electron configurations and identify the elements.

- a. Arrange these atoms in order of increasing size:  $[\text{Kr}]5s^24d^{10}5p^6$ ;  $[\text{Kr}]5s^24d^{10}5p^1$ ;  $[\text{Kr}]5s^24d^{10}5p^3$ .
- b. Arrange these atoms in order of decreasing first ionization energy:  $[\text{Ne}]3s^23p^5$ ;  $[\text{Ar}]4s^23d^{10}4p^3$ ;  $[\text{Ar}]4s^23d^{10}4p^5$ .

## Marathon Problem\*

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

- 141.** From the information below, identify element X.

- a. The wavelength of the radio waves sent by an FM station broadcasting at 97.1 MHz is 30.0 million ( $3.00 \times 10^7$ ) times greater than the wavelength corresponding to the energy difference between a particular excited state of the hydrogen atom and the ground state.
- b. Let  $V$  represent the principal quantum number for the valence shell of element X. If an electron in the hydrogen atom falls from shell  $V$  to the inner shell corresponding to the excited state mentioned above in part a, the wavelength of light emitted is the same as the wavelength of an electron moving at a speed of 570. m/s.
- c. The number of unpaired electrons for element X in the ground state is the same as the maximum number of electrons in an atom that can have the quantum number designations  $n = 2$ ,  $m_\ell = -1$ , and  $m_s = -\frac{1}{2}$ .
- d. Let  $A$  equal the charge of the stable ion that would form when the undiscovered element 120 forms ionic compounds. This value of  $A$  also represents the angular momentum quantum number for the subshell containing the unpaired electron(s) for element X.



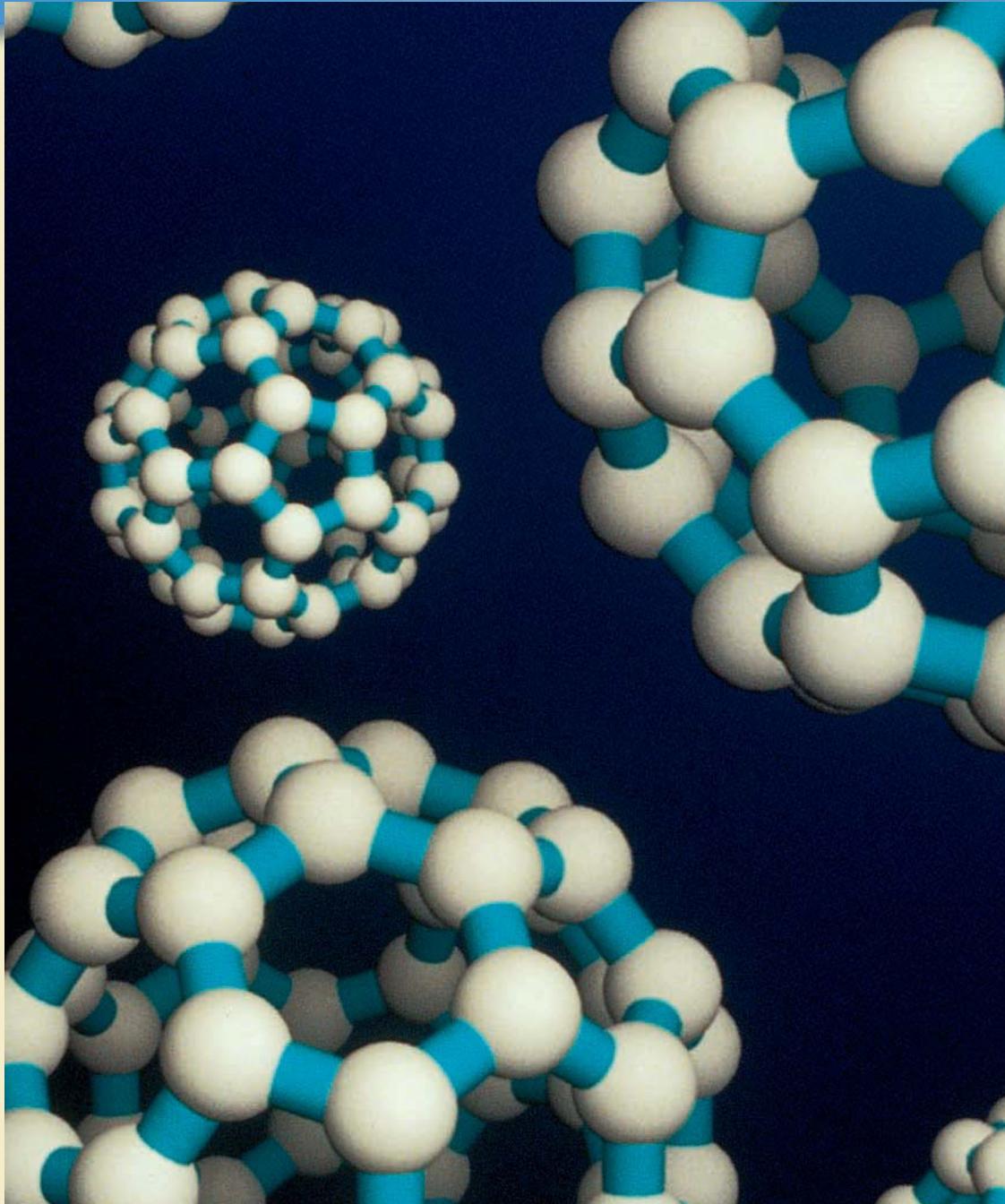
Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmco.com/PIC/zumdahl17e](http://college.hmco.com/PIC/zumdahl17e).

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# 8 Bonding: General Concepts

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Carbon forms very stable spherical C<sub>60</sub> molecules.

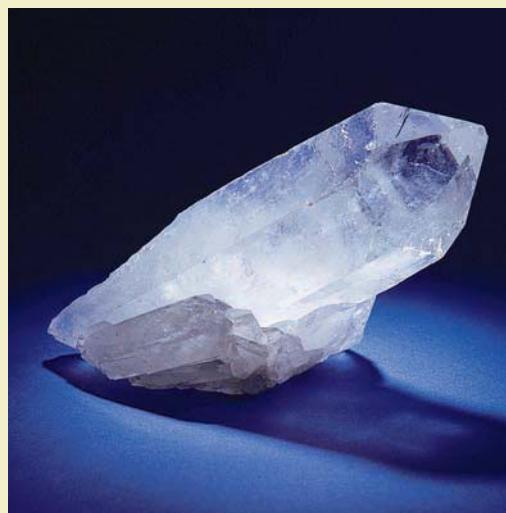
**A**s we examine the world around us, we find it to be composed almost entirely of compounds and mixtures of compounds: Rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together. Substances composed of unbound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

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

Silicon and carbon are next to each other in Group 4A of the periodic table. From our knowledge of periodic trends, we might expect  $\text{SiO}_2$  and  $\text{CO}_2$  to be very similar. But  $\text{SiO}_2$  is the empirical formula of silica, which is found in sand and quartz, and carbon dioxide is a gas, a product of respiration. Why are they so different? We will be able to answer this question after we have developed models for bonding.

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

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



Quartz grows in beautiful, regular crystals.

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

## 8.1 Types of Chemical Bonds

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

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

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

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

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

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

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.

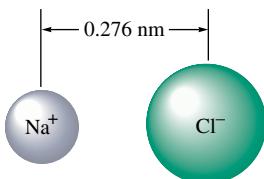
For example, in solid sodium chloride the distance between the centers of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions is 2.76 Å (0.276 nm), and the ionic energy per pair of ions is

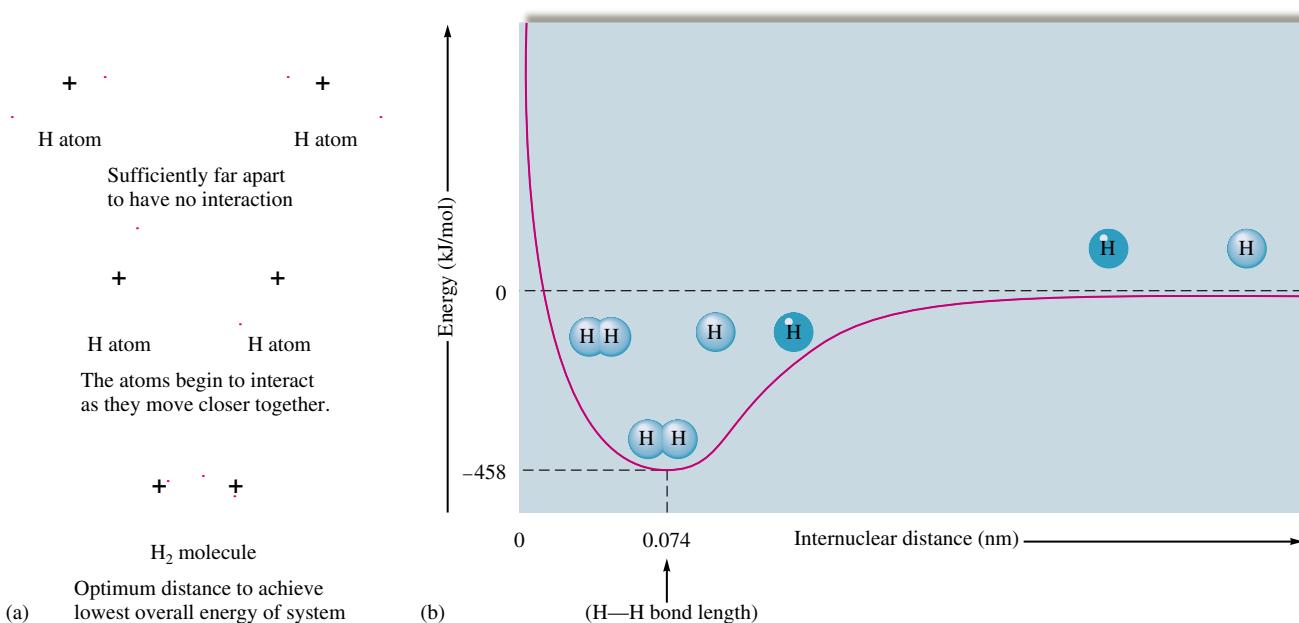
$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left[ \frac{(+1)(-1)}{0.276 \text{ nm}} \right] = -8.37 \times 10^{-19} \text{ J}$$

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

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

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



**FIGURE 8.1**

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

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

Potential energy was discussed in Chapter 6.

identical atoms? Let's explore this situation from a very simple point of view by considering the energy terms that result when two hydrogen atoms are brought close together, as shown in Fig. 8.1(a). When hydrogen atoms are brought close together, there are two unfavorable potential energy terms, proton–proton repulsion and electron–electron repulsion, and one favorable term, proton–electron attraction. Under what conditions will the H<sub>2</sub> molecule be favored over the separated hydrogen atoms? That is, what conditions will favor bond formation? The answer lies in the strong tendency in nature for any system to achieve the lowest possible energy. A bond will form (that is, the two hydrogen atoms will exist as a molecular unit) if the system can lower its total energy in the process.

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

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

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

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

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

In the H<sub>2</sub> molecule, the electrons reside primarily in the space between the two nuclei, where they are attracted simultaneously by both protons. This positioning is precisely what leads to the stability of the H<sub>2</sub> molecule compared with two separated hydrogen



## CHEMICAL IMPACT

### No Lead Pencils

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

Originally, chunks of graphite from Borrowdale, called marking stones, were used as writing instruments. Later,

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

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

atoms. The potential energy of each electron is lowered because of the increased attractive forces in this area. When we say that a bond is formed between the hydrogen atoms, we mean that the H<sub>2</sub> molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy).

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

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

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



where  $\delta$  (lowercase delta) is used to indicate a fractional charge. This same effect was noted in Chapter 4, where many of water’s unusual properties were attributed to the polar O—H bonds in the H<sub>2</sub>O molecule.

The most logical explanation for the development of the partial positive and negative charges on the atoms (bond polarity) in such molecules as HF and H<sub>2</sub>O is that the

Ionic and covalent bonds are the extreme bond types.



Visualization: Polar Molecules

is blended for several days, it is dried, ground up again, and mixed with more water to give a gray paste. The paste is extruded through a metal tube to form thin rods, which are then cut into pencil-length pieces called “leads.” These leads are heated in an oven to 1000°C until they are smooth and hard. The ratio of clay to graphite is adjusted to vary the hardness of the lead—the more clay in the mix, the harder the lead and the lighter the line it makes.

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

Modern pencils are simple but amazing instruments. The average pencil can write approximately 45,000 words,

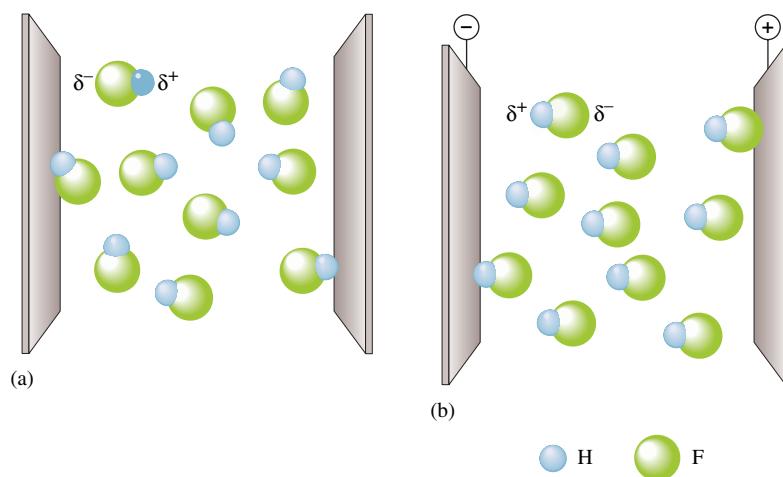
which is equivalent to a line 35 miles long. The graphite in a pencil is easily transferred to paper because graphite contains layers of carbon atoms bound together in a “chicken-wire” structure. Although the bonding *within* each layer is very strong, the bonding *between* layers is weak, giving graphite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

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

electrons in the bonds are not shared equally. For example, we can account for the polarity of the HF molecule by assuming that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom. Likewise, in the H<sub>2</sub>O molecule the oxygen atom appears to attract the shared electrons more strongly than the hydrogen atoms do. Because bond polarity has important chemical implications, we find it useful to quantify the ability of an atom to attract shared electrons. In the next section we show how this is done.

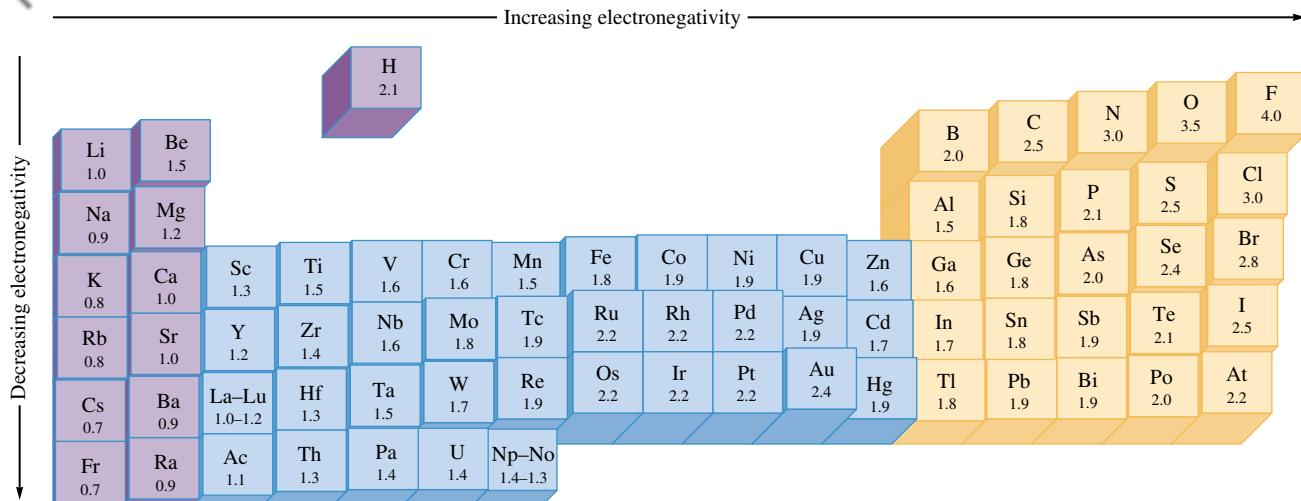
## 8.2 Electronegativity

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



**FIGURE 8.2**

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

**FIGURE 8.3**

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

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

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

The difference ( $\Delta$ ) between the actual (measured) and expected bond energies is

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

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



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

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

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

**TABLE 8.1** The Relationship Between Electronegativity and Bond Type

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

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

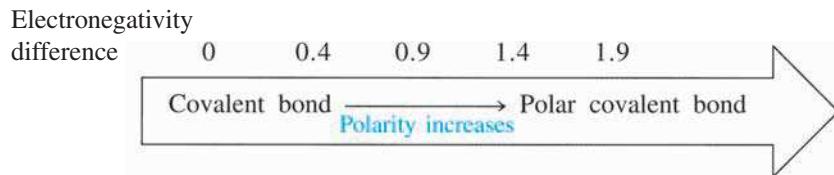
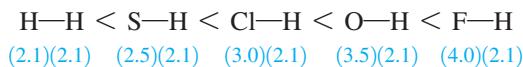
### Sample Exercise 8.1

### Relative Bond Polarities

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

#### Solution

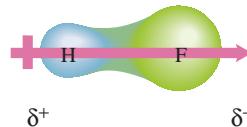
The polarity of the bond increases as the difference in electronegativity increases. From the electronegativity values in Fig. 8.3, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):

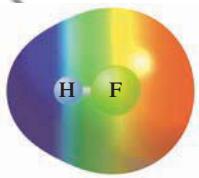


*See Exercises 8.31 and 8.32.*

## 8.3 Bond Polarity and Dipole Moments

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



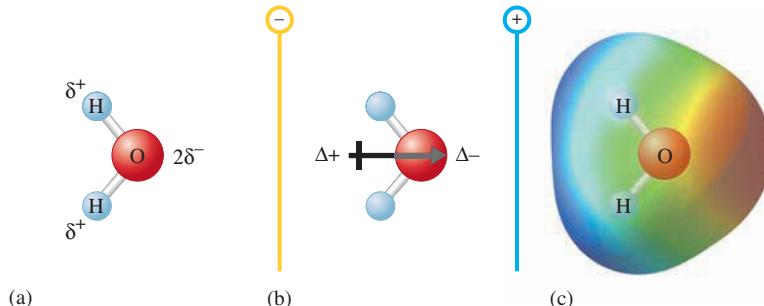
**FIGURE 8.4**

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

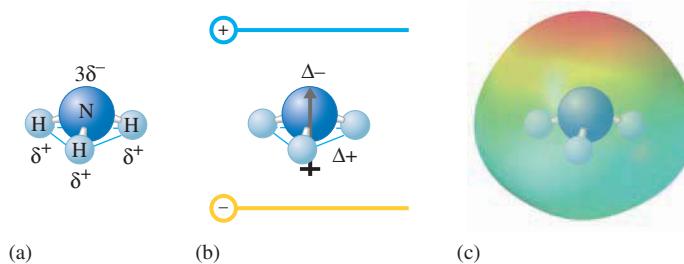
Another way to represent the charge distribution in HF is by an electrostatic potential diagram (see Fig. 8.4). For this representation the colors of visible light are used to show the variation in charge distribution. Red indicates the most electron-rich region of the molecule and blue indicates the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

Of course, any diatomic (two-atom) molecule that has a polar bond also will show a molecular dipole moment. Polyatomic molecules also can exhibit dipolar behavior. For example, because the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms, the molecular charge distribution is that shown in Fig. 8.5(a). Because of this charge distribution, the water molecule behaves in an electric field as if it had two centers of charge—one positive and one negative—as shown in Fig. 8.5(b). The water molecule has a dipole moment. The same type of behavior is observed for the NH<sub>3</sub> molecule (Fig. 8.6). Some molecules have polar bonds but do not have a dipole moment. This occurs when the individual bond polarities are arranged in such a way that they cancel each other out. An example is the CO<sub>2</sub> molecule, which is a linear molecule that has the charge distribution shown in Fig. 8.7. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment. There is no preferential way for this molecule to line up in an electric field. (Try to find a preferred orientation to make sure you understand this concept.)

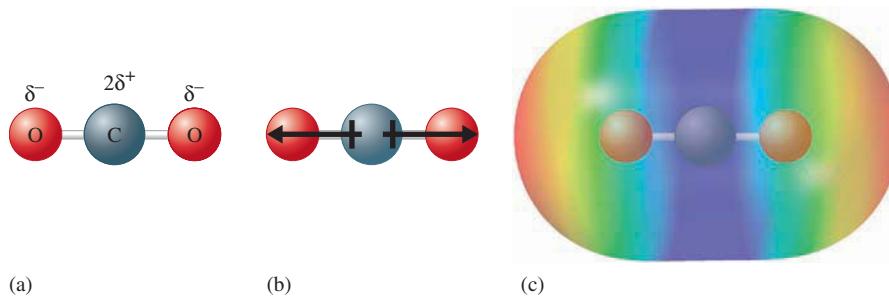
There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are shown in Table 8.2.

**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.

**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 Moment**

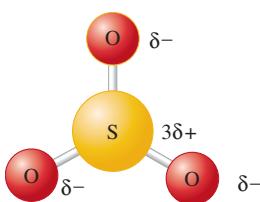
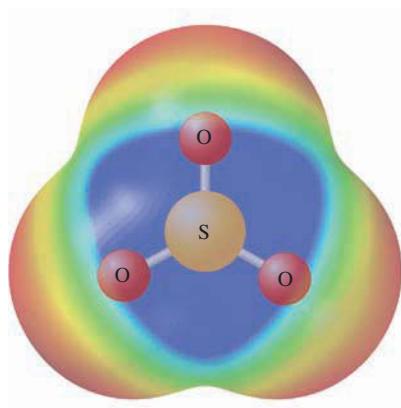
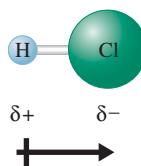
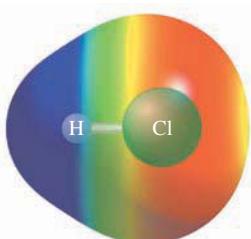
Type		Cancellation of Polar Bonds	Example	Ball-and-Stick Model
Linear molecules with two identical bonds	B—A—B $\text{CO}_2$	$\longleftrightarrow + + \rightarrow$		
Planar molecules with three identical bonds 120 degrees apart			$\text{SO}_3$	
Tetrahedral molecules with four identical bonds 109.5 degrees apart			$\text{CCl}_4$	

**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<sub>2</sub>, SO<sub>3</sub> (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH<sub>4</sub> [tetrahedral (see Table 8.2) with the carbon atom at the center], and H<sub>2</sub>S (V-shaped with the sulfur atom at the point).

**Solution**

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



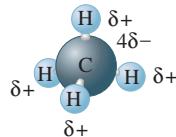
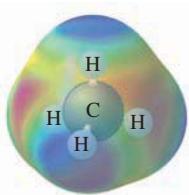
*The Cl<sub>2</sub> molecule:* The two chlorine atoms share the electrons equally. No bond polarity occurs, and the Cl<sub>2</sub> molecule has no dipole moment.

*The SO<sub>3</sub> molecule:* The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5). This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge:

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

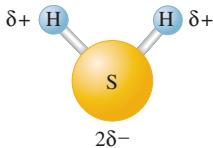
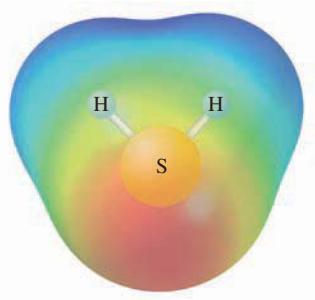
The bond polarities arranged symmetrically as shown cancel, and the molecule has no dipole moment. This molecule is the second type shown in Table 8.2.

*The CH<sub>4</sub> molecule:* Carbon has a slightly higher electronegativity (2.5) than does hydrogen (2.1). This leads to small partial positive charges on the hydrogen atoms and a small partial negative charge on the carbon:

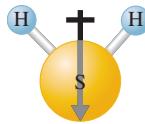


This case is similar to the third type in Table 8.2, and the bond polarities cancel. The molecule has no dipole moment.

*The H<sub>2</sub>S molecule:* Since the electronegativity of sulfur (2.5) is slightly greater than that of hydrogen (2.1), the sulfur will have a partial negative charge, and the hydrogen atoms will have a partial positive charge, which can be represented as



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



*See Exercise 8.114.*

## 8.4 Ions: Electron Configurations and Sizes

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

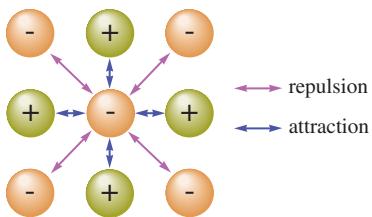
- When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations.

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

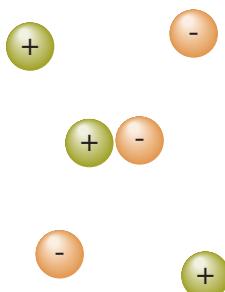
- When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom and the valence orbitals of the metal are emptied. In this way both ions achieve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

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

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



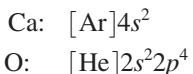
In the gas phase of an ionic substance the ions would be relatively far apart and would not contain large groups of ions:



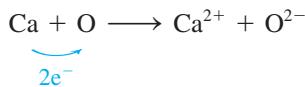
## Predicting Formulas of Ionic Compounds

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

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



From Fig. 8.3 we see that the electronegativity of oxygen (3.5) is much greater than that of calcium (1.0). Because of this large difference, electrons will be transferred from calcium to oxygen to form oxygen anions and calcium cations in the compound. How many electrons are transferred? We can base our prediction on the observation that noble gas configurations are generally the most stable. Note that oxygen needs two electrons to fill its  $2s$  and  $2p$  valence orbitals and to achieve the configuration of neon ( $1s^22s^22p^6$ ). And by losing two electrons, calcium can achieve the configuration of argon. Two electrons are therefore transferred:



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

The same principles can be applied to many other cases. For example, consider the compound formed between aluminum and oxygen. Because aluminum has the configuration  $[\text{Ne}]3s^23p^1$ , it loses three electrons to form the  $\text{Al}^{3+}$  ion and thus achieves the neon



Visualization: Formation of Ionic Compounds



A bauxite mine. Bauxite contains  $\text{Al}_2\text{O}_3$ , the main source of aluminum.

configuration. Therefore, the  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  ions form in this case. Since the compound must be electrically neutral, there must be three  $\text{O}^{2-}$  ions for every two  $\text{Al}^{3+}$  ions, and the compound has the empirical formula  $\text{Al}_2\text{O}_3$ .

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

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

### Sizes of Ions

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

**TABLE 8.3 Common Ions with Noble Gas Configurations in Ionic Compounds**

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

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

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

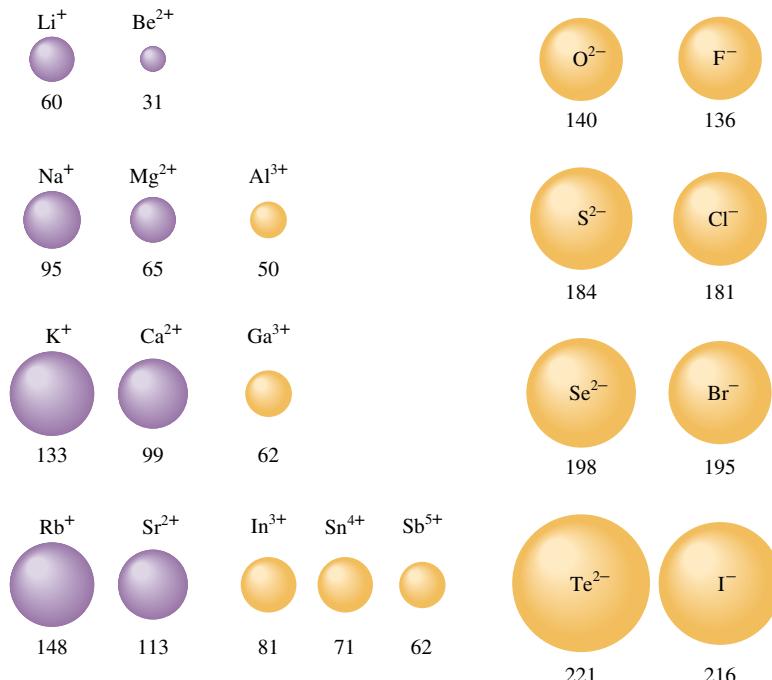
It is also important to know how the sizes of ions vary depending on the positions of the parent elements in the periodic table. Figure 8.8 shows the sizes of the most important ions (each with a noble gas configuration) and their position in the periodic table. Note that ion size increases down a group.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

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



Visualization: Ionic Radii

For isoelectronic ions, size decreases as  $Z$  increases.



**FIGURE 8.8**

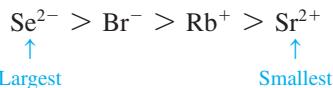
Sizes of ions related to positions of the elements on the periodic table. Note that size generally increases down a group. Also note that in a series of isoelectronic ions, size decreases with increasing atomic number. The ionic radii are given in units of picometers.

**Sample Exercise 8.3****Relative Ion Size I**

Arrange the ions  $\text{Se}^{2-}$ ,  $\text{Br}^-$ ,  $\text{Rb}^+$ , and  $\text{Sr}^{2+}$  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  $\text{Se}^{2-}$ , 35 for  $\text{Br}^-$ , 37 for  $\text{Rb}^+$ , and 38 for  $\text{Sr}^{2+}$ . Since the nuclear charge is greatest for  $\text{Sr}^{2+}$ , it is the smallest of these ions. The  $\text{Se}^{2-}$  ion is largest:



*See Exercises 8.37 and 8.38.*

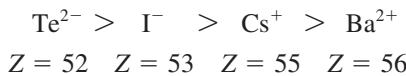
**Sample Exercise 8.4****Relative Ion Size II**

Choose the largest ion in each of the following groups.

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

**Solution**

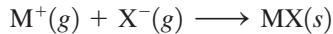
- a. The ions are all from Group 1A elements. Since size increases down a group (the ion with the greatest number of electrons is largest),  $\text{Cs}^+$  is the largest ion.
- b. This is an isoelectronic series of ions, all of which have the xenon electron configuration. The ion with the smallest nuclear charge is largest:



*See Exercises 8.39 and 8.40.*

## 8.5 Energy Effects in Binary Ionic Compounds

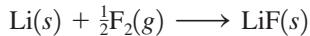
In this section we will introduce the factors that influence the stability and the structures of solid binary ionic compounds. We know that metals and nonmetals react by transferring electrons to form cations and anions that are mutually attractive. The resulting ionic solid forms because the aggregated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



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

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

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



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

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



The enthalpy of sublimation for  $\text{Li}(s)$  is 161 kJ/mol.

→ 2 Ionization of lithium atoms to form  $\text{Li}^+$  ions in the gas phase:



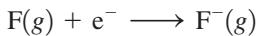
This process corresponds to the first ionization energy for lithium, which is 520 kJ/mol.

→ 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  $\text{F}_2$  molecules:



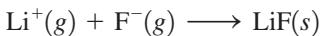
The energy required to break this bond is 154 kJ/mol. In this case we are breaking the bonds in a half mole of fluorine, so the energy required for this step is  $(154 \text{ kJ})/2$ , or 77 kJ.

→ 4 Formation of  $\text{F}^-$  ions from fluorine atoms in the gas phase:



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

→ 5 Formation of solid lithium fluoride from the gaseous  $\text{Li}^+$  and  $\text{F}^-$  ions:



This corresponds to the lattice energy for  $\text{LiF}$ , which is  $-1047 \text{ kJ/mol}$ .

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

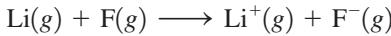
Process	Energy Change (kJ)
$\text{Li}(s) \rightarrow \text{Li}(g)$	161
$\text{Li}(g) \rightarrow \text{Li}^+(g) + \text{e}^-$	520
$\frac{1}{2}\text{F}_2(g) \rightarrow \text{F}(g)$	77
$\text{F}(g) + \text{e}^- \rightarrow \text{F}^-(g)$	$-328$
$\text{Li}^+(g) + \text{F}^-(g) \rightarrow \text{LiF}(s)$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



Lithium fluoride.

In doing this calculation, we have ignored the small difference between  $\Delta H_{\text{sub}}$  and  $\Delta E_{\text{sub}}$ .

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



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



Visualization: Born–Haber Cycle for NaCl(s)

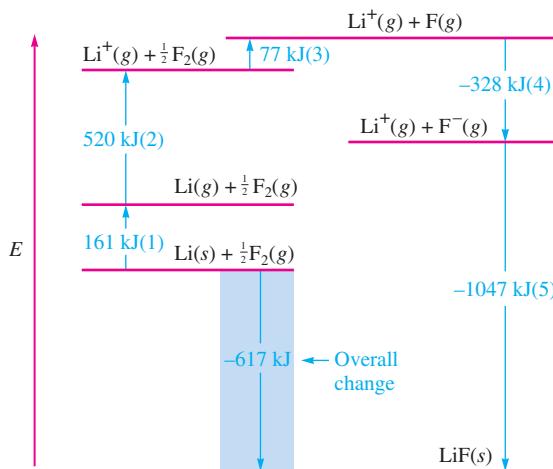
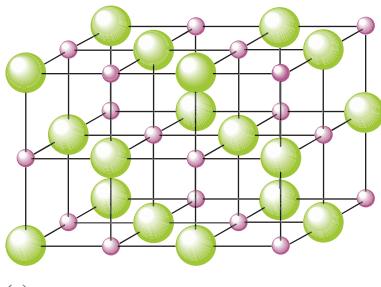
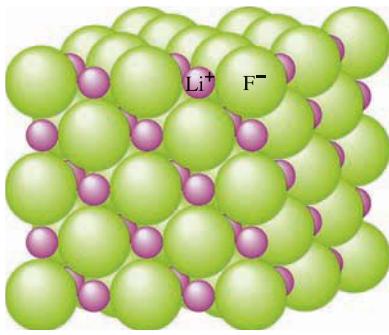


FIGURE 8.9

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



(a)



(b)

FIGURE 8.10

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

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

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

### Lattice Energy Calculations

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

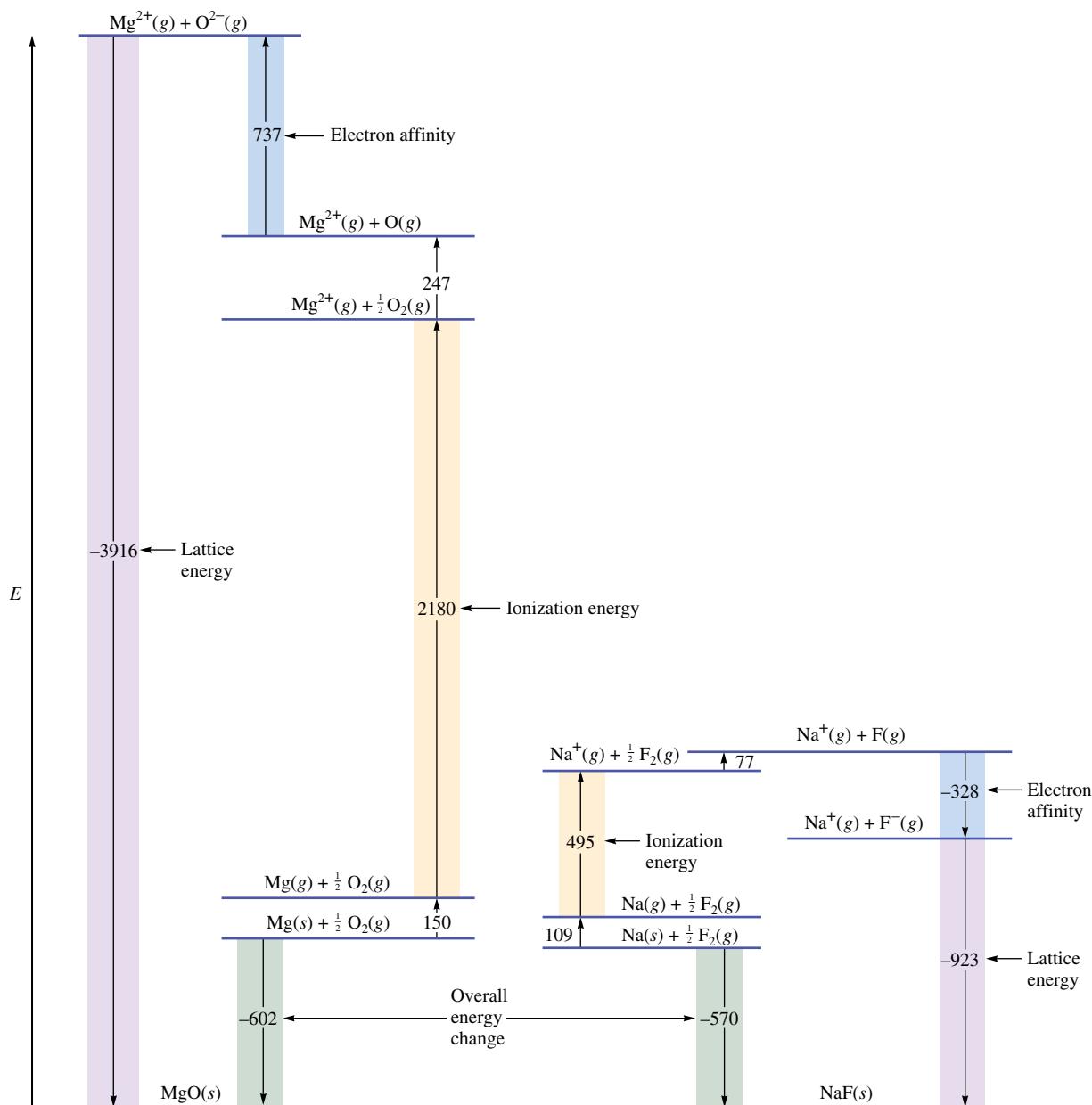
$$\text{Lattice energy} = k \left( \frac{Q_1 Q_2}{r} \right)$$

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

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

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

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

**FIGURE 8.11**

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

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

In view of the facts that twice as much energy is required to remove the second electron from magnesium as to remove the first and that addition of an electron to the gaseous  $\text{O}^-$  ion is quite endothermic, it seems puzzling that magnesium oxide contains  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions rather than  $\text{Mg}^+$  and  $\text{O}^-$  ions. The answer lies in the lattice energy. Note that the lattice energy for combining gaseous  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions to form  $\text{MgO}(s)$  is 3000 kJ/mol

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Since the equation for lattice energy contains the product  $Q_1 Q_2$ , the lattice energy for a solid with  $2+$  and  $2-$  ions should be four times that for a solid with  $1+$  and  $1-$  ions. That is,

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

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

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

more negative than that for combining gaseous  $\text{Na}^+$  and  $\text{F}^-$  ions to form  $\text{NaF}(s)$ . Thus the energy released in forming a solid containing  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions rather than  $\text{Mg}^+$  and  $\text{O}^-$  ions more than compensates for the energies required for the processes that produce the  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions.

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

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

## 8.6 Partial Ionic Character of Covalent Bonds

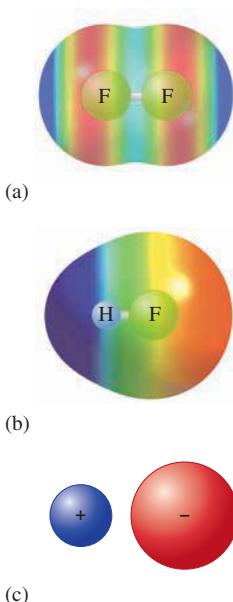
Recall that when atoms with different electronegativities react to form molecules, the electrons are not shared equally. The possible result is a polar covalent bond or, in the case of a large electronegativity difference, a complete transfer of one or more electrons to form ions. The cases are summarized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

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

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

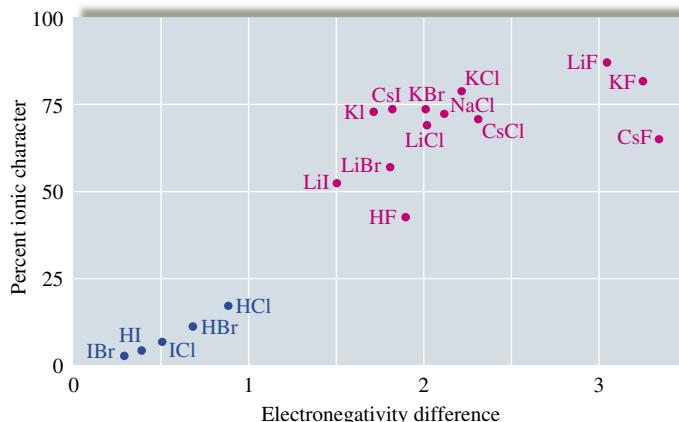
Application of this definition to various compounds (in the gas phase) gives the results shown in Fig. 8.13, where percent ionic character is plotted versus the difference in the electronegativity values of X and Y. Note from this plot that ionic character increases with electronegativity difference,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

Another complication in identifying ionic compounds is that many substances contain polyatomic ions. For example,  $\text{NH}_4\text{Cl}$  contains  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions, and  $\text{Na}_2\text{SO}_4$  contains  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions. The ammonium and sulfate ions are held together by covalent bonds. Thus, calling  $\text{NH}_4\text{Cl}$  and  $\text{Na}_2\text{SO}_4$  ionic compounds is somewhat ambiguous.



**FIGURE 8.12**

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

**FIGURE 8.13**

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

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

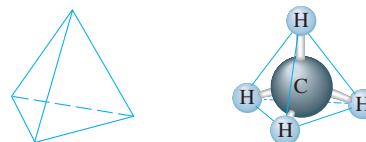
## 8.7 The Covalent Chemical Bond: A Model

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

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

*Why do chemical bonds occur?* There is no principle of nature that states that bonds are favored or disfavored. Bonds are neither inherently “good” nor inherently “bad” as far as nature is concerned; *bonds result from the tendency of a system to seek its lowest possible energy*. From a simplistic point of view, bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms. For example, approximately 1652 kJ of energy is required to break a mole of methane ( $\text{CH}_4$ ) molecules into separate C and H atoms. Or, taking the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms. Thus we can say that 1 mole of  $\text{CH}_4$  molecules in the gas phase is 1652 kJ lower in energy than 1 mole of carbon atoms plus 4 moles of hydrogen atoms. Methane is therefore a stable molecule relative to its separated atoms.

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



Given this structure, it is natural to envision four individual C—H interactions (we call them *bonds*). The energy of stabilization of  $\text{CH}_4$  is divided equally among the four bonds to give an average C—H bond energy per mole of C—H bonds:

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

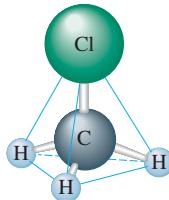
A tetrahedron has four equal triangular faces.



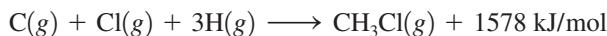
Molten NaCl conducts an electric current, indicating the presence of mobile  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

Bonding is a model proposed to explain molecular stability.

Next, consider methyl chloride, which consists of  $\text{CH}_3\text{Cl}$  molecules having the structure



Experiments have shown that approximately 1578 kJ of energy is required to break down 1 mole of gaseous  $\text{CH}_3\text{Cl}$  molecules into gaseous carbon, chlorine, and hydrogen atoms. The reverse process can be represented as



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

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

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

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

## Models: An Overview

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

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

In natural processes there is a tendency toward lower energy. Collections of atoms therefore occur because the aggregated state has lower energy than the separated atoms. Why? As we saw earlier in this chapter, the best explanations for the energy change involve

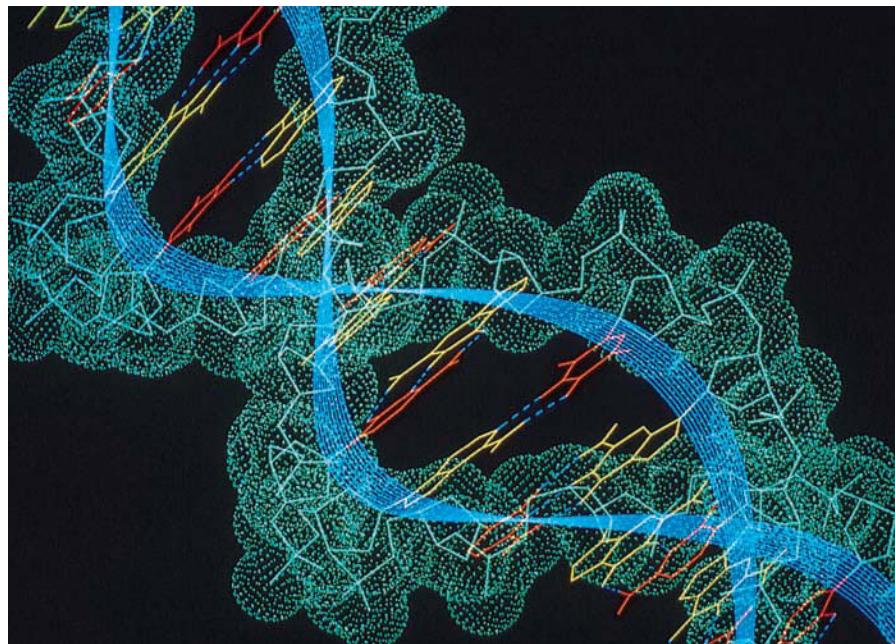
atoms sharing electrons or atoms transferring electrons to become ions. In the case of electron sharing, we find it convenient to assume that individual bonds occur between pairs of atoms. Let's explore the validity of this assumption and see how it is useful.

In a diatomic molecule such as H<sub>2</sub>, it is natural to assume that a bond exists between the atoms, holding them together. It is also useful to assume that individual bonds are present in polyatomic molecules such as CH<sub>4</sub>. Therefore, instead of thinking of CH<sub>4</sub> as a unit with a stabilization energy of 1652 kJ per mole, we choose to think of CH<sub>4</sub> as containing four C—H bonds, each worth 413 kJ of energy per mole of bonds. Without this concept of individual bonds in molecules, chemistry would be hopelessly complicated. There are millions of different chemical compounds, and if each of these compounds had to be considered as an entirely new entity, the task of understanding chemical behavior would be overwhelming.

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

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

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



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

### Fundamental Properties of Models

- Models are human inventions, always based on an incomplete understanding of how nature works. A *model does not equal reality*.
  - Models are often wrong. This property derives from the first property. Models are based on speculation and are always oversimplifications.
  - Models tend to become more complicated as they age. As flaws are discovered in our models, we “patch” them and thus add more detail.
  - It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can be expected to yield only qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.
- For a model to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple aufbau principle used to account for the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper, for example, do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the simple model. However, this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we must apply it with caution and not expect it to be correct in every case.
- When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes. (Try to remember this when you get back your next chemistry test.)

## 8.8 Covalent Bond Energies and Chemical Reactions

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

Process	Energy Required (kJ/mol)
$\text{CH}_4(g) \rightarrow \text{CH}_3(g) + \text{H}(g)$	435
$\text{CH}_3(g) \rightarrow \text{CH}_2(g) + \text{H}(g)$	453
$\text{CH}_2(g) \rightarrow \text{CH}(g) + \text{H}(g)$	425
$\text{CH}(g) \rightarrow \text{C}(g) + \text{H}(g)$	339
	Total = 1652
	Average = $\frac{1652}{4} = 413$

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

**TABLE 8.4 Average Bond Energies (kJ/mol)**

Single Bonds				Multiple Bonds	
H—H	432	N—H	391	I—I	149
H—F	565	N—N	160	I—Cl	208
H—Cl	427	N—F	272	I—Br	175
H—Br	363	N—Cl	200	O=O	495
H—I	295	N—Br	243	C=O*	745
		N—O	201	C=O	1072
C—H	413	O—H	467	S—H	347
C—C	347	O—O	146	S—Cl	253
C—N	305	O—F	190	S—Br	218
C—O	358	O—Cl	203	S—S	266
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<sub>2</sub>) = 799

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

Molecule	Measured C—H Bond Energy (kJ/mol)
HCB <sub>3</sub>	380
HCCl <sub>3</sub>	380
HCF <sub>3</sub>	430
C <sub>2</sub> H <sub>6</sub>	410

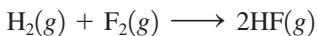
These data show that the C—H bond strength varies significantly with its environment, but the concept of an average C—H bond strength remains useful to chemists. The average values of bond energies for various types of bonds are listed in Table 8.4.

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

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

### Bond Energy and Enthalpy

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



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

**TABLE 8.5 Bond Lengths for Selected Bonds**

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

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

$$\Delta H = \text{sum of the energies required to break old bonds (positive signs)} \\ \text{plus the sum of the energies released in the formation of new bonds (negative signs)}$$

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  $\Sigma$  represents the sum of terms, and  $D$  represents the bond energy per mole of bonds. ( $D$  always has a positive sign.)

In the case of the formation of HF,

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

Thus, when 1 mol  $\text{H}_2(g)$  and 1 mol  $\text{F}_2(g)$  react to form 2 mol  $\text{HF}(g)$ , 544 kJ of energy should be released.

This result can be compared with the calculation of  $\Delta H$  for this reaction from the standard enthalpy of formation for HF (-271 kJ/mol):

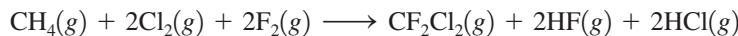
$$\Delta H^\circ = 2 \text{ mol} \times (-271 \text{ kJ/mol}) = -542 \text{ kJ}$$

Thus the use of bond energies to calculate  $\Delta H$  works quite well in this case.

### Sample Exercise 8.5

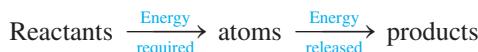
### $\Delta H$ from Bond Energies

Using the bond energies listed in Table 8.4, calculate  $\Delta H$  for the reaction of methane with chlorine and fluorine to give Freon-12 ( $\text{CF}_2\text{Cl}_2$ ).



#### 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:



We then combine the energy changes to calculate  $\Delta H$ :

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

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

#### Reactant Bonds Broken:

$\text{CH}_4$ :	4 mol C—H	$4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$
$2\text{Cl}_2$ :	2 mol Cl—Cl	$2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$
$2\text{F}_2$ :	2 mol F—F	$2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = 308 \text{ kJ}$
Total energy required		= 2438 kJ

#### Product Bonds Formed:

$\text{CF}_2\text{Cl}_2$ :	2 mol C—F	$2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = 970 \text{ kJ}$
and		
	$2 \text{ mol C—Cl}$	$2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = 3678 \text{ kJ}$
	$2 \text{ mol H—F}$	$2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = 1130 \text{ kJ}$
	$2 \text{ mol H—Cl}$	$2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = 3854 \text{ kJ}$
Total energy released		= 3632 kJ

We now can calculate  $\Delta H$ :

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

Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of  $\text{CF}_2\text{Cl}_2$  formed.

*See Exercises 8.53 through 8.60.*

## 8.9 The Localized Electron Bonding Model

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

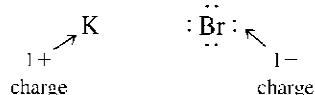
As we will apply it, the LE model has three parts:

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

## 8.10 Lewis Structures

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

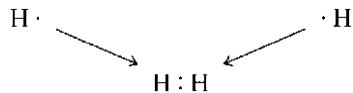
We have already seen that when metals and nonmetals react to form binary ionic compounds, electrons are transferred and the resulting ions typically have noble gas electron configurations. An example is the formation of KBr, where the  $K^+$  ion has the [Ar] electron configuration and the  $Br^-$  ion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



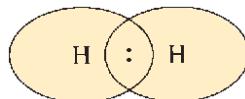
No dots are shown on the  $K^+$  ion because it has no valence electrons. The  $Br^-$  ion is shown with eight electrons because it has a filled valence shell.

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

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



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



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

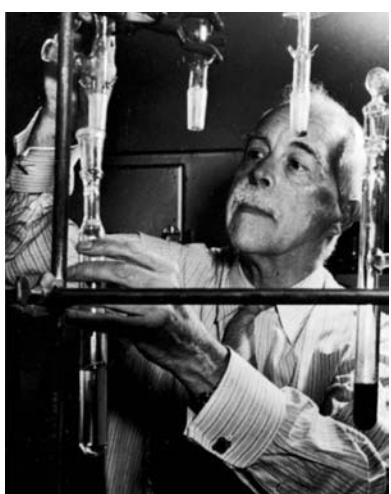
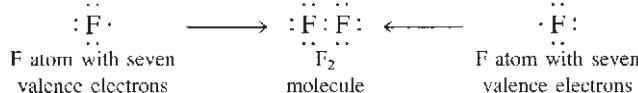


FIGURE 8.14

G. N. Lewis (1875–1946).

- The second-row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the 2s and the three 2p 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<sub>2</sub> molecule, which has the following Lewis structure:

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



Note that each fluorine atom in F<sub>2</sub> is, in effect, surrounded by eight electrons, two of which are shared with the other atom. This is a *bonding pair* of electrons, as discussed earlier. Each fluorine atom also has three pairs of electrons not involved in bonding. These are the *lone pairs*.

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



Note that only the valence electrons of the neon atom (2s<sup>2</sup>2p<sup>6</sup>) are represented by the Lewis structure. The 1s<sup>2</sup> electrons are core electrons and are not shown.

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

### Steps for Writing Lewis Structures

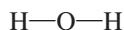
- 1 Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
- 2 Use a pair of electrons to form a bond between each pair of bound atoms.
- 3 Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

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

- 1 We sum the *valence* electrons for H<sub>2</sub>O as shown:

$$\begin{array}{r} 1 + 1 + 6 = 8 \text{ valence electrons} \\ \swarrow \quad \swarrow \quad \swarrow \\ \text{H} \quad \text{H} \quad \text{O} \end{array}$$

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

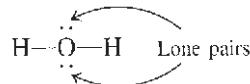


Note that a *line instead of a pair of dots* is used to indicate each pair of bonding electrons. This is the standard notation.

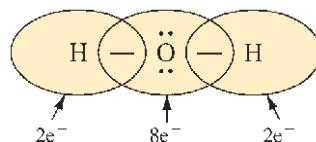
- 3 We distribute the remaining electrons to achieve a noble gas electron configuration for each atom. Since four electrons have been used in forming the two bonds, four electrons (8 – 4) remain to be distributed. Hydrogen is satisfied with two electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration. Thus the remaining

four electrons are added to oxygen as two lone pairs. Dots are used to represent the lone pairs:

$\text{H}-\text{O}-\text{H}$  represents  $\text{H}_2\text{O}$



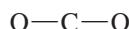
This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight, as shown below:



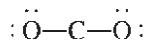
As a second example, let's write the Lewis structure for carbon dioxide. Summing the valence electrons gives

$$\begin{array}{c} 4 + 6 + 6 = 16 \\ \text{C} \quad \text{O} \quad \text{O} \\ \swarrow \quad \uparrow \quad \uparrow \\ \end{array}$$

After forming a bond between the carbon and each oxygen,



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



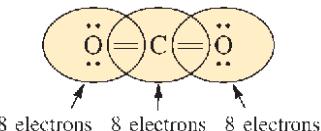
Is this correct? To answer this question, we need to check two things:

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

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

$\cdot \ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$  represents

$\ddot{\text{O}}:\text{C}:\ddot{\text{O}}$



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

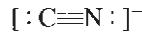
Finally, let's consider the Lewis structure of the  $\text{CN}^-$  (cyanide) ion. Summing the valence electrons, we have

$$\begin{array}{c} \text{CN}^- \\ \swarrow \quad \uparrow \\ \text{4} + \text{5} + \text{1} = \text{10} \end{array}$$

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



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



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

### Sample Exercise 8.6

### Writing Lewis Structures

Give the Lewis structure for each of the following.

- |                  |                  |
|------------------|------------------|
| a. HF            | d. $\text{CH}_4$ |
| b. $\text{N}_2$  | e. $\text{CF}_4$ |
| c. $\text{NH}_3$ | f. $\text{NO}^+$ |

#### Solution

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

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	$1 + 7 = 8$	H—F	6	H—F:	H, 2 F, 8
b. $\text{N}_2$	$5 + 5 = 10$	N—N	8	:N≡N:	N, 8
c. $\text{NH}_3$	$5 + 3(1) = 8$	H— $\begin{array}{c} \text{N} \\   \\ \text{H} \end{array}$ —H	2	H— $\begin{array}{c} \cdot \\   \\ \text{N} \\   \\ \cdot \end{array}$ —H	H, 2 N, 8
d. $\text{CH}_4$	$4 + 4(1) = 8$	$\begin{array}{c} \text{H} \\   \\ \text{H}—\text{C}—\text{H} \\   \\ \text{H} \end{array}$	0	H— $\begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array}$ —H	H, 2 C, 8
e. $\text{CF}_4$	$4 + 4(7) = 32$	F— $\begin{array}{c} \text{C} \\   \\ \text{F} \\   \\ \text{F} \end{array}$ —F	24	:F:— $\begin{array}{c} \cdot \\   \\ \text{C} \\   \\ \cdot \end{array}$ —F:	F, 8 C, 8
f. $\text{NO}^+$	$5 + 6 - 1 = 10$	N—O	8	[:N≡O:] <sup>+</sup>	N, 8 O, 8

*See Exercises 8.67 and 8.68.*



## CHEMICAL IMPACT

### Nitrogen Under Pressure

The element nitrogen exists at normal temperatures and pressures as a gas containing  $\text{N}_2$ , a molecule with a very strong triple bond. In the gas phase the diatomic molecules move around independently with almost no tendency to associate with each other. Under intense pressure, however, nitrogen changes to a dramatically different form. This conclusion was reached at the Carnegie Institution in Washington, D.C., by Mikhail Eremets and his colleagues, who subjected nitrogen to a pressure of 2.4 million atmospheres in a special diamond anvil press. Under this tremendous pressure the bonds of the  $\text{N}_2$  molecules break and a substance containing an aggregate of nitrogen atoms forms. In other words, under great pressure elemental nitrogen changes from a substance containing diatomic molecules to one containing many nitrogen atoms bonded to each other. Interestingly, this substance remains intact even after the pressure is released—as long as the temperature remains at 100 K. This new form of nitrogen has a very high potential energy relative to  $\text{N}_2$ . Thus this substance would be an extraordinarily powerful propellant or explosive if enough of it could be made. This new form of nitrogen is also a semiconductor for electricity; normal nitrogen gas is an insulator.

The newly discovered form of nitrogen is significant for several reasons. For one thing, it may help us understand the nature of the interiors of the giant gas planets such as Jupiter. Also, their success in changing nitrogen to an atomic solid encourages high-pressure scientists who are trying to



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

accomplish the same goal with hydrogen. It is surprising that nitrogen, which has diatomic molecules containing bonds more than twice as strong as those in hydrogen, will form an atomic solid at these pressures but hydrogen does not. Hydrogen remains a molecular solid at far greater pressures than nitrogen can endure.

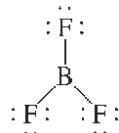
When writing Lewis structures, do not worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all the available valence electrons of the atoms to achieve the lowest possible energy.\* The valence electrons belong to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

## 8.11 Exceptions to the Octet Rule

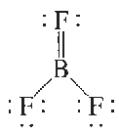
The localized electron model is a simple but very successful model, and the rules we have used for Lewis structures apply to most molecules. However, with such a simple model, some exceptions are inevitable. Boron, for example, tends to form compounds in which the boron atom has fewer than eight electrons around it—it does not have a complete octet. Boron trifluoride ( $\text{BF}_3$ ), a gas at normal temperatures and pressures, reacts very

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

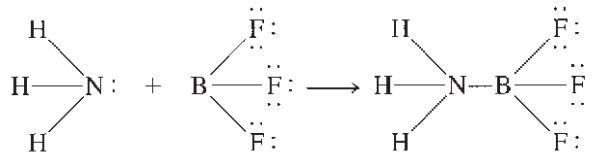
energetically with molecules such as water and ammonia that have available electron pairs (lone pairs). The violent reactivity of  $\text{BF}_3$  with electron-rich molecules arises because the boron atom is electron-deficient. Boron trifluoride has 24 valence electrons. The Lewis structure often drawn for  $\text{BF}_3$  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  $\text{BF}_3$ . However, the boron atom in  $\text{BF}_3$  certainly behaves as if it is electron-deficient, as indicated by the reactivity of  $\text{BF}_3$  toward electron-rich molecules, for example, toward  $\text{NH}_3$  to form  $\text{H}_3\text{NBF}_3$ :



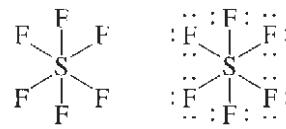
In this stable compound, boron has an octet of electrons.

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

Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond. To see how this arises, we will consider the Lewis structure for sulfur hexafluoride ( $\text{SF}_6$ ), a well-known and very stable molecule. The sum of the valence electrons is

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

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



We have used 12 electrons to form the S—F bonds, which leaves 36 electrons. Since fluorine always follows the octet rule, we complete the six fluorine octets to give the structure on the right above. This structure uses all 48 valence electrons for  $\text{SF}_6$ , but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule. How can this happen?

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



Third-row elements can exceed the octet rule.

The localized electron model assumes that the empty  $3d$  orbitals can be used to accommodate extra electrons. Thus the sulfur atom in  $\text{SF}_6$  can have 12 electrons around it by using the  $3s$  and  $3p$  orbitals to hold 8 electrons, with the extra 4 electrons placed in the formerly empty  $3d$  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-deficient compounds are very reactive.
- The second-row elements never exceed the octet rule, since their valence orbitals ( $2s$  and  $2p$ ) 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).

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

### Sample Exercise 8.7

### Lewis Structures for Molecules That Violate the Octet Rule I

Write the Lewis structure for  $\text{PCl}_5$ .

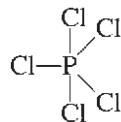
#### Solution

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

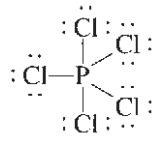
→ 1 Sum the valence electrons.

$$\begin{array}{c} 5 + 5(7) = 40 \text{ electrons} \\ \uparrow \quad \uparrow \\ \text{P} \quad \text{Cl} \end{array}$$

→ 2 Indicate single bonds between bound atoms.



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



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

*See Exercises 8.71 and 8.72.*

In the  $\text{PCl}_5$  and  $\text{SF}_6$  molecules, the central atoms (P and S, respectively) must have the extra electrons. However, in molecules having more than one atom that can exceed the octet rule, it is not always clear which atom should have the extra electrons. Consider

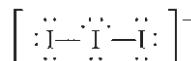
the Lewis structure for the triiodide ion ( $I_3^-$ ), which has

$$\begin{array}{c} 3(7) + 1 = 22 \text{ valence electrons} \\ \uparrow \quad \uparrow \\ I \quad I - \text{charge} \end{array}$$

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

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

Thus for  $I_3^-$  the Lewis structure is



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

### Sample Exercise 8.8

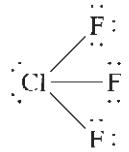
### Lewis Structures for Molecules That Violate the Octet Rule II

Write the Lewis structure for each molecule or ion.

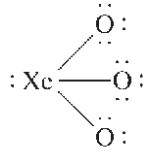
- a.  $\text{ClF}_3$     b.  $\text{XeO}_3$     c.  $\text{RnCl}_2$     d.  $\text{BeCl}_2$     e.  $\text{ICl}_4^-$

#### Solution

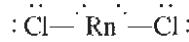
- a. The chlorine atom (third row) accepts the extra electrons.



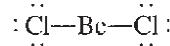
- b. All atoms obey the octet rule.



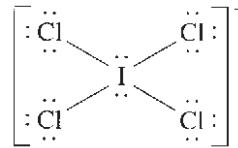
- c. Radon, a noble gas in Period 6, accepts the extra electrons.



- d. Beryllium is electron-deficient.



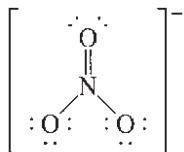
- e. Iodine exceeds the octet rule.



*See Exercises 8.71 and 8.72.*

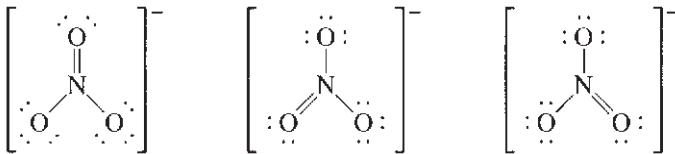
## 8.12 Resonance

Sometimes more than one valid Lewis structure (one that obeys the rules we have outlined) is possible for a given molecule. Consider the Lewis structure for the nitrate ion ( $\text{NO}_3^-$ ), which has 24 valence electrons. To achieve an octet of electrons around each atom, a structure like this is required:



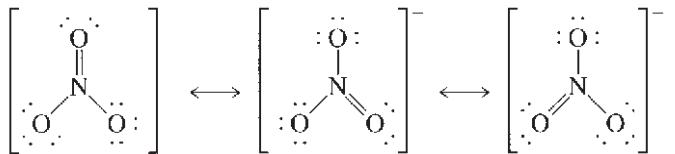
If this structure accurately represents the bonding in  $\text{NO}_3^-$ , there should be two types of N--O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds). However, experiments clearly show that  $\text{NO}_3^-$  exhibits only *one* type of N--O bond with a length and strength *between* those expected for a single bond and a double bond. Thus, although the structure we have shown above is a valid Lewis structure, it does *not* correctly represent the bonding in  $\text{NO}_3^-$ . This is a serious problem, and it means that the model must be modified.

Look again at the proposed Lewis structure for  $\text{NO}_3^-$ . There is no reason for choosing a particular oxygen atom to have the double bond. There are really three valid Lewis structures:



Is any of these structures a correct description of the bonding in  $\text{NO}_3^-$ ? No, because  $\text{NO}_3^-$  does not have one double and two single bonds—it has three equivalent bonds. We can solve this problem by making the following assumption: The correct description of  $\text{NO}_3^-$  is *not given by any one* of the three Lewis structures but is given only by the *superposition of all three*.

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



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

The concept of resonance is necessary because the localized electron model postulates that electrons are localized between a given pair of atoms. However, nature does not really operate this way. Electrons are really delocalized—they can move around the entire molecule. The valence electrons in the  $\text{NO}_3^-$  molecule distribute themselves to provide equivalent N--O bonds. Resonance is necessary to compensate for the defective assumption of the localized electron model. However, this model is so useful that we retain the

concept of localized electrons and add resonance to allow the model to treat species such as  $\text{NO}_3^-$ .

### Sample Exercise 8.9

### Resonance Structures

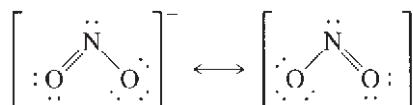
Describe the electron arrangement in the nitrite anion ( $\text{NO}_2^-$ ) using the localized electron model.

#### Solution

We will follow the usual procedure for obtaining the Lewis structure for the  $\text{NO}_2^-$  ion. In  $\text{NO}_2^-$  there are  $5 + 2(6) + 1 = 18$  valence electrons. Indicating the single bonds gives the structure



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



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

*See Exercises 8.73 through 8.78.*

### Odd-Electron Molecules

Relatively few molecules formed from nonmetals contain odd numbers of electrons. One common example is nitric oxide (NO), which is formed when nitrogen and oxygen gases react at the high temperatures in automobile engines. Nitric oxide is emitted into the air, where it immediately reacts with oxygen to form gaseous nitrogen dioxide ( $\text{NO}_2$ ), another odd-electron molecule.

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

### Formal Charge

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

In Chapter 4 we discussed one system for obtaining charges, called *oxidation states*. However, in assigning oxidation states, we always count *both* the shared electrons as belonging to the more electronegative atom in a bond. This practice leads to highly exaggerated estimates of charge. In other words, although oxidation states are useful for bookkeeping electrons in redox reactions, they are not realistic estimates of the actual

Equivalent Lewis structures contain the same numbers of single and multiple bonds. For example, the resonance structures for  $\text{O}_3$



are equivalent Lewis structures. These are equally important in describing the bonding in  $\text{O}_3$ . Nonequivalent Lewis structures contain different numbers of single and multiple bonds.

charges on individual atoms in a molecule, so they are not suitable for judging the appropriateness of Lewis structures. Another definition of the charge on an atom in a molecule, the formal charge, can, however, be used to evaluate Lewis structures. As we will see below, the **formal charge** of an atom in a molecule is *the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule*.

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

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

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

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

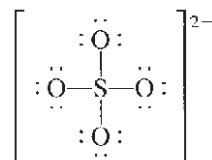
To compute the formal charge of an atom in a molecule, we assign the valence electrons in the molecule to the various atoms, making the following assumptions:

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

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

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

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



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

$$\text{Valence electrons assigned to each oxygen} = 6 \text{ plus } \frac{1}{2}(2) = 7$$

↑              ↑  
 Lone        Shared  
 pair        electrons  
 electrons

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

↑  
 Valence electrons  
 on a free O atom  
 ↓  
 Valence electrons  
 assigned to each O  
 in  $\text{SO}_4^{2-}$

The formal charge on each oxygen is  $-1$ .

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

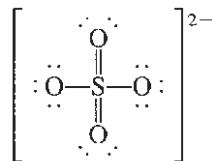
$$\text{Valence electrons assigned to sulfur} = 0 \text{ plus } \frac{1}{2}(8) = 4$$

↑  
 Lone pair electrons  
 Shared electrons

$$\text{Formal charge on sulfur} = 6 \text{ minus } 4 = 2$$

↑  
 Valence electrons on a free S atom  
 ↓  
 Valence electrons assigned to S in  $\text{SO}_4^{2-}$

A second possible Lewis structure is



In this case the formal charges are as follows:

*For oxygen atoms with single bonds:*

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

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

*For oxygen atoms with double bonds:*

$$\text{Valence electrons assigned} = 4 + \frac{1}{2}(4) = 6$$

↑  
 Each double bond has 4 electrons

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

*For the sulfur atom:*

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

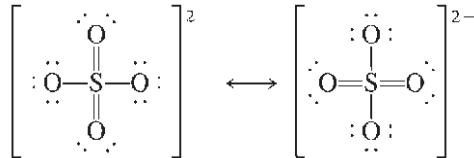
$$\text{Formal charge} = 6 - 6 = 0$$

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

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

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

the  $-1$  formal charges are on electronegative oxygen atoms. Thus, for the sulfate ion, we might expect resonance structures such as



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

### Rules Governing Formal Charge

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

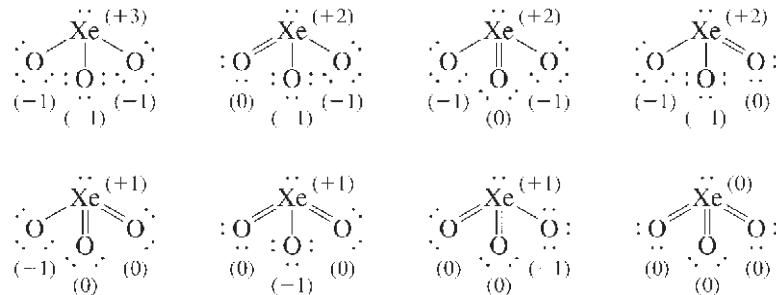
#### Sample Exercise 8.10

### Formal Charges

Give possible Lewis structures for  $\text{XeO}_3$ , an explosive compound of xenon. Which Lewis structure or structures are most appropriate according to the formal charges?

#### Solution

For  $\text{XeO}_3$  (26 valence electrons) we can draw the following possible Lewis structures (formal charges are indicated in parentheses):



Based on the ideas of formal charge, we would predict that the Lewis structures with the lower values of formal charge would be most appropriate for describing the bonding in  $\text{XeO}_3$ .

*See Exercises 8.81 through 8.86.*

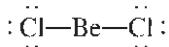
As a final note, there are a couple of cautions about formal charge to keep in mind. First, although formal charges are closer to actual atomic charges in molecules than are oxidation states, formal charges still provide only *estimates* of charge—they should not

be taken as actual atomic charges. Second, the evaluation of Lewis structures using formal charge ideas can lead to erroneous predictions. Tests based on experiments must be used to make the final decisions on the correct description of the bonding in a molecule or polyatomic ion.

## 8.13 Molecular Structure: The VSEPR Model

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

Many accurate methods now exist for determining **molecular structure**, the three-dimensional arrangement of the atoms in a molecule. These methods must be used if precise information about structure is required. However, it is often useful to be able to predict the approximate molecular structure of a molecule. In this section we consider a simple model that allows us to do this. This model, called the **valence shell electron-pair repulsion (VSEPR) model**, is useful in predicting the geometries of molecules formed from nonmetals. The main postulate of this model is that *the structure around a given atom is determined principally by minimizing electron-pair repulsions*. The idea here is that the bonding and nonbonding pairs around a given atom will be positioned as far apart as possible. To see how this model works, we will first consider the molecule BeCl<sub>2</sub>, which has the Lewis structure



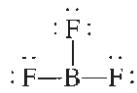
Note that there are two pairs of electrons around the beryllium atom. What arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsions? Clearly, the best arrangement places the pairs on opposite sides of the beryllium atom at 180 degrees from each other:



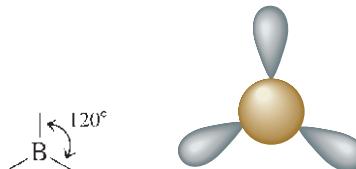
This is the maximum possible separation for two electron pairs. Once we have determined the optimal arrangement of the electron pairs around the central atom, we can specify the molecular structure of BeCl<sub>2</sub>, that is, the positions of the atoms. Since each electron pair on beryllium is shared with a chlorine atom, the molecule has a **linear structure** with a 180-degree bond angle:



Next, let's consider BF<sub>3</sub>, which has the Lewis structure



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



Visualization: VSEPR

BeCl<sub>2</sub> has only four electrons around Be and is expected to be very reactive with electron-pair donors.

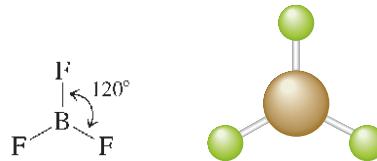


Visualization: VSEPR: Two Electron Pairs



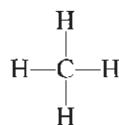
Visualization: VSEPR: Three Electron Pairs

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

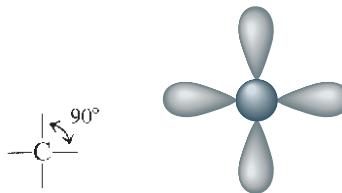


This is a planar (flat) and triangular molecule, which is commonly described as a **trigonal planar structure**.

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

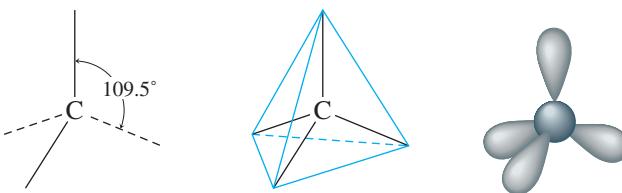


There are four pairs of electrons around the central carbon atom. What arrangement of these electron pairs best minimizes the repulsions? First, let's try a square planar arrangement:



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

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



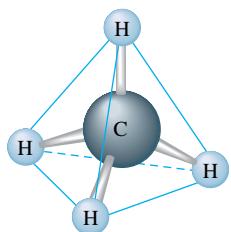
It can be shown that this is the maximum possible separation of four pairs around a given atom. This means that *whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally*.

Now that we have the electron-pair arrangement that gives the least repulsion, we can determine the positions of the atoms and thus the molecular structure of  $\text{CH}_4$ . In methane, each of the four electron pairs is shared between the carbon atom and a hydrogen atom. Thus the hydrogen atoms are placed as in Fig. 8.15, and the molecule has a tetrahedral structure with the carbon atom at the center.

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



Visualization: VSEPR: Four Electron Pairs



**FIGURE 8.15**

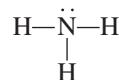
The molecular structure of methane. The tetrahedral arrangement of electron pairs produces a tetrahedral arrangement of hydrogen atoms.

### 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 ( $\text{NH}_3$ ) using this stepwise approach.

- 1 Draw the Lewis structure:



- 2 Count the pairs of electrons and arrange them to minimize repulsions. The  $\text{NH}_3$  molecule has four pairs of electrons: three bonding pairs and one nonbonding pair. From the discussion of the methane molecule, we know that the best arrangement of four electron pairs is a tetrahedral array, as shown in Fig. 8.16(a).
- 3 Determine the positions of the atoms. The three H atoms share electron pairs, as shown in Fig. 8.16(b).
- 4 Name the molecular structure. It is very important to recognize that the *name* of the molecular structure is always based on the *positions of the atoms*. The placement of the electron pairs determines the structure, but the name is based on the positions of the atoms. Thus it is incorrect to say that the  $\text{NH}_3$  molecule is tetrahedral. It has a tetrahedral arrangement of electron pairs but not a tetrahedral arrangement of atoms. The molecular structure of ammonia is a **trigonal pyramid** (one side is different from the other three) rather than a tetrahedron, as shown in Fig. 8.16(c).



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

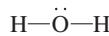
### Sample Exercise 8.11

### Prediction of Molecular Structure I

Describe the molecular structure of the water molecule.

#### Solution

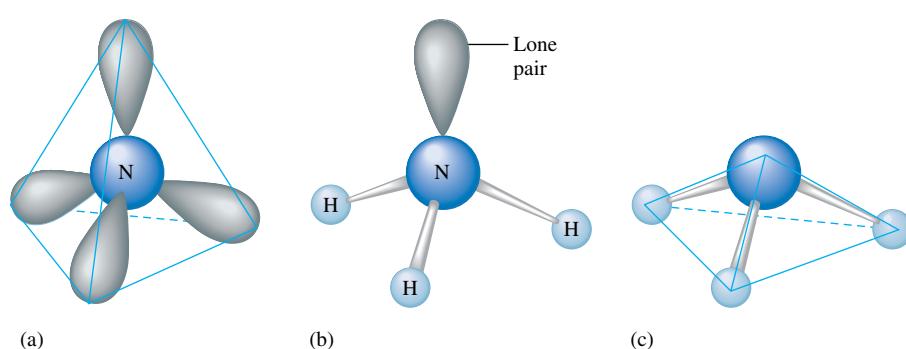
The Lewis structure for water is

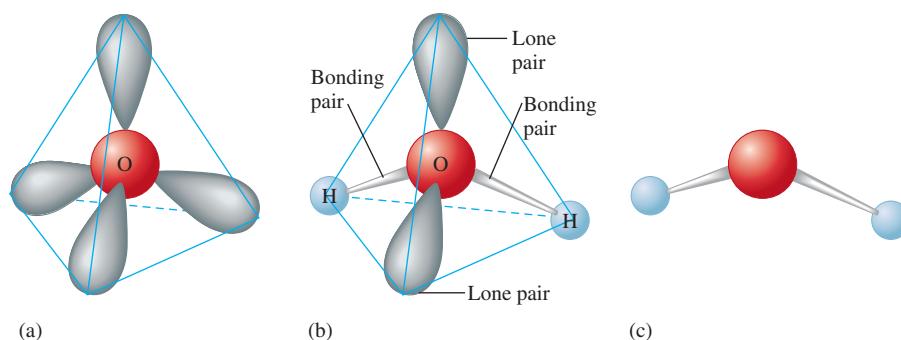


There are four pairs of electrons: two bonding pairs and two nonbonding pairs. To minimize repulsions, these are best arranged in a tetrahedral array, as shown in Fig. 8.17(a).

**FIGURE 8.16**

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



**FIGURE 8.17**

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

Although  $\text{H}_2\text{O}$  has a tetrahedral arrangement of electron pairs, it is not a tetrahedral molecule. The atoms in the  $\text{H}_2\text{O}$  molecule form a V shape, as shown in Fig. 8.17(b) and (c).

*See Exercises 8.91 and 8.92.*

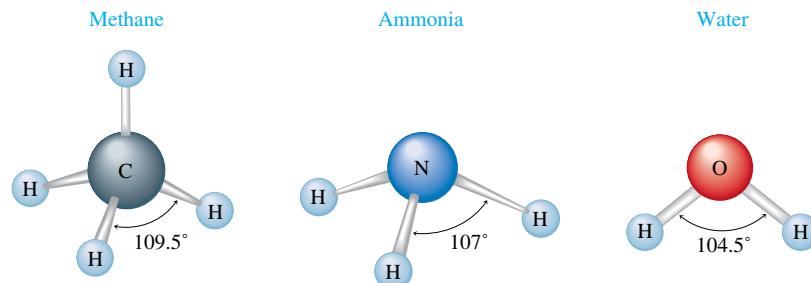
From Sample Exercise 8.11 we see that the  $\text{H}_2\text{O}$  molecule is V-shaped, or bent, because of the presence of the lone pairs. If no lone pairs were present, the molecule would be linear, the polar bonds would cancel, and the molecule would have no dipole moment. This would make water very different from the polar substance so familiar to us.

From the previous discussion we would predict that the H—X—H bond angle (where X is the central atom) in  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  should be the tetrahedral angle of 109.5 degrees. Experimental studies, however, show that the actual bond angles are those given in Fig. 8.18. What significance do these results have for the VSEPR model? One possible point of view is that we should be pleased to have the observed angles so close to the tetrahedral angle. The opposite view is that the deviations are significant enough to require modification of the simple model so that it can more accurately handle similar cases. We will take the latter view.

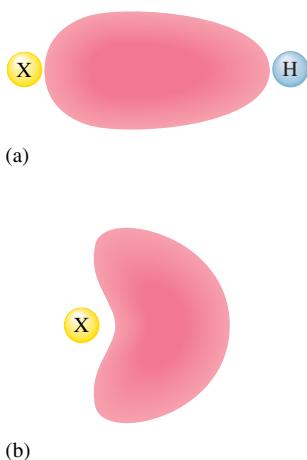
Let us examine the following data:

	$\text{CH}_4$	$\text{NH}_3$	$\text{H}_2\text{O}$
<b>Number of Lone Pairs</b>	0	1	2
<b>Bond Angle</b>	109.5°	107°	104.5°

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

**FIGURE 8.18**

The bond angles in the  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  molecules. Note that the bond angle between bonding pairs decreases as the number of lone pairs increases. Note that all of the angles in  $\text{CH}_4$  are 109.5 degrees and all of the angles in  $\text{NH}_3$  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.

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

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

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

Table 8.7 summarizes the structures possible for molecules in which there are four electron pairs around the central atom with various numbers of atoms bonded to it. Note that molecules with four pairs of electrons around the central atom can be tetrahedral ( $\text{AB}_4$ ), trigonal pyramidal ( $\text{AB}_3$ ), and V-shaped ( $\text{AB}_2$ ).

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

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

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

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

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

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

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

has two different angles, 90 degrees and 120 degrees. As the name suggests, the structure formed by this arrangement of pairs consists of two trigonal-based pyramids that share a common base. Table 8.8 summarizes the structures possible for molecules in which there are five electron pairs around the central atom with various numbers of atoms bonded to it. Note that molecules with five pairs of electrons around the central atom can be trigonal bipyramidal ( $\text{AB}_5$ ), see-saw ( $\text{AB}_4$ ), T-shaped ( $\text{AB}_3$ ), and linear ( $\text{AB}_2$ ).

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

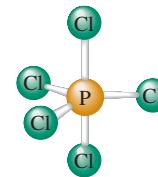
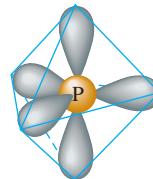
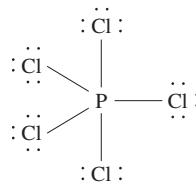
To use the VSEPR model to determine the geometric structures of molecules, you should memorize the relationships between the number of electron pairs and their best arrangement.

**Sample Exercise 8.12****Prediction of Molecular Structure II**

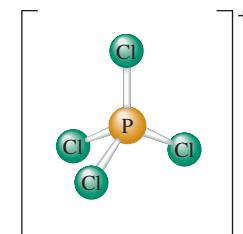
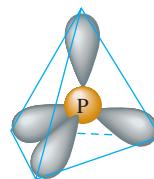
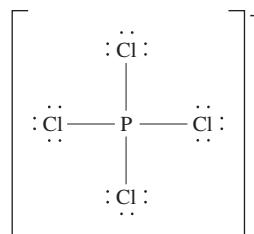
When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride ( $\text{PCl}_5$ ) is formed. In the gaseous and liquid states, this substance consists of  $\text{PCl}_5$  molecules, but in the solid state it consists of a 1 : 1 mixture of  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions. Predict the geometric structures of  $\text{PCl}_5$ ,  $\text{PCl}_4^+$ , and  $\text{PCl}_6^-$ .

**Solution**

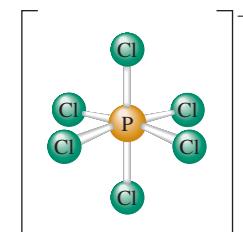
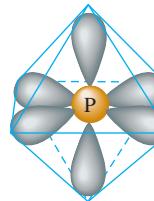
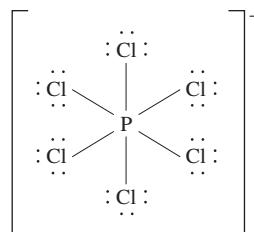
The Lewis structure for  $\text{PCl}_5$  is shown. Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement (see Table 8.6). When the chlorine atoms are included, a trigonal bipyramidal molecule results:



The Lewis structure for the  $\text{PCl}_4^+$  ion (5 + 4(7) - 1 = 32 valence electrons) is shown below. There are four pairs of electrons surrounding the phosphorus atom in the  $\text{PCl}_4^+$  ion, which requires a tetrahedral arrangement of the pairs. Since each pair is shared with a chlorine atom, a tetrahedral  $\text{PCl}_4^+$  cation results.



The Lewis structure for  $\text{PCl}_6^-$  (5 + 6(7) + 1 = 48 valence electrons) is shown below. Since phosphorus is surrounded by six pairs of electrons, an octahedral arrangement is required to minimize repulsions, as shown below in the center. Since each electron pair is shared with a chlorine atom, an octahedral  $\text{PCl}_6^-$  anion is predicted.



*See Exercises 8.89, 8.90, 8.93, and 8.94.*

**Sample Exercise 8.13****Prediction of Molecular Structure III**

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

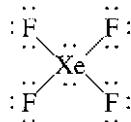


Visualization: VSEPR: Iodine Pentafluoride

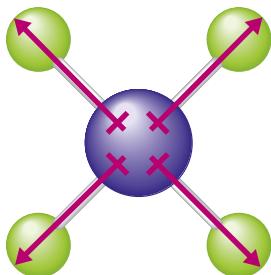
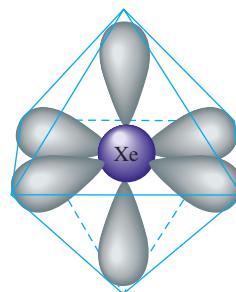
Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride ( $\text{XeF}_4$ ). Predict its structure and whether it has a dipole moment.

**Solution**

The Lewis structure for  $\text{XeF}_4$  is



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

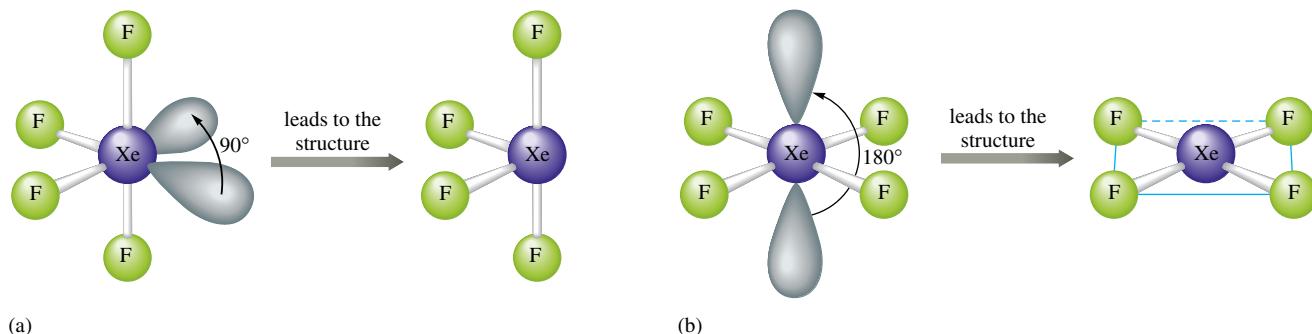


The structure predicted for this molecule will depend on how the lone pairs and bonding pairs are arranged. Consider the two possibilities shown in Fig. 8.20. The bonding pairs are indicated by the presence of the fluorine atoms. Since the structure predicted differs in the two cases, we must decide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

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

Thus  $\text{XeF}_4$  has no dipole moment, as shown in the margin.

**See Exercises 8.95 through 8.98.**

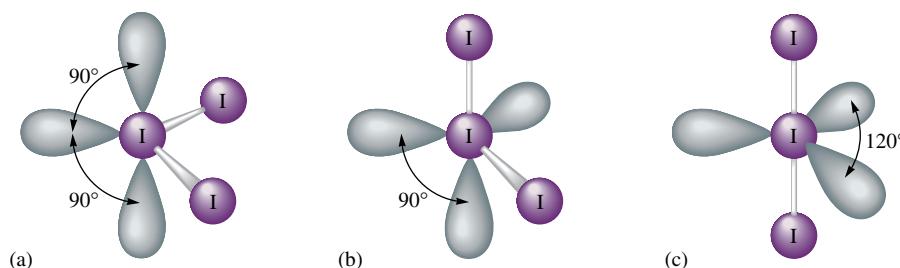


(a)

(b)

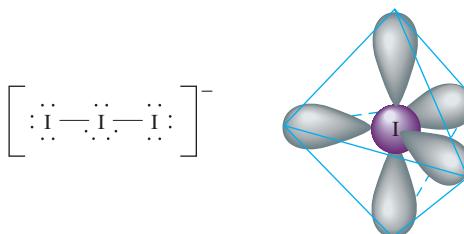
**FIGURE 8.20**

Possible electron-pair arrangements for  $\text{XeF}_4$ . 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.

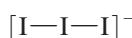
**FIGURE 8.21**

Three possible arrangements of the electron pairs in the  $\text{I}_3^-$  ion. Arrangement (c) is preferred because there are no 90-degree lone pair–lone pair interactions.

We can further illustrate the use of the VSEPR model for molecules or ions with lone pairs by considering the triiodide ion ( $\text{I}_3^-$ ).

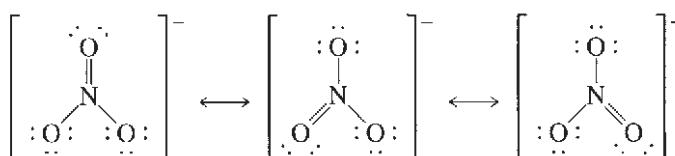


The central iodine atom has five pairs around it, which requires a trigonal bipyramidal arrangement. Several possible arrangements of lone pairs are shown in Fig. 8.21. Note that structures (a) and (b) have lone pairs at 90 degrees, whereas in (c) all lone pairs are at 120 degrees. Thus structure (c) is preferred. The resulting molecular structure for  $\text{I}_3^-$  is linear:

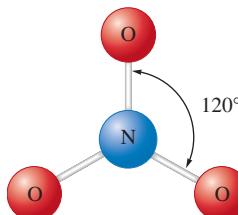


### The VSEPR Model and Multiple Bonds

So far in our treatment of the VSEPR model we have not considered any molecules with multiple bonds. To see how these molecules are handled by this model, let's consider the  $\text{NO}_3^-$  ion, which requires three resonance structures to describe its electronic structure:



The  $\text{NO}_3^-$  ion is known to be planar with 120-degree bond angles:



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

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

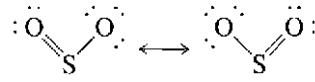
### Sample Exercise 8.14

### Structures of Molecules with Multiple Bonds

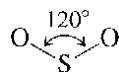
Predict the molecular structure of the sulfur dioxide molecule. Is this molecule expected to have a dipole moment?

#### Solution

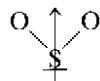
First, we must determine the Lewis structure for the SO<sub>2</sub> molecule, which has 18 valence electrons. The expected resonance structures are



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



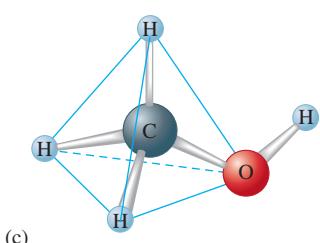
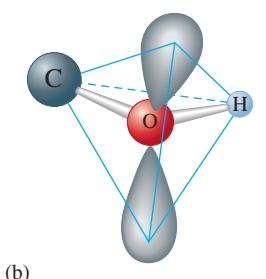
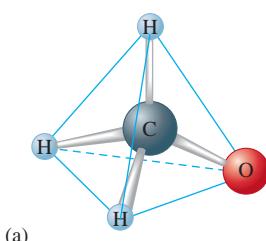
Thus the structure of the SO<sub>2</sub> molecule is expected to be V-shaped, with a 120-degree bond angle. The molecule has a dipole moment directed as shown:



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

*See Exercises 8.99 and 8.100.*

It should be noted at this point that lone pairs that are oriented at least 120 degrees from other pairs do not produce significant distortions of bond angles. For example, the angle in the SO<sub>2</sub> molecule is actually quite close to 120 degrees. We will follow the

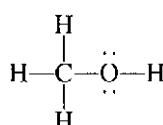
**FIGURE 8.22**

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.

general principle that a 120-degree angle provides lone pairs with enough space so that distortions do not occur. Angles less than 120 degrees are distorted when lone pairs are present.

### Molecules Containing No Single Central Atom

So far we have considered molecules consisting of one central atom surrounded by other atoms. The VSEPR model can be readily extended to more complicated molecules, such as methanol ( $\text{CH}_3\text{OH}$ ). This molecule is represented by the following Lewis structure:



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

### Summary of the VSEPR Model

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

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

### The VSEPR Model—How Well Does It Work?

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



## CHEMICAL IMPACT

### Chemical Structure and Communication: Semiochemicals

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

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



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

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

however, fail in a few instances. For example, phosphine ( $\text{PH}_3$ ), which has a Lewis structure analogous to that of ammonia,



would be predicted to have a molecular structure similar to that for  $\text{NH}_3$ , with bond angles of approximately 107 degrees. However, the bond angles of phosphine are actually 94 degrees. There are ways of explaining this structure, but more rules have to be added to the model.

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

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

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

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

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

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

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

*Kairomones* are chemical messengers that bring advantageous news to the receiver, and the floral scents are kairomones from the honeybees’ viewpoint. Many predators are guided by kairomones emitted by their food. For example, apple skins exude a chemical that attracts the codling moth larva. In some cases kairomones help the underdog.

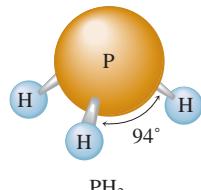
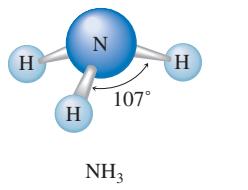
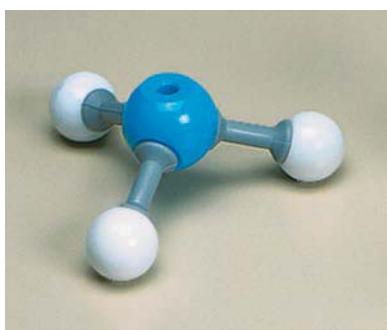
Certain marine mollusks can pick up the “scent” of their predators, the sea stars, and make their escape.

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

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

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

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



## Key Terms

### Section 8.1

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

### Section 8.2

electronegativity

### Section 8.3

dipolar  
dipole moment

### Section 8.4

isoelectronic ions

### Section 8.5

lattice energy

### Section 8.8

single bond  
double bond  
triple bond

### Section 8.9

localized electron (LE) model  
lone pair  
bonding pair

### Section 8.10

Lewis structure  
duet rule  
octet rule

### Section 8.12

resonance  
resonance structure  
formal charge

### Section 8.13

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

## For Review

### Chemical bonds

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

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

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

### Ionic bonding

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

### Bond energy

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

### Lewis structures

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

### VSEPR model

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

### REVIEW QUESTIONS

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

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

2. When an element forms an anion, what happens to the radius? When an element forms a cation, what happens to the radius? Why? Define the term *isoelectronic*. When comparing sizes of ions, which ion has the largest radius and which ion has the smallest radius in an isoelectronic series? Why?
3. Define the term *lattice energy*. Why, energetically, do ionic compounds form? Figure 8.11 illustrates the energy changes involved in the formation of  $\text{MgO}(s)$  and  $\text{NaF}(s)$ . Why is the lattice energy of  $\text{MgO}(s)$  so different from that of  $\text{NaF}(s)$ ? The magnesium oxide is composed of  $\text{Mg}^{2+}$  and  $\text{O}^{2-}$  ions. Energetically, why does  $\text{Mg}^{2+}\text{O}^{2-}$  form and not  $\text{Mg}^+\text{O}^-$ ? Why doesn't  $\text{Mg}^{3+}\text{O}^{3-}$  form?
4. Explain how bond energies can be used to estimate  $\Delta H$  for a reaction. Why is this an estimate of  $\Delta H$ ? How do the product bond strengths compare to the reactant bond strengths for an exothermic reaction? For an endothermic reaction? What is the relationship between the number of bonds between two atoms and bond strength? Bond length?
5. Give a rationale for the octet rule and the duet rule for H in terms of orbitals. Give the steps for drawing a Lewis structure for a molecule or ion. In general, molecules and ions always follow the octet rule unless it is impossible. The three types of exceptions are molecules/ions with too few electrons, molecules/ions with an odd number of electrons, and molecules/ions with too many electrons. Which atoms sometimes have fewer than 8 electrons around them? Give an example. Which atoms sometimes have more than 8 electrons around them? Give some examples. Why are odd-electron species generally very reactive and uncommon? Give an example of an odd-electron molecule.
6. Explain the terms *resonance* and *delocalized electrons*. When a substance exhibits resonance, we say that none of the individual Lewis structures accurately portrays the bonding in the substance. Why do we draw resonance structures?
7. Define formal charge and explain how to calculate it. What is the purpose of the formal charge? Organic compounds are composed mostly of carbon and hydrogen, but also may have oxygen, nitrogen, and/or halogens in the formula. Formal charge arguments work very well for organic compounds when drawing the best Lewis structure. How do C, H, N, O, and Cl satisfy the octet rule in organic compounds so as to have a formula charge of zero?
8. Explain the main postulate of the VSEPR model. List the five base geometries (along with bond angles) that most molecules or ions adopt to minimize electron-pair repulsions. Why are bond angles sometimes slightly less than predicted in actual molecules as compared to what is predicted by the VSEPR model?
9. Give two requirements that should be satisfied for a molecule to be polar. Explain why  $\text{CF}_4$  and  $\text{XeF}_4$  are nonpolar compounds (have no dipole moments) while  $\text{SF}_4$  is polar (has a dipole moment). Is  $\text{CO}_2$  polar? What about  $\text{COS}$ ? Explain.
10. Consider the following compounds:  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{KrF}_2$ ,  $\text{SO}_3$ ,  $\text{NF}_3$ ,  $\text{IF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_4$ ,  $\text{XeF}_4$ ,  $\text{PF}_5$ ,  $\text{IF}_5$ , and  $\text{SCl}_6$ . These 12 compounds are all examples of different molecular structures. Draw the Lewis structures for each and predict the molecular structure. Predict the bond angles and the polarity of each. (A polar molecule has a dipole moment, while a nonpolar molecule does not.) See Exercises 89 and 90 for the molecular structures based on the trigonal bipyramidal and the octahedral geometries.

## Active Learning Questions

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

1. Explain the electronegativity trends across a row and down a column of the periodic table. Compare these trends with those of ionization energies and atomic radii. How are they related?
2. The ionic compound AB is formed. The charges on the ions may be +1, -1; +2, -2; +3, -3; or even larger. What are the factors that determine the charge for an ion in an ionic compound?
3. Using only the periodic table, predict the most stable ion for Na, Mg, Al, S, Cl, K, Ca, and Ga. Arrange these from largest to smallest radius, and explain why the radius varies as it does. Compare your predictions with Fig. 8.8.
4. The bond energy for a C—H bond is about 413 kJ/mol in CH<sub>4</sub> but 380 kJ/mol in CHBr<sub>3</sub>. Although these values are relatively close in magnitude, they are different. Explain why they are different. Does the fact that the bond energy is lower in CHBr<sub>3</sub> make any sense? Why?
5. Consider the following statement: “Because oxygen wants to have a negative two charge, the second electron affinity is more negative than the first.” Indicate everything that is correct in this statement. Indicate everything that is incorrect. Correct the incorrect statements and explain.
6. Which has the greater bond lengths: NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>? Explain.
7. The following ions are best described with resonance structures. Draw the resonance structures, and using formal charge arguments, predict the best Lewis structure for each ion.
  - a. NCO<sup>-</sup>
  - b. CNO<sup>-</sup>
8. Would you expect the electronegativity of titanium to be the same in the species Ti, Ti<sup>2+</sup>, Ti<sup>3+</sup>, and Ti<sup>4+</sup>? Explain.
9. The second electron affinity values for both oxygen and sulfur are unfavorable (endothermic). Explain.
10. What is meant by a chemical bond? Why do atoms form bonds with each other? Why do some elements exist as molecules in nature instead of as free atoms?
11. Why are some bonds ionic and some covalent?
12. Does a Lewis structure tell which electrons come from which atoms? Explain.

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

## Questions

13. Some plant fertilizer compounds are (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, and KCl. Which of these compounds contain both ionic and covalent bonds?
14. Some of the important properties of ionic compounds are as follows:
  - i. low electrical conductivity as solids and high conductivity in solution or when molten
  - ii. relatively high melting and boiling points
  - iii. brittleness
  - iv. solubility in polar solvents

- How does the concept of ionic bonding discussed in this chapter account for these properties?
15. What is the electronegativity trend? Where does hydrogen fit into the electronegativity trend for the other elements in the periodic table?
  16. Give one example of a compound having a linear molecular structure that has an overall dipole moment (is polar) and one example that does not have an overall dipole moment (is non-polar). Do the same for molecules that have trigonal planar and tetrahedral molecular structures.
  17. When comparing the size of different ions, the general radii trend discussed in Chapter 7 is generally not very useful. What do you concentrate on when comparing sizes of ions to each other or when comparing the size of an ion to its neutral atom?
  18. In general, the higher the charge on the ions in an ionic compound, the more favorable the lattice energy. Why do some stable ionic compounds have +1 charged ions even though +4, +5, +6, charged ions would have a more favorable lattice energy?
  19. Combustion reactions of fossil fuels provide most of the energy needs of the world. Why are combustion reactions of fossil fuels so exothermic?
  20. Which of the following statements is(are) true? Correct the false statements.
    - a. It is impossible to satisfy the octet rule for all atoms in XeF<sub>2</sub>.
    - b. Because SF<sub>4</sub> exists, then OF<sub>4</sub> should also exist because oxygen is in the same family as sulfur.
    - c. The bond in NO<sup>+</sup> should be stronger than the bond in NO<sup>-</sup>.
    - d. As predicted from the two Lewis structures for ozone, one oxygen-oxygen bond is stronger than the other oxygen-oxygen bond.
  21. Three resonance structures can be drawn for CO<sub>2</sub>. Which resonance structure is best from a formal charge standpoint?
  22. Which of the following statements is(are) true? Correct the false statements.
    - a. The molecules SeS<sub>3</sub>, SeS<sub>2</sub>, PCl<sub>5</sub>, TeCl<sub>4</sub>, ICl<sub>3</sub>, and XeCl<sub>2</sub> all exhibit at least one bond angle which is approximately 120°.
    - b. The bond angle in SO<sub>2</sub> should be similar to the bond angle in CS<sub>2</sub> or SCl<sub>2</sub>.
    - c. Of the compounds CF<sub>4</sub>, KrF<sub>4</sub>, and SeF<sub>4</sub>, only SeF<sub>4</sub> exhibits an overall dipole moment (is polar).
    - d. Central atoms in a molecule adopt a geometry of the bonded atoms and lone pairs about the central atom in order to maximize electron repulsions.

## Exercises

In this section similar exercises are paired.

### Chemical Bonds and Electronegativity

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

24. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements.

- a. Na, K, Rb
- c. F, Cl, Br
- b. B, O, Ga
- d. S, O, F

25. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.

- a. C—F, Si—F, Ge—F
- b. P—Cl or S—Cl
- c. S—F, S—Cl, S—Br
- d. Ti—Cl, Si—Cl, Ge—Cl

26. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar.

- a. C—H, Si—H, Sn—H
- b. Al—Br, Ga—Br, In—Br, Tl—Br
- c. C—O or Si—O
- d. O—F or O—Cl

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

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

29. Which of the following incorrectly shows the bond polarity? Show the correct bond polarity for those that are incorrect.

- a.  $\delta^+H-F\delta^-$
- d.  $\delta^+Br-Br\delta^-$
- b.  $\delta^+Cl-I\delta^-$
- e.  $\delta^+O-P\delta^-$
- c.  $\delta^+Si-S\delta^-$

30. Indicate the bond polarity (show the partial positive and partial negative ends) in the following bonds.

- a. C—O
- d. Br—Te
- b. P—H
- e. Se—S
- c. H—Cl

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

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

### Ions and Ionic Compounds

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

34. Write electron configurations for

- a. the cations  $Mg^{2+}$ ,  $K^+$ , and  $Al^{3+}$ .
- b. the anions  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$ , and  $Te^{2-}$ .

35. Which of the following ions have noble gas electron configurations?

- a.  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Sc^{3+}$ ,  $Co^{3+}$
- b.  $Tl^+$ ,  $Te^{2-}$ ,  $Cr^{3+}$
- c.  $Pu^{4+}$ ,  $Ce^{4+}$ ,  $Ti^{4+}$
- d.  $Ba^{2+}$ ,  $Pt^{2+}$ ,  $Mn^{2+}$

36. What noble gas has the same electron configuration as each of the ions in the following compounds?

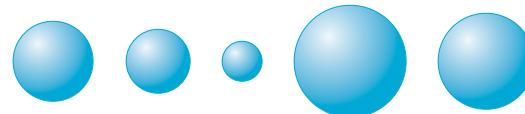
- a. cesium sulfide
- b. strontium fluoride

c. calcium nitride

d. aluminum bromide

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

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



39. For each of the following groups, place the atoms and/or ions in order of decreasing size.

- a. Cu,  $Cu^+$ ,  $Cu^{2+}$
- b.  $Ni^{2+}$ ,  $Pd^{2+}$ ,  $Pt^{2+}$
- c. O,  $O^-$ ,  $O^{2-}$
- d.  $La^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Yb^{3+}$
- e.  $Te^{2-}$ ,  $I^-$ ,  $Cs^+$ ,  $Ba^{2+}$ ,  $La^{3+}$

40. For each of the following groups, place the atoms and/or ions in order of decreasing size.

- a. V,  $V^{2+}$ ,  $V^{3+}$ ,  $V^{5+}$
- b.  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$
- c.  $Te^{2-}$ ,  $I^-$ ,  $Cs^+$ ,  $Ba^{2+}$
- d. P,  $P^-$ ,  $P^{2-}$ ,  $P^{3-}$
- e.  $O^{2-}$ ,  $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$

41. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.

- a. Al and S
- c. Mg and Cl
- b. K and N
- d. Cs and Br

42. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.

- a. Ga and I
- c. Sr and F
- b. Na and O
- d. Ca and P

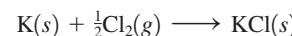
43. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.

- a.  $NaCl$ ,  $KCl$
- b.  $LiF$ ,  $LiCl$
- c.  $Mg(OH)_2$ ,  $MgO$
- d.  $Fe(OH)_2$ ,  $Fe(OH)_3$
- e.  $NaCl$ ,  $Na_2O$
- f.  $MgO$ ,  $BaS$

44. Which compound in each of the following pairs of ionic substances has the most exothermic lattice energy? Justify your answers.

- a.  $LiF$ ,  $CsF$
- b.  $NaBr$ ,  $NaI$
- c.  $BaCl_2$ ,  $BaO$
- d.  $Na_2SO_4$ ,  $CaSO_4$
- e.  $KF$ ,  $K_2O$
- f.  $Li_2O$ ,  $Na_2S$

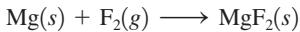
45. Use the following data to estimate  $\Delta H_f^\circ$  for potassium chloride.



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Lattice energy	-690. kJ/mol
Ionization energy for K	419 kJ/mol
Electron affinity of Cl	-349 kJ/mol
Bond energy of $\text{Cl}_2$	239 kJ/mol
Enthalpy of sublimation for K	64 kJ/mol

46. Use the following data to estimate  $\Delta H_f^\circ$  for magnesium fluoride.



Lattice energy	-3916 kJ/mol
First ionization energy of Mg	735 kJ/mol
Second ionization energy of Mg	1445 kJ/mol
Electron affinity of F	-328 kJ/mol
Bond energy of $\text{F}_2$	154 kJ/mol
Enthalpy of sublimation of Mg	150. kJ/mol

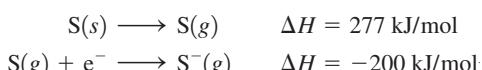
47. Consider the following energy changes:

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

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

48. Compare the electron affinity of fluorine to the ionization energy of sodium. Is the process of an electron being “pulled” from the sodium atom to the fluorine atom exothermic or endothermic? Why is NaF a stable compound? Is the overall formation of NaF endothermic or exothermic? How can this be?
49. LiI(s) has a heat of formation of -272 kJ/mol and a lattice energy of -753 kJ/mol. The ionization energy of  $\text{Li}(g)$  is 520. kJ/mol, the bond energy of  $\text{I}_2(g)$  is 151 kJ/mol, and the electron affinity of  $\text{I}(g)$  is -295 kJ/mol. Use these data to determine the heat of sublimation of  $\text{Li}(s)$ .
50. Use the following data to estimate  $\Delta H$  for the reaction  $\text{S}^-(g) + e^- \rightarrow \text{S}^{2-}(g)$ . Include an estimate of uncertainty.

	$\Delta H_f^\circ$	Lattice Energy	I.E. of M	$\Delta H_{\text{sub}}$ of M
$\text{Na}_2\text{S}$	-365	-2203	495	109
$\text{K}_2\text{S}$	-381	-2052	419	90
$\text{Rb}_2\text{S}$	-361	-1949	409	82
$\text{Cs}_2\text{S}$	-360	-1850	382	78



Assume that all values are known to  $\pm 1$  kJ/mol.

51. Rationalize the following lattice energy values:

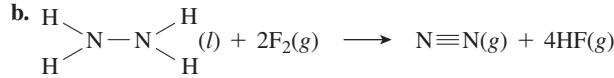
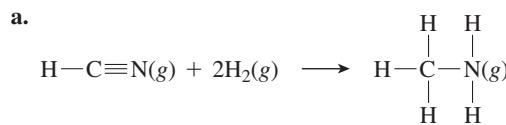
Compound	Lattice Energy (kJ/mol)
CaSe	-2862
$\text{Na}_2\text{Se}$	-2130
CaTe	-2721
$\text{Na}_2\text{Te}$	-2095

52. The lattice energies of  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ , and  $\text{Fe}_2\text{O}_3$  are (in no particular order) -2631, -5359, and -14,774 kJ/mol. Match the appropriate formula to each lattice energy. Explain.

### Bond Energies

53. Use bond energy values (Table 8.4) to estimate  $\Delta H$  for each of the following reactions in the gas phase.
- $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$
  - $\text{N} \equiv \text{N} + 3\text{H}_2 \rightarrow 2\text{NH}_3$

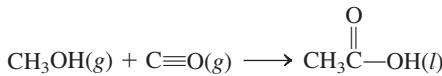
54. Use bond energy values (Table 8.4) to estimate  $\Delta H$  for each of the following reactions.



55. Use bond energies (Table 8.4) to predict  $\Delta H$  for the isomerization of methyl isocyanide to acetonitrile:

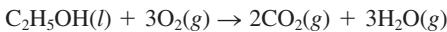


56. Acetic acid is responsible for the sour taste of vinegar. It can be manufactured using the following reaction:



Use tabulated values of bond energies (Table 8.4) to estimate  $\Delta H$  for this reaction.

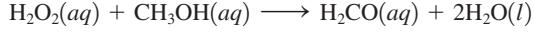
57. Use bond energies to predict  $\Delta H$  for the combustion of ethanol:



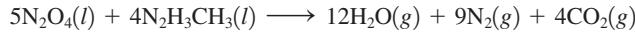
58. Use bond energies to estimate  $\Delta H$  for the combustion for one mole of acetylene:



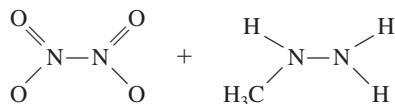
59. Use bond energies to estimate  $\Delta H$  for the following reaction:



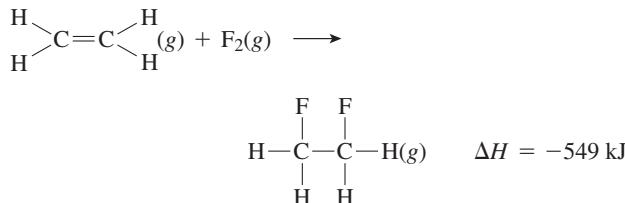
60. The space shuttle orbiter utilizes the oxidation of methyl hydrazine by dinitrogen tetroxide for propulsion:



Use bond energies to estimate  $\Delta H$  for this reaction. The structures for the reactants are:



61. Consider the following reaction:



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

62. Consider the following reaction:



The bond energy for  $\text{A}_2$  is one-half the amount of the AB bond energy. The bond energy of  $\text{B}_2 = 432$  kJ/mol. What is the bond energy of  $\text{A}_2$ ?

63. Compare your answers from parts a and b of Exercise 53 with  $\Delta H$  values calculated for each reaction using standard enthalpies of formation in Appendix 4. Do enthalpy changes calculated from bond energies give a reasonable estimate of the actual values?
64. Compare your answer from Exercise 56 to the  $\Delta H$  value calculated from standard enthalpies of formation in Appendix 4. Explain any discrepancies.
65. The standard enthalpies of formation for  $\text{S}(\text{g})$ ,  $\text{F}(\text{g})$ ,  $\text{SF}_4(\text{g})$ , and  $\text{SF}_6(\text{g})$  are +278.8, +79.0, −775, and −1209 kJ/mol, respectively.
- Use these data to estimate the energy of an S–F bond.
  - Compare your calculated values to the value given in Table 8.4. What conclusions can you draw?
  - Why are the  $\Delta H_f^\circ$  values for  $\text{S}(\text{g})$  and  $\text{F}(\text{g})$  not equal to zero, since sulfur and fluorine are elements?
66. Use the following standard enthalpies of formation to estimate the N–H bond energy in ammonia:  $\text{N}(\text{g})$ , 472.7 kJ/mol;  $\text{H}(\text{g})$ , 216.0 kJ/mol;  $\text{NH}_3(\text{g})$ , −46.1 kJ/mol. Compare your value to the one in Table 8.4.

### Lewis Structures and Resonance

67. Write Lewis structures that obey the octet rule for each of the following.
- $\text{HCN}$
  - $\text{NH}_4^+$
  - $\text{CO}_2$
  - $\text{PH}_3$
  - $\text{H}_2\text{CO}$
  - $\text{O}_2$
  - $\text{CHCl}_3$
  - $\text{SeF}_2$
  - $\text{HBr}$
- Except for HCN and  $\text{H}_2\text{CO}$ , the first atom listed is the central atom. For HCN and  $\text{H}_2\text{CO}$ , carbon is the central atom.
68. Write Lewis structures that obey the octet rule for each of the following molecules and ions. (In each case the first atom listed is the central atom.)
- $\text{POCl}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{XeO}_4$ ,  $\text{PO}_4^{3-}$ ,  $\text{ClO}_4^-$
  - $\text{NF}_3$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_3^{3-}$ ,  $\text{ClO}_3^-$

- c.  $\text{ClO}_2^-$ ,  $\text{SCl}_2$ ,  $\text{PCl}_2^-$

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

69. One type of exception to the octet rule are compounds with central atoms having fewer than eight electrons around them.  $\text{BeH}_2$  and  $\text{BH}_3$  are examples of this type of exception. Draw the Lewis structures for  $\text{BeH}_2$  and  $\text{BH}_3$ .

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

- Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.
- Boron trihydride accepts a pair of electrons from ammonia, forming  $\text{BH}_3\text{NH}_3$ .

Give a possible explanation for why these two reactions occur.

71. The most common type of exception to the octet rule are compounds or ions with central atoms having more than eight electrons around them.  $\text{PF}_5$ ,  $\text{SF}_4$ ,  $\text{ClF}_3$  and  $\text{Br}_3^-$  are examples of this type of exception. Draw the Lewis structure for these compounds or ions. Which elements, when they have to, can have more than eight electrons around them? How is this rationalized?

72.  $\text{SF}_6$ ,  $\text{ClF}_5$ , and  $\text{XeF}_4$  are three compounds whose central atoms do not follow the octet rule. Draw Lewis structures for these compounds.

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

- $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{N}_2\text{O}_4$  ( $\text{N}_2\text{O}_4$  exists as  $\text{O}_2\text{N}-\text{NO}_2$ )
- $\text{OCN}^-$ ,  $\text{SCN}^-$ ,  $\text{N}_3^-$  (Carbon is the central atom in  $\text{OCN}^-$  and  $\text{SCN}^-$ .)

74. Some of the important pollutants in the atmosphere are ozone ( $\text{O}_3$ ), sulfur dioxide, and sulfur trioxide. Write Lewis structures for these three molecules. Show all resonance structures where applicable.

75. Benzene ( $\text{C}_6\text{H}_6$ ) consists of a six-membered ring of carbon atoms with one hydrogen bonded to each carbon. Write Lewis structures for benzene, including resonance structures.

76. Borazine ( $\text{B}_3\text{N}_3\text{H}_6$ ) has often been called “inorganic” benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms with one hydrogen bonded to each boron and nitrogen.

77. An important observation supporting the concept of resonance in the localized electron model was that there are only three different structures of dichlorobenzene ( $\text{C}_6\text{H}_4\text{Cl}_2$ ). How does this fact support the concept of resonance (see Exercise 75)?

78. Consider the following bond lengths:



In the  $\text{CO}_3^{2-}$  ion, all three C–O bonds have identical bond lengths of 136 pm. Why?

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



( $\text{N}_2\text{F}_4$  exists as  $\text{F}_2\text{N}-\text{NF}_2$ , and  $\text{N}_2\text{F}_2$  exists as  $\text{FN}-\text{NF}$ .)

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



What is the order from the weakest to the strongest carbon–oxygen bond? ( $\text{CH}_3\text{OH}$  exists as  $\text{H}_3\text{C}—\text{OH}$ .)

### Formal Charge

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

- a.  $\text{POCl}_3$
- e.  $\text{SO}_2\text{Cl}_2$
- b.  $\text{SO}_4^{2-}$
- f.  $\text{XeO}_4$
- c.  $\text{ClO}_4^-$
- g.  $\text{ClO}_3^-$
- d.  $\text{PO}_4^{3-}$
- h.  $\text{NO}_4^{3-}$

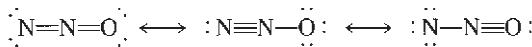
- 82.** Write Lewis structures for the species in Exercise 81 that involve minimum formal charges.

- 83.** Write the Lewis structure for  $\text{O}_2\text{F}_2$  ( $\text{O}_2\text{F}_2$  exists as  $\text{F}—\text{O}—\text{O}—\text{F}$ ). Assign oxidation states and formal charges to the atoms in  $\text{O}_2\text{F}_2$ . This compound is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or formal charges more useful in accounting for these properties of  $\text{O}_2\text{F}_2$ ?

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

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

- 86.** Nitrous oxide ( $\text{N}_2\text{O}$ ) has three possible Lewis structures:



Given the following bond lengths,

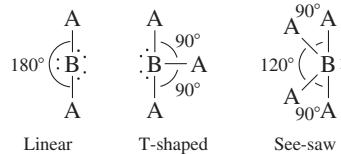
N—N	167 pm	N=O	115 pm
N=N	120 pm	N—O	147 pm
N≡N	110 pm		

rationalize the observations that the N—N bond length in  $\text{N}_2\text{O}$  is 112 pm and that the N—O bond length is 119 pm. Assign formal charges to the resonance structures for  $\text{N}_2\text{O}$ . Can you eliminate any of the resonance structures on the basis of formal charges? Is this consistent with observation?

### Molecular Structure and Polarity

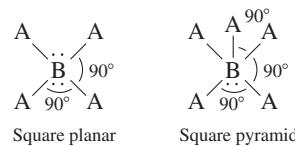
- 87.** Predict the molecular structure and bond angles for each molecule or ion in Exercises 67 and 73.
- 88.** Predict the molecular structure and bond angles for each molecule or ion in Exercises 68 and 74.

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



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

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



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

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

- a.  $\text{SeO}_3$
- b.  $\text{SeO}_2$

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

- a.  $\text{PCl}_3$
- b.  $\text{SCl}_2$
- c.  $\text{SiF}_4$

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

- a.  $\text{XeCl}_2$
- b.  $\text{ICl}_3$
- c.  $\text{TeF}_4$
- d.  $\text{PCl}_5$

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

- a.  $\text{ICl}_5$
- b.  $\text{XeCl}_4$
- c.  $\text{SeCl}_6$

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

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

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

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

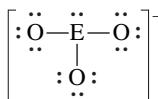
- 99.** Write Lewis structures and predict the molecular structures of the following. (See Exercises 89 and 90.)

- a.  $\text{OCl}_2$ ,  $\text{KrF}_2$ ,  $\text{BeH}_2$ ,  $\text{SO}_2$
- b.  $\text{SO}_3$ ,  $\text{NF}_3$ ,  $\text{IF}_3$
- c.  $\text{CF}_4$ ,  $\text{SeF}_4$ ,  $\text{KrF}_4$
- d.  $\text{IF}_5$ ,  $\text{AsF}_5$

Which of these compounds are polar?

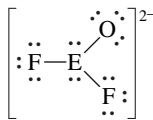
- 100.** Write Lewis structures and predict whether each of the following is polar or nonpolar.
- HOCN (exists as HO—CN)
  - COS
  - XeF<sub>2</sub>
  - CF<sub>2</sub>Cl<sub>2</sub>
  - SeF<sub>6</sub>
  - H<sub>2</sub>CO (C is the central atom.)

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



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

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



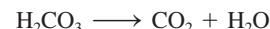
What are some possible identities for element E? Predict the molecular structure (including bond angles) for this ion. (See Exercises 89 and 90.)

- 103.** The molecules BF<sub>3</sub>, CF<sub>4</sub>, CO<sub>2</sub>, PF<sub>5</sub>, and SF<sub>6</sub> are all nonpolar, even though they all contain polar bonds. Why?
- 104.** Two different compounds have the formula XeF<sub>2</sub>Cl<sub>2</sub>. Write Lewis structures for these two compounds, and describe how measurement of dipole moments might be used to distinguish between them.

## Additional Exercises

- 105.** Arrange the following in order of increasing radius and increasing ionization energy.
- N<sup>+</sup>, N, N<sup>-</sup>
  - Se, Se<sup>-</sup>, Cl, Cl<sup>+</sup>
  - Br<sup>-</sup>, Rb<sup>+</sup>, Sr<sup>2+</sup>
- 106.** For each of the following, write an equation that corresponds to the energy given.
- lattice energy of NaCl
  - lattice energy of NH<sub>4</sub>Br
  - lattice energy of MgS
  - O=O double bond energy beginning with O<sub>2</sub>(g) as a reactant
- 107.** Use bond energies (Table 8.4), values of electron affinities (Table 7.7), and the ionization energy of hydrogen (1312 kJ/mol) to estimate  $\Delta H$  for each of the following reactions.
- HF(g) → H<sup>+</sup>(g) + F<sup>-</sup>(g)
  - HCl(g) → H<sup>+</sup>(g) + Cl<sup>-</sup>(g)
  - HI(g) → H<sup>+</sup>(g) + I<sup>-</sup>(g)
  - H<sub>2</sub>O(g) → H<sup>+</sup>(g) + OH<sup>-</sup>(g)
- (Electron affinity of OH(g) = -180. kJ/mol.)

- 108.** Write Lewis structures for CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>CO<sub>3</sub>. When acid is added to an aqueous solution containing carbonate or bicarbonate ions, carbon dioxide gas is formed. We generally say that carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is unstable. Use bond energies to estimate  $\Delta H$  for the reaction (in the gas phase)



Specify a possible cause for the instability of carbonic acid.

- 109.** Which member of the following pairs would you expect to be more energetically stable? Justify each choice.

- NaBr or NaBr<sub>2</sub>
- ClO<sub>4</sub> or ClO<sub>4</sub><sup>-</sup>
- SO<sub>4</sub> or XeO<sub>4</sub>
- OF<sub>4</sub> or SeF<sub>4</sub>

- 110.** What do each of the following sets of compounds/ions have in common with each other?

- SO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>
- O<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub><sup>-</sup>

- 111.** What do each of the following sets of compounds/ions have in common with each other? See your Lewis structures for Exercises 91 through 94.

- XeCl<sub>4</sub>, XeCl<sub>2</sub>
- ICl<sub>5</sub>, TeF<sub>4</sub>, ICl<sub>3</sub>, PCl<sub>3</sub>, SCl<sub>2</sub>, SeO<sub>2</sub>

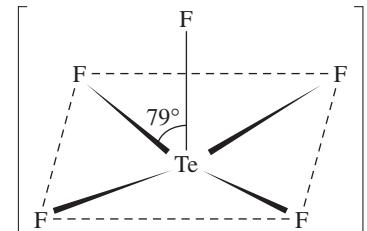
- 112.** Although both Br<sub>3</sub><sup>-</sup> and I<sub>3</sub><sup>-</sup> ions are known, the F<sub>3</sub><sup>-</sup> ion has not been observed. Explain.

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

- 114.** Which of the following molecules have dipole moments? For the molecules that are polar, indicate the polarity of each bond and the direction of the net dipole moment of the molecule.

- CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, CCl<sub>4</sub>
- CO<sub>2</sub>, N<sub>2</sub>O
- PH<sub>3</sub>, NH<sub>3</sub>

- 115.** The structure of TeF<sub>5</sub><sup>-</sup> is



Draw a complete Lewis structure for TeF<sub>5</sub><sup>-</sup>, and explain the distortion from the ideal square pyramidal structure. (See Exercise 90.)

## Challenge Problems

- 116.** An alternative definition of electronegativity is

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

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

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

- 117.** Calculate the standard heat of formation of the compound  $\text{ICl}(g)$  at  $25^\circ\text{C}$ , and show your work. (*Hint:* Use Table 8.4 and Appendix 4.)

- 118.** Given the following information:

Heat of sublimation of  $\text{Li}(s) = 166 \text{ kJ/mol}$   
 Bond energy of  $\text{HCl} = 427 \text{ kJ/mol}$   
 Ionization energy of  $\text{Li}(g) = 520 \text{ kJ/mol}$   
 Electron affinity of  $\text{Cl}(g) = -349 \text{ kJ/mol}$   
 Lattice energy of  $\text{LiCl}(s) = -829 \text{ kJ/mol}$   
 Bond energy of  $\text{H}_2 = 432 \text{ kJ/mol}$

Calculate the net change in energy for the following reaction:



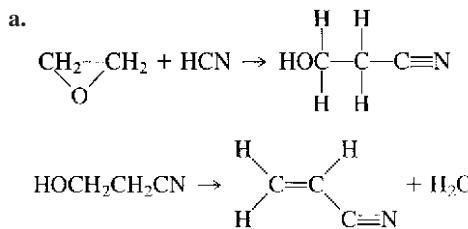
- 119.** Use data in this chapter (and Chapter 7) to discuss why  $\text{MgO}$  is an ionic compound but  $\text{CO}$  is not an ionic compound.

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

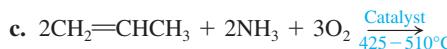
- a. What is the sign of the energy change for each of these three processes?
- b. In general, what is the sign of the sum of the first two processes? Use examples to support your answer.
- c. What must be the sign of the sum of the three processes?
- d. Given your answer to part c, why do ionic bonds occur?
- e. Given your above explanations, why is  $\text{NaCl}$  stable but not  $\text{Na}_2\text{Cl}$ ?  $\text{NaCl}_2$ ? What about  $\text{MgO}$  compared to  $\text{MgO}_2$ ?  $\text{Mg}_2\text{O}$ ?

- 121.** The compound  $\text{NF}_3$  is quite stable, but  $\text{NCl}_3$  is very unstable ( $\text{NCl}_3$  was first synthesized in 1811 by P. L. Dulong, who lost three fingers and an eye studying its properties). The compounds  $\text{NBr}_3$  and  $\text{NI}_3$  are unknown, although the explosive compound  $\text{NI}_3 \cdot \text{NH}_3$  is known. Account for the instability of these halides of nitrogen.

- 122.** Three processes that have been used for the industrial manufacture of acrylonitrile ( $\text{CH}_2\text{CHCN}$ ), an important chemical used in the manufacture of plastics, synthetic rubber, and fibers, are shown below. Use bond energy values (Table 8.4) to estimate  $\Delta H$  for each of the reactions.

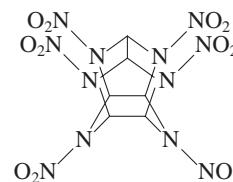


The nitrogen–oxygen bond energy in nitric oxide (NO) is 630. kJ/mol.



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

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



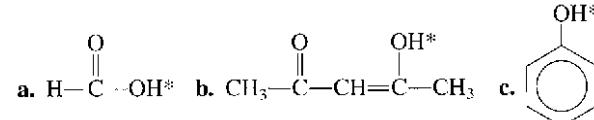
CL-20

In such shorthand structures, each point where lines meet represents a carbon atom. In addition, the hydrogens attached to the carbon atoms are omitted; each of the six carbon atoms has one hydrogen atom attached. Finally, assume that the two O atoms in the  $\text{NO}_2$  groups are attached to N with one single bond and one double bond.

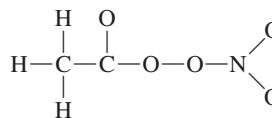
Three possible reactions for the explosive decomposition of CL-20 are

- i.  $\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}(s) \rightarrow 6\text{CO}(g) + 6\text{N}_2(g) + 3\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2(g)$
- ii.  $\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}(s) \rightarrow 3\text{CO}(g) + 3\text{CO}_2(g) + 6\text{N}_2(g) + 3\text{H}_2\text{O}(g)$
- iii.  $\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}(s) \rightarrow 6\text{CO}_2(g) + 6\text{N}_2(g) + 3\text{H}_2(g)$
- a. Use bond energies to estimate  $\Delta H$  for these three reactions.
- b. Which of the above reactions releases the largest amount of energy per kilogram of CL-20?

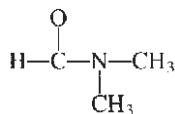
- 124.** Many times extra stability is characteristic of a molecule or ion in which resonance is possible. How could this be used to explain the acidities of the following compounds? (The acidic hydrogen is marked with an asterisk.) Part c shows resonance in the  $\text{C}_6\text{H}_5$  ring.



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



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



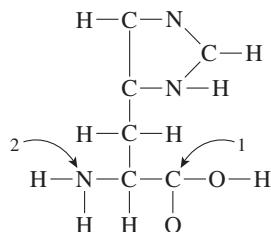
Various types of evidence lead to the conclusion that there is some double bond character to the C—N bond. Draw one or more resonance structures that support this observation.

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

- a.  $\text{BrFI}_2$
- b.  $\text{XeO}_2\text{F}_2$
- c.  $\text{TeF}_2\text{Cl}_3^-$

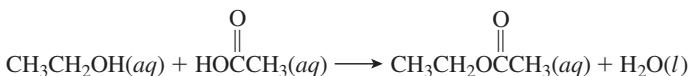
For each formula there are at least two different structures that can be drawn using the same central atom. Draw all possible structures for each formula.

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

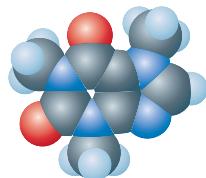


Draw a complete Lewis structure for histidine in which all atoms have a formal charge of zero. What should be the approximate bond angles about the carbon atom labeled 1 and the nitrogen atom labeled 2?

- 129.** Using bond energies, estimate  $\Delta H$  for the following reaction:



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



●	H
●	O
●	N
●	C

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

## Integrative Problems

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

- 131.** A compound,  $\text{XF}_5$ , is 42.81% fluorine by mass. Identify the element X. What is the molecular structure of  $\text{XF}_5$ ?
- 132.** A polyatomic ion is composed of C, N, and an unknown element X. The skeletal Lewis structure of this polyatomic ion is  $[\text{X}-\text{C}-\text{N}]^-$ . The ion  $\text{X}^{2-}$  has an electron configuration of  $[\text{Ar}]4s^23d^{10}4p^6$ . What is element X? Knowing the identity of X, complete the Lewis structure of the polyatomic ion, including all important resonance structures.
- 133.** Identify the following elements based on their electron configurations and rank them in order of increasing electronegativity:  $[\text{Ar}]4s^13d^5$ ;  $[\text{Ne}]3s^23p^3$ ;  $[\text{Ar}]4s^23d^{10}4p^3$ ;  $[\text{Ne}]3s^23p^5$ .

## Marathon Problem

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

- 134.** Identify the five compounds of H, N, and O described below. For each compound, write a Lewis structure that is consistent with the information given.
- a. All the compounds are electrolytes, although not all of them are strong electrolytes. Compounds C and D are ionic and compound B is covalent.
  - b. Nitrogen occurs in its highest possible oxidation state in compounds A and C; nitrogen occurs in its lowest possible oxidation state in compounds C, D, and E. The formal charge on both nitrogens in compound C is +1; the formal charge on the only nitrogen in compound B is 0.
  - c. Compounds A and E exist in solution. Both solutions give off gases. Commercially available concentrated solutions of compound A are normally 16 M. The commercial, concentrated solution of compound E is 15 M.
  - d. Commercial solutions of compound E are labeled with a misnomer that implies that a binary, gaseous compound of nitrogen and hydrogen has reacted with water to produce ammonium ions and hydroxide ions. Actually, this reaction occurs to only a slight extent.
  - e. Compound D is 43.7% N and 50.0% O by mass. If compound D were a gas at STP, it would have a density of 2.86 g/L.
  - f. A formula unit of compound C has one more oxygen than a formula unit of compound D. Compounds C and A have one ion in common when compound A is acting as a strong electrolyte.
  - g. Solutions of compound C are weakly acidic; solutions of compound A are strongly acidic; solutions of compounds B and E are basic. The titration of 0.726 g of compound B requires 21.98 mL of 1.000 M HCl for complete neutralization.

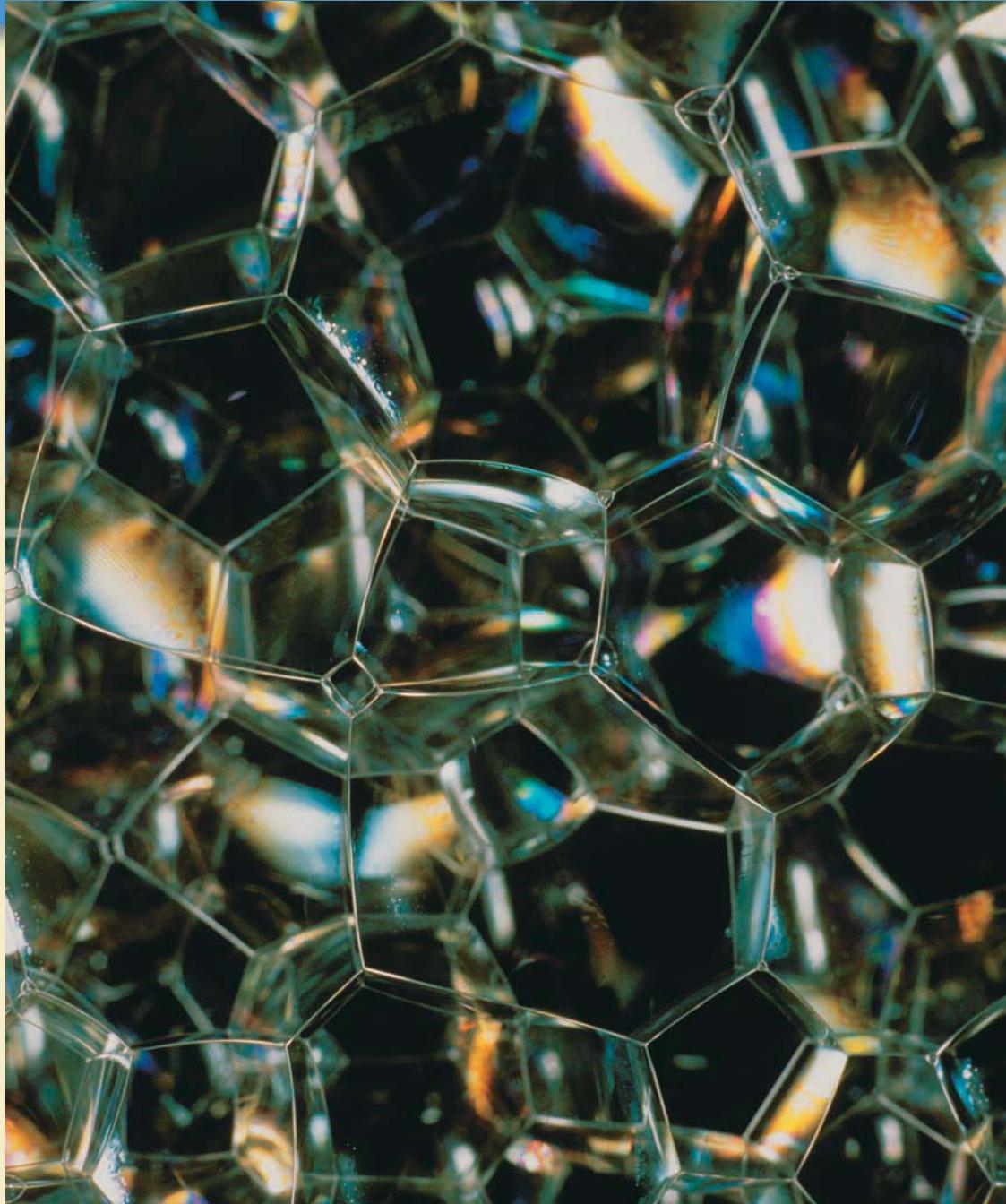


Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at [college.hmco.com/PIC/zumdahl\\_7e](http://college.hmco.com/PIC/zumdahl_7e).

# 9 Covalent Bonding: Orbitals

## Contents

- 9.1 Hybridization and the Localized Electron Model**
  - $sp^3$  Hybridization
  - $sp^2$  Hybridization
  - $sp$  Hybridization
  - $dsp^3$  Hybridization
  - $d^2sp^3$  Hybridization
  - The Localized Electron Model: A Summary
- 9.2 The Molecular Orbital Model**
  - Bond Order
- 9.3 Bonding in Homonuclear Diatomic Molecules**
  - Paramagnetism
- 9.4 Bonding in Heteronuclear Diatomic Molecules**
- 9.5 Combining the Localized Electron and Molecular Orbital Models**



A close-up of soap bubbles reveals their geometric shapes.

**I**

In Chapter 8 we discussed the fundamental concepts of bonding and introduced the most widely used simple model for covalent bonding: the localized electron model. We saw the usefulness of a bonding model as a means for systematizing chemistry by allowing us to look at molecules in terms of individual bonds. We also saw that molecular structure can be predicted by minimizing electron-pair repulsions. In this chapter we will examine bonding models in more detail, particularly focusing on the role of orbitals.

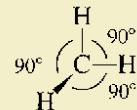
## 9.1 Hybridization and the Localized Electron Model

As we saw in Chapter 8, the localized electron model views a molecule as a collection of atoms bound together by sharing electrons between their atomic orbitals. The arrangement of valence electrons is represented by the Lewis structure (or structures, where resonance occurs), and the molecular geometry can be predicted from the VSEPR model. In this section we will describe the atomic orbitals used to share electrons and hence to form the bonds.

### *sp<sup>3</sup>* Hybridization

Let us reconsider the bonding in methane, which has the Lewis structure and molecular geometry shown in Fig. 9.1. In general, we assume that bonding involves only the valence orbitals. This means that the hydrogen atoms in methane use  $1s$  orbitals. The valence orbitals of a carbon atom are the  $2s$  and  $2p$  orbitals shown in Fig. 9.2. In thinking about how carbon can use these orbitals to bond to the hydrogen atoms, we can see two related problems:

1. Using the  $2p$  and  $2s$  atomic orbitals will lead to two different types of C—H bonds: (a) those from the overlap of a  $2p$  orbital of carbon and a  $1s$  orbital of hydrogen (there will be three of these) and (b) those from the overlap of a  $2s$  orbital of carbon and a  $1s$  orbital of hydrogen (there will be one of these). This is a problem because methane is known to have four identical C—H bonds.
2. Since the carbon  $2p$  orbitals are mutually perpendicular, we might expect the three C—H bonds formed with these orbitals to be oriented at 90-degree angles:



However, the methane molecule is known by experiment to be tetrahedral with bond angles of 109.5 degrees.

This analysis leads to one of two conclusions: Either the simple localized electron model is wrong or carbon adopts a set of atomic orbitals other than its “native”  $2s$  and  $2p$  orbitals to bond to the hydrogen atoms in forming the methane molecule. The second conclusion seems more reasonable. The  $2s$  and  $2p$  orbitals present on an *isolated* carbon atom may not be the best set of orbitals for bonding; a new set of atomic

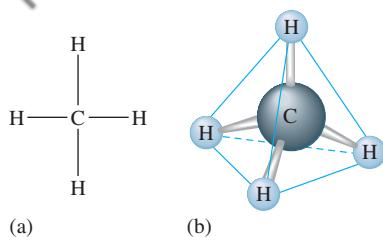


#### Visualization: Hybridization: $sp^3$

The valence orbitals are the orbitals associated with the highest principal quantum level that contains electrons on a given atom.

Hybridization is a modification of the localized electron model to account for the observation that atoms often seem to use special atomic orbitals in forming molecules.

$sp^3$  hybridization gives a tetrahedral set of orbitals.



**FIGURE 9.1**

(a) The Lewis structure of the methane molecule. (b) The tetrahedral molecular geometry of the methane molecule.

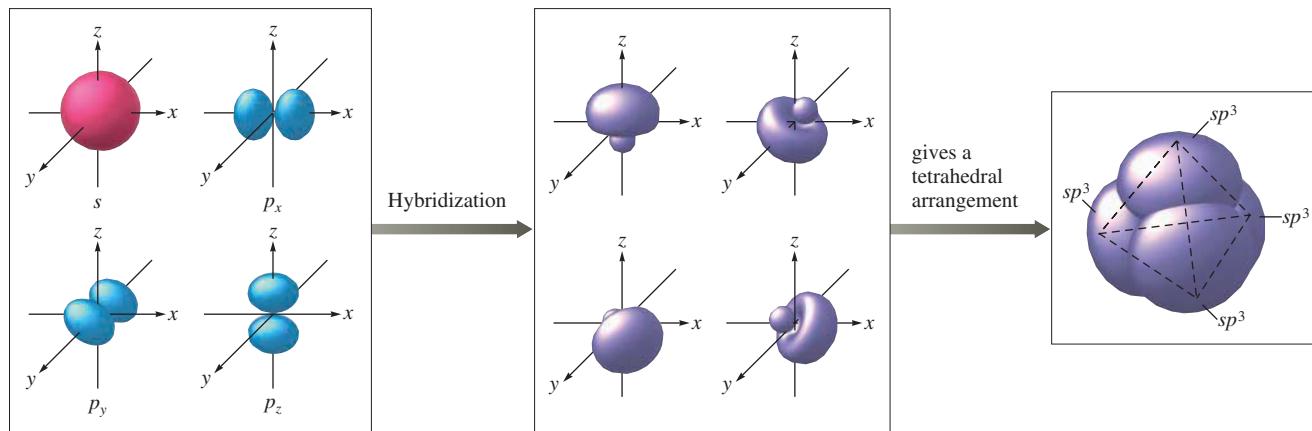
orbitals might better serve the carbon atom in forming molecules. To account for the known structure of methane, it makes sense to assume that the carbon atom has four equivalent atomic orbitals, arranged tetrahedrally. In fact, such a set of orbitals can be obtained quite readily by combining the carbon 2s and 2p orbitals, as shown schematically in Fig. 9.3. This mixing of the native atomic orbitals to form special orbitals for bonding is called **hybridization**. The four new orbitals are called  $sp^3$  orbitals because they are formed from one 2s and three 2p orbitals ( $s^1p^3$ ). We say that the carbon atom undergoes  $sp^3$  hybridization or is  $sp^3$  hybridized. The four  $sp^3$  orbitals are identical in shape, each one having a large lobe and a small lobe (see Fig. 9.4). The four orbitals are oriented in space so that the large lobes form a tetrahedral arrangement, as shown in Fig. 9.3.

The hybridization of the carbon 2s and 2p orbitals also can be represented by an orbital energy-level diagram, as shown in Fig. 9.5. Note that electrons have been omitted because we do not need to be concerned with the electron arrangements on the individual atoms—it is the total number of electrons and the arrangement of these electrons in the *molecule* that are important. We are assuming that carbon's atomic orbitals are rearranged to accommodate the best electron arrangement for the molecule as a whole. The new  $sp^3$  atomic orbitals on carbon are used to share electron pairs with the 1s orbitals from the four hydrogen atoms, as shown in Fig. 9.6 on page 393.

At this point let's summarize the bonding in the methane molecule. The experimentally known structure of this molecule can be explained if we assume that the carbon atom adopts a special set of atomic orbitals. These new orbitals are obtained by combining the  $2s$  and the three  $2p$  orbitals of the carbon atom to produce four identically shaped orbitals that are oriented toward the corners of a tetrahedron and are used to bond to the hydrogen atoms. Thus the four  $sp^3$  orbitals on carbon in methane are postulated to account for its known structure.

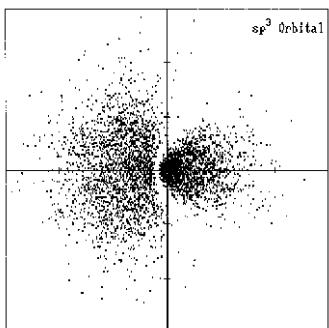
Remember this principle: Whenever a set of equivalent tetrahedral atomic orbitals is required by an atom, this model assumes that the atom adopts a set of  $sp^3$  orbitals; the atom becomes  $sp^3$  hybridized.

It is really not surprising that an atom in a molecule might adopt a different set of atomic orbitals (called **hybrid orbitals**) from those it has in the free state. It does not seem unreasonable that to achieve minimum energy, an atom uses one set of atomic orbitals in the free state and a different set in a molecule. This is consistent with the idea that a molecule is more than simply a sum of its parts. What the atoms in a molecule were



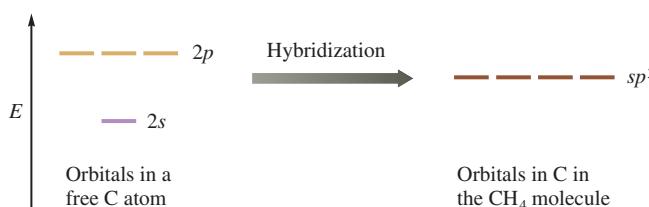
## FIGURE 9.3

The “native” 2s and three 2p atomic orbitals characteristic of a free carbon atom are combined to form a new set of four  $sp^3$  orbitals. The small lobes of the orbitals are usually omitted from diagrams for clarity.

**FIGURE 9.4**

Cross section of an  $sp^3$  orbital. This shows a “slice” of the electron density of the  $sp^3$  orbitals illustrated in the center diagram of Fig. 9.3.

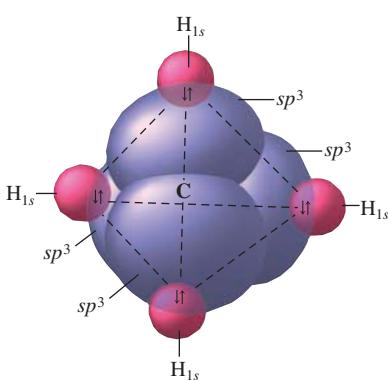
(Generated from a program by Robert Allendoerfer on Project SERAPHIM disk PC2402; printed with permission.)

**FIGURE 9.5**

An energy-level diagram showing the formation of four  $sp^3$  orbitals.

like before the molecule was formed is not as important as how the electrons are best arranged in the molecule. Therefore, this model assumes that the individual atoms respond as needed to achieve the minimum energy for the molecule.

### Sample Exercise 9.1

**FIGURE 9.6**

The tetrahedral set of four  $sp^3$  orbitals of the carbon atom are used to share electron pairs with the four 1s orbitals of the hydrogen atoms to form the four equivalent C–H bonds. This accounts for the known tetrahedral structure of the  $\text{CH}_4$  molecule.

### The Localized Electron Model I

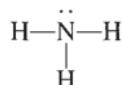
Describe the bonding in the ammonia molecule using the localized electron model.

#### Solution

A complete description of the bonding involves three steps:

1. Writing the Lewis structure
2. Determining the arrangement of electron pairs using the VSEPR model
3. Determining the hybrid atomic orbitals needed to describe the bonding in the molecule

The Lewis structure for  $\text{NH}_3$  is

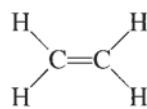


The four electron pairs around the nitrogen atom require a tetrahedral arrangement to minimize repulsions. We have seen that a tetrahedral set of  $sp^3$  hybrid orbitals is obtained by combining the 2s and three 2p orbitals. In the  $\text{NH}_3$  molecule three of the  $sp^3$  orbitals are used to form bonds to the three hydrogen atoms, and the fourth  $sp^3$  orbital holds the lone pair, as shown in Fig. 9.7.

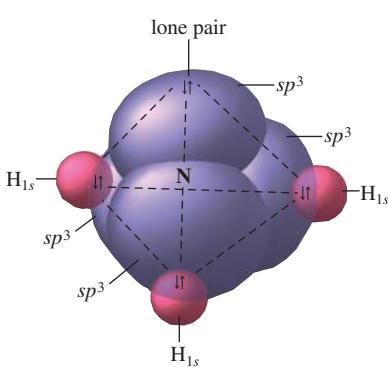
*See Exercise 9.15.*

### $sp^2$ Hybridization

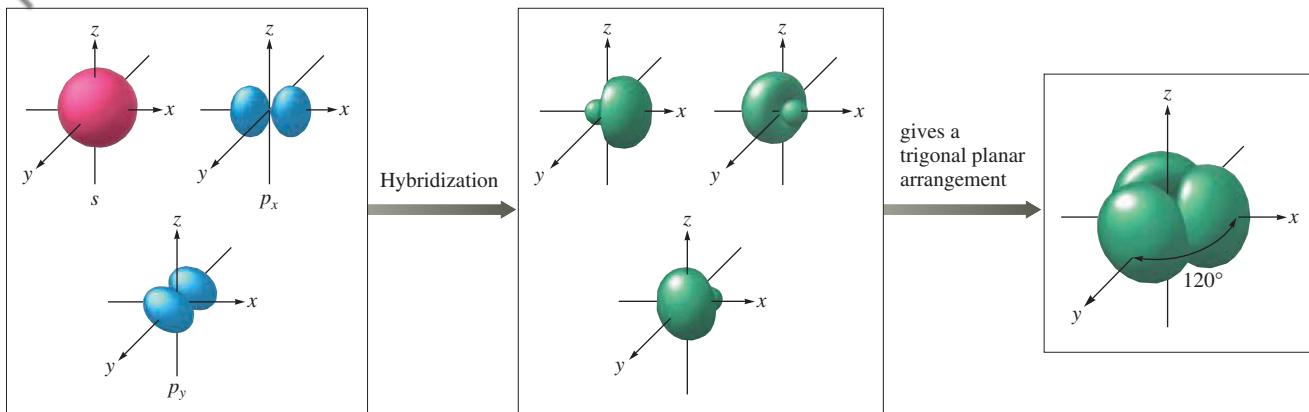
Ethylene ( $\text{C}_2\text{H}_4$ ) is an important starting material in the manufacture of plastics. The  $\text{C}_2\text{H}_4$  molecule has 12 valence electrons and the following Lewis structure:



We saw in Chapter 8 that a double bond acts as one effective pair, so in the ethylene molecule each carbon is surrounded by three effective pairs. This requires a trigonal planar arrangement with bond angles of 120 degrees. What orbitals do the carbon atoms in this molecule employ? The molecular geometry requires a set of orbitals in one plane at angles

**FIGURE 9.7**

The nitrogen atom in ammonia is  $sp^3$  hybridized.

**FIGURE 9.8**

The hybridization of the  $s$ ,  $p_x$ , and  $p_y$  atomic orbitals results in the formation of three  $sp^2$  orbitals centered in the  $xy$  plane. The large lobes of the orbitals lie in the plane at angles of 120 degrees and point toward the corners of a triangle.

**A double bond acts as one effective electron pair.**

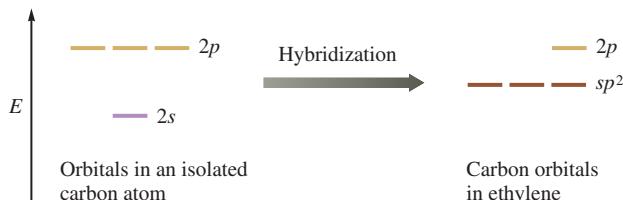
of 120 degrees. Since the  $2s$  and  $2p$  valence orbitals of carbon do not have the required arrangement, we need a set of hybrid orbitals.

The  $sp^3$  orbitals we have just considered will not work because they are at angles of 109.5 degrees rather than the required 120 degrees. In ethylene the carbon atom must hybridize in a different manner. A set of three orbitals arranged at 120-degree angles in the same plane can be obtained by combining one  $s$  orbital and two  $p$  orbitals, as shown in Fig. 9.8. The orbital energy-level diagram for this arrangement is shown in Fig. 9.9. Since one  $2s$  and two  $2p$  orbitals are used to form these hybrid orbitals, this is called  **$sp^2$  hybridization**. Note from Fig. 9.8 that the plane of the  $sp^2$  hybridized orbitals is determined by which  $p$  orbitals are used. Since in this case we have arbitrarily decided to use the  $p_x$  and  $p_y$  orbitals, the hybrid orbitals are centered in the  $xy$  plane.

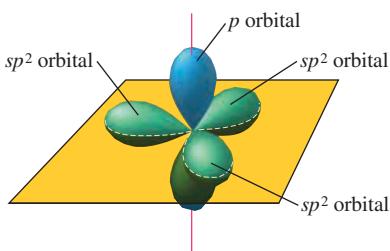
In forming the  $sp^2$  orbitals, one  $2p$  orbital on carbon has not been used. This remaining  $p$  orbital ( $p_z$ ) is oriented perpendicular to the plane of the  $sp^2$  orbitals, as shown in Fig. 9.10.

Now we will see how these orbitals can be used to account for the bonds in ethylene. The three  $sp^2$  orbitals on each carbon can be used to share electrons, as shown in Fig. 9.11. In each of these bonds, the electron pair is shared in an area centered on a line running between the atoms. This type of covalent bond is called a **sigma ( $\sigma$ ) bond**. In the ethylene molecule, the  $\sigma$  bonds are formed using  $sp^2$  orbitals on each carbon atom and the  $1s$  orbital on each hydrogen atom.

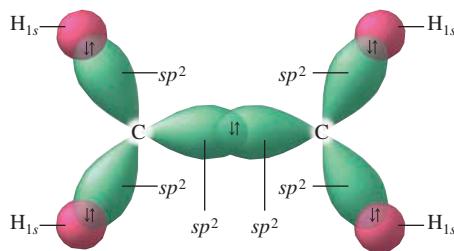
How can we explain the double bond between the carbon atoms? In the  $\sigma$  bond the electron pair occupies the space between the carbon atoms. The second bond must therefore result from sharing an electron pair in the space *above and below* the  $\sigma$  bond. This type of bond can be formed using the  $2p$  orbital perpendicular to the  $sp^2$  hybrid orbitals on each carbon atom (refer to Fig. 9.10). These parallel  $p$  orbitals can share an electron pair, which occupies the space above and below a line joining the atoms, to form a **pi ( $\pi$ ) bond**, as shown in Fig. 9.12.

**FIGURE 9.9**

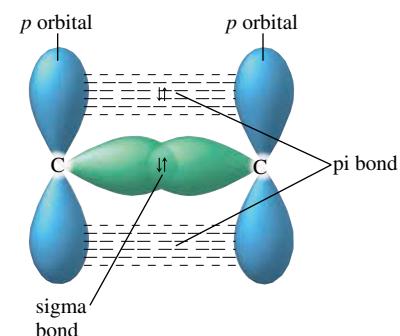
An orbital energy-level diagram for  $sp^2$  hybridization. Note that one  $p$  orbital remains unchanged.

**FIGURE 9.10**

When an *s* and two *p* orbitals are mixed to form a set of three  $sp^2$  orbitals, one *p* orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals. Note that in this figure and those that follow, the orbitals are drawn with narrowed lobes to show their orientations more clearly.

**FIGURE 9.11**

The  $\sigma$  bonds in ethylene. Note that for each bond the shared electron pair occupies the region directly between the atoms.

**FIGURE 9.12**

A carbon–carbon double bond consists of a  $\sigma$  bond and a  $\pi$  bond. In the  $\sigma$  bond the shared electrons occupy the space directly between the atoms. The  $\pi$  bond is formed from the unhybridized *p* orbitals on the two carbon atoms. In a  $\pi$  bond the shared electron pair occupies the space above and below a line joining the atoms.

Visualization: Hybridization:  $sp^2$ 

Visualization: Formation of C=C Double Bond in Ethylene

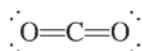
Note that  $\sigma$  bonds are formed from orbitals whose lobes point toward each other, but  $\pi$  bonds result from parallel orbitals. A *double bond* always consists of one  $\sigma$  bond, where the electron pair is located directly between the atoms, and one  $\pi$  bond, where the shared pair occupies the space above and below the  $\sigma$  bond.

We can now completely specify the orbitals that this model assumes are used to form the bonds in the ethylene molecule. As shown in Fig. 9.13, the carbon atoms use  $sp^2$  hybrid orbitals to form the  $\sigma$  bonds to the hydrogen atoms and to each other, and they use *p* to form the  $\pi$  bond with each other. Note that we have accounted fully for the Lewis structure of ethylene with its carbon–carbon double bond and carbon–hydrogen single bonds.

This example illustrates an important general principle of this model: *Whenever an atom is surrounded by three effective pairs, a set of  $sp^2$  hybrid orbitals is required.*

### *sp* Hybridization

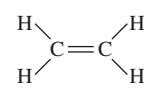
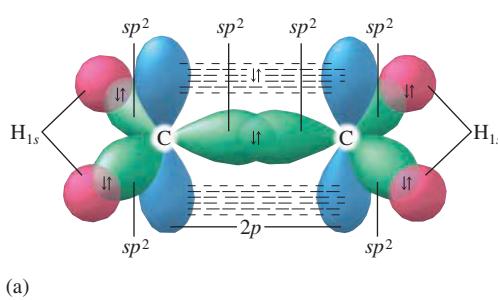
Another type of hybridization occurs in carbon dioxide, which has the following Lewis structure:



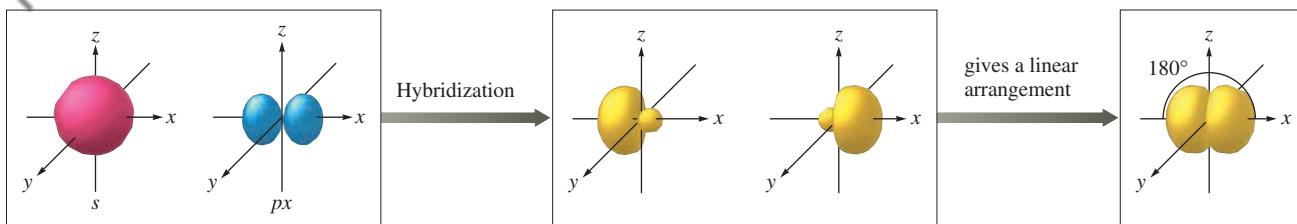
In the  $\text{CO}_2$  molecule the carbon atom has two effective pairs that will be arranged at an angle of 180 degrees. We therefore need a pair of atomic orbitals oriented in opposite directions. This requires a new type of hybridization, since neither  $sp^3$  nor  $sp^2$  hybrid

Visualization: Hybridization:  $sp$ **FIGURE 9.13**

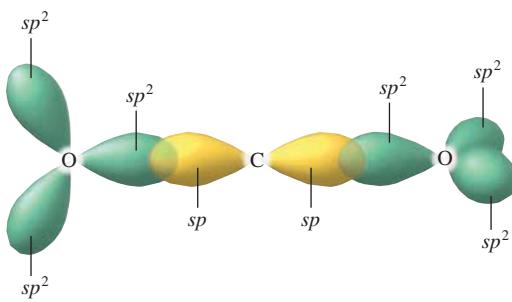
(a) The orbitals used to form the bonds in ethylene. (b) The Lewis structure for ethylene.



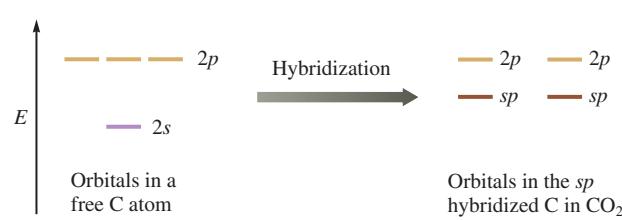
(b)

**FIGURE 9.14**

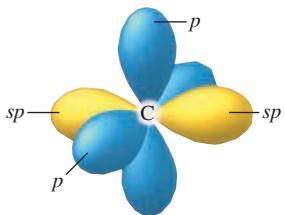
When one  $s$  orbital and one  $p$  orbital are hybridized, a set of two  $sp$  orbitals oriented at 180 degrees results.

**FIGURE 9.15**

The hybrid orbitals in the  $\text{CO}_2$  molecule.

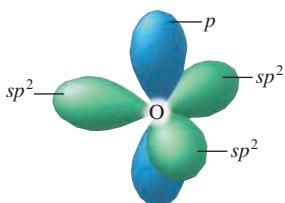
**FIGURE 9.16**

The orbital energy-level diagram for the formation of  $sp$  hybrid orbitals on carbon.

**FIGURE 9.17**

The orbitals of an  $sp$  hybridized carbon atom.

More rigorous theoretical models of  $\text{CO}_2$  indicate that each of the oxygen atoms uses two  $p$  orbitals simultaneously to form the pi bonds to the carbon atom, thus leading to unusually strong  $\text{C}=\text{O}$  bonds.

**FIGURE 9.18**

The orbital arrangement for an  $sp^2$  hybridized oxygen atom.

orbitals will fit this case. To obtain two hybrid orbitals arranged at 180 degrees requires  **$sp$  hybridization**, involving one  $s$  orbital and one  $p$  orbital, as shown in Fig. 9.14.

In terms of this model, *two effective pairs around an atom will always require  $sp$  hybridization of that atom*. The  $sp$  orbitals of carbon in carbon dioxide can be seen in Fig. 9.15, and the corresponding orbital energy-level diagram for their formation is given in Fig. 9.16. These  $sp$  hybrid orbitals are used to form the  $\sigma$  bonds between the carbon and the oxygen atoms. Note that two  $2p$  orbitals remain unchanged on the  $sp$  hybridized carbon. These are used to form the  $\pi$  bonds with the oxygen atoms.

In the  $\text{CO}_2$  molecule each oxygen atom\* has three effective pairs around it, requiring a trigonal planar arrangement of the pairs. Since a trigonal set of hybrid orbitals requires  $sp^2$  hybridization, each oxygen atom is  $sp^2$  hybridized. One  $p$  orbital on each oxygen is unchanged and is used for the  $\pi$  bond with the carbon atom.

Now we are ready to use our model to describe the bonding in carbon dioxide. The  $sp$  orbitals on carbon form  $\sigma$  bonds with the  $sp^2$  orbitals on the two oxygen atoms (Fig. 9.15). The remaining  $sp^2$  orbitals on the oxygen atoms hold lone pairs. The  $\pi$  bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel  $2p$  orbitals. The  $sp$  hybridized carbon atom has two unhybridized  $p$  orbitals, pictured in Fig. 9.17. Each of these  $p$  orbitals is used to form a  $\pi$  bond with an oxygen atom (see Fig. 9.18). The total bonding picture for the  $\text{CO}_2$  molecule is shown in Fig. 9.19. Note that this picture of the bonding neatly explains the arrangement of electrons predicted by the Lewis structure.

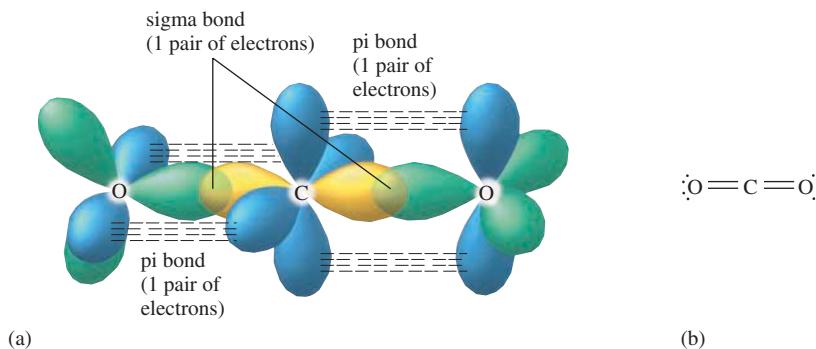
Another molecule whose bonding can be described by  $sp$  hybridization is acetylene ( $\text{C}_2\text{H}_2$ ), which has the systematic name ethyne. The Lewis structure for acetylene is



\*We will assume that minimizing electron repulsions also is important for the peripheral atoms in a molecule and apply the VSEPR model to these atoms as well.

**FIGURE 9.19**

(a) The orbitals used to form the bonds in carbon dioxide. Note that the carbon–oxygen double bonds each consist of one  $\sigma$  bond and one  $\pi$  bond. (b) The Lewis structure for carbon dioxide.



Because the triple bond counts as one effective repulsive unit, each carbon has two effective pairs, which requires a linear arrangement. Thus each carbon atom requires  $sp$  hybridization, leaving two unchanged  $p$  orbitals (see Fig. 9.16). One of the oppositely oriented (see Fig. 9.14)  $sp$  orbitals is used to form a bond to the hydrogen atom; the other  $sp$  orbital overlaps with the similar  $sp$  orbital on the other carbon to form the sigma bond. The two  $\pi$  bonds are formed from the overlap of the two  $p$  orbitals on each carbon. This accounts for the triple bond (one sigma and two  $\pi$  bonds) in acetylene.

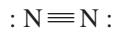
### Sample Exercise 9.2

### The Localized Electron Model II

Describe the bonding in the  $\text{N}_2$  molecule.

#### Solution

The Lewis structure for the nitrogen molecule is

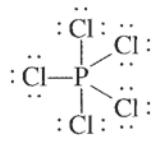


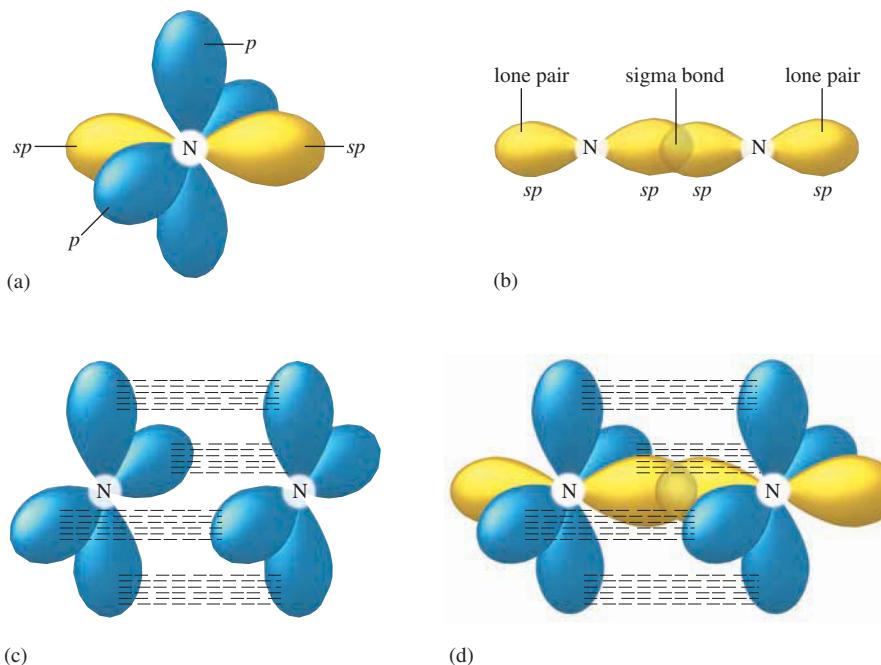
where each nitrogen atom is surrounded by two effective pairs. (Remember that a multiple bond counts as one effective pair.) This gives a linear arrangement (180 degrees) requiring a pair of oppositely directed orbitals. This situation requires  $sp$  hybridization. Each nitrogen atom in the nitrogen molecule has two  $sp$  hybrid orbitals and two unchanged  $p$  orbitals, as shown in Fig. 9.20(a). The  $sp$  orbitals are used to form the  $\sigma$  bond between the nitrogen atoms and to hold lone pairs, as shown in Fig. 9.20(b). The  $p$  orbitals are used to form the two  $\pi$  bonds [see Fig. 9.20(c)]; each pair of overlapping parallel  $p$  orbitals holds one electron pair. Such bonding accounts for the electron arrangement given by the Lewis structure. The triple bond consists of a  $\sigma$  bond (overlap of two  $sp$  orbitals) and two  $\pi$  bonds (each one from an overlap of two  $p$  orbitals). In addition, a lone pair occupies an  $sp$  orbital on each nitrogen atom.

*See Exercises 9.17 and 9.18.*

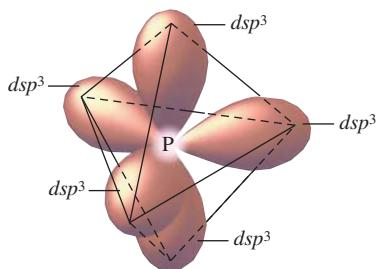
### $dsp^3$ Hybridization

To illustrate the treatment of a molecule in which the central atom exceeds the octet rule, consider the bonding in the phosphorus pentachloride molecule ( $\text{PCl}_5$ ). The Lewis structure



**FIGURE 9.20**

(a) An  $sp$  hybridized nitrogen atom. There are two  $sp$  hybrid orbitals and two unhybridized  $p$  orbitals. (b) The  $\sigma$  bond in the  $N_2$  molecule. (c) The two  $\pi$  bonds in  $N_2$  are formed when electron pairs are shared between two sets of parallel  $p$  orbitals. (d) The total bonding picture for  $N_2$ .

**FIGURE 9.21**

A set of  $dsp^3$  hybrid orbitals on a phosphorus atom. Note that the set of five  $dsp^3$  orbitals has a trigonal bipyramidal arrangement. (Each  $dsp^3$  orbital also has a small lobe that is not shown in this diagram.)

shows that the phosphorus atom is surrounded by five electron pairs. Since five pairs require a trigonal bipyramidal arrangement, we need a trigonal bipyramidal set of atomic orbitals on phosphorus. Such a set of orbitals is formed by  **$dsp^3$  hybridization** of one  $d$  orbital, one  $s$  orbital, and three  $p$  orbitals, as shown in Fig. 9.21.

The  $dsp^3$  hybridized phosphorus atom in the  $PCl_5$  molecule uses its five  $dsp^3$  orbitals to share electrons with the five chlorine atoms. *Note that a set of five effective pairs around a given atom always requires a trigonal bipyramidal arrangement, which in turn requires  $dsp^3$  hybridization of that atom.*

The Lewis structure for  $PCl_5$  shows that each chlorine atom is surrounded by four electron pairs. This requires a tetrahedral arrangement, which in turn requires a set of four  $sp^3$  orbitals on each chlorine atom.

Now we can describe the bonding in the  $PCl_5$  molecule. The five P—Cl  $\sigma$  bonds are formed by sharing electrons between a  $dsp^3$  orbital\* on the phosphorus atom and an  $sp^3$  orbital on each chlorine.<sup>†</sup> The other  $sp^3$  orbitals on each chlorine hold lone pairs. This is shown in Fig. 9.22.

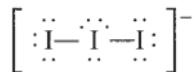
### Sample Exercise 9.3

### The Localized Electron Model III

Describe the bonding in the triiodide ion ( $I_3^-$ ).

#### Solution

The Lewis structure for  $I_3^-$



\*There is considerable controversy about whether the  $d$  orbitals are as heavily involved in the bonding in these molecules as this model predicts. However, this matter is beyond the scope of this text.

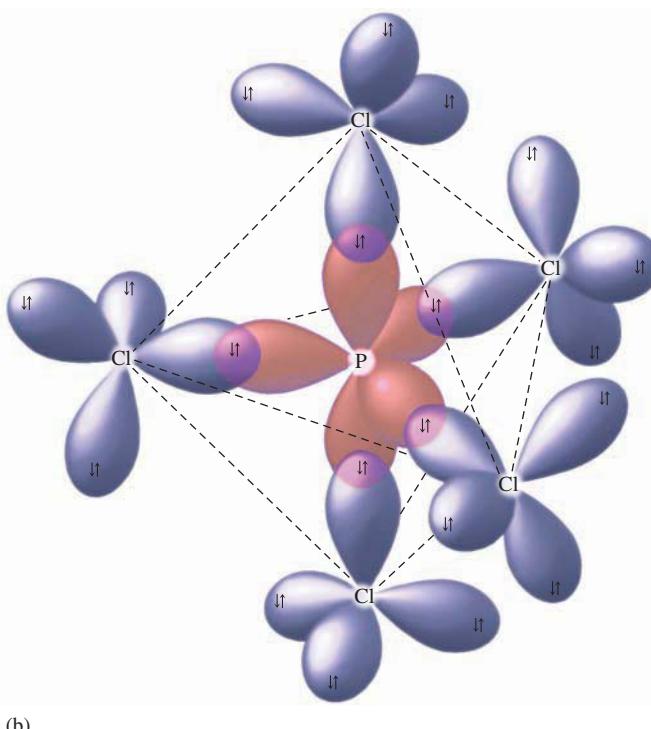
<sup>†</sup>Although we have no way of proving conclusively that each chlorine is  $sp^3$  hybridized, we assume that minimizing electron-pair repulsions is as important for peripheral atoms as for the central atom. Thus we will apply the VSEPR model and hybridization to both central and peripheral atoms.



(a)

**FIGURE 9.22**

- (a) The structure of the  $\text{PCl}_5$  molecule.  
 (b) The orbitals used to form the bonds in  $\text{PCl}_5$ . The phosphorus uses a set of five  $d\text{sp}^3$  orbitals to share electron pairs with  $sp^3$  orbitals on the five chlorine atoms. The other  $sp^3$  orbitals on each chlorine atom hold lone pairs.



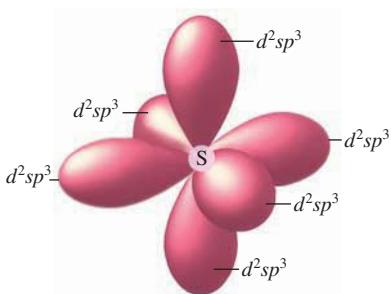
(b)

shows that the central iodine atom has five pairs of electrons (see Section 8.11). A set of five pairs requires a trigonal bipyramidal arrangement, which in turn requires a set of  $d\text{sp}^3$  orbitals. The outer iodine atoms have four pairs of electrons, which calls for a tetrahedral arrangement and  $sp^3$  hybridization.

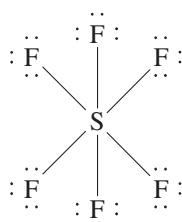
Thus the central iodine is  $d\text{sp}^3$  hybridized. Three of these hybrid orbitals hold lone pairs, and two of them overlap with  $sp^3$  orbitals of the other two iodine atoms to form  $\sigma$  bonds.

*See Exercise 9.23.*

$d^2\text{sp}^3$  hybridization gives six orbitals arranged octahedrally.

**FIGURE 9.23**

An octahedral set of  $d^2\text{sp}^3$  orbitals on a sulfur atom. The small lobe of each hybrid orbital has been omitted for clarity.



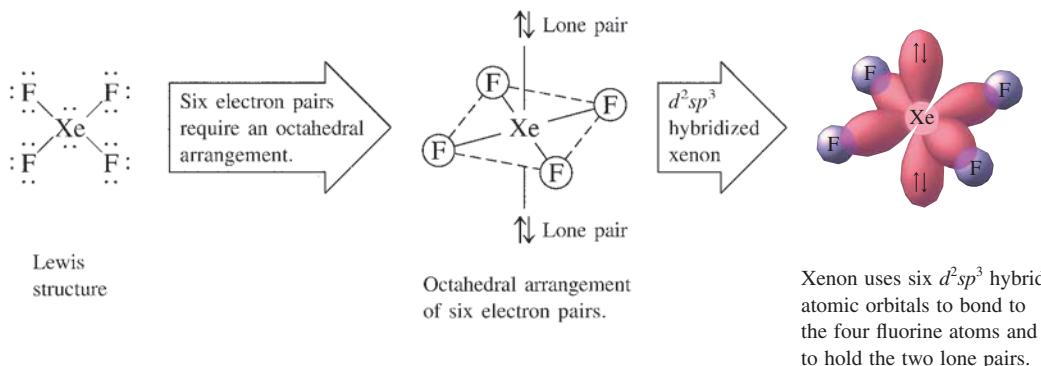
This requires an octahedral arrangement of pairs and in turn an octahedral set of six hybrid orbitals, or  **$d^2\text{sp}^3$  hybridization**, in which two  $d$  orbitals, one  $s$  orbital, and three  $p$  orbitals are combined (see Fig. 9.23). Note that *six electron pairs around an atom are always arranged octahedrally and require  $d^2\text{sp}^3$  hybridization of the atom*. Each of the  $d^2\text{sp}^3$  orbitals on the sulfur atom is used to bond to a fluorine atom. Since there are four pairs on each fluorine atom, the fluorine atoms are assumed to be  $sp^3$  hybridized.

**Sample Exercise 9.4****The Localized Electron Model IV**

How is the xenon atom in  $\text{XeF}_4$  hybridized?

**Solution**

As seen in Sample Exercise 8.13,  $\text{XeF}_4$  has six pairs of electrons around xenon that are arranged octahedrally to minimize repulsions. An octahedral set of six atomic orbitals is required to hold these electrons, and the xenon atom is  $d^2sp^3$  hybridized.



*See Exercise 9.24.*

**The Localized Electron Model: A Summary**

The description of a molecule using the localized electron model involves three distinct steps.

**Localized Electron Model**

- 1 Draw the Lewis structure(s).
- 2 Determine the arrangement of electron pairs using the VSEPR model.
- 3 Specify the hybrid orbitals needed to accommodate the electron pairs.

It is important to do the steps in this order. For a model to be successful, it must follow nature's priorities. In the case of bonding, it seems clear that the tendency for a molecule to minimize its energy is more important than the maintenance of the characteristics of atoms as they exist in the free state. The atoms adjust to meet the "needs" of the molecule. When considering the bonding in a particular molecule, therefore, we always start with the molecule rather than the component atoms. In the molecule the electrons will be arranged to give each atom a noble gas configuration, where possible, and to minimize electron-pair repulsions. We then assume that the atoms adjust their orbitals by hybridization to allow the molecule to adopt the structure that gives the minimum energy.

In applying the localized electron model, we must remember not to overemphasize the characteristics of the separate atoms. It is not where the valence electrons originate that is important; it is where they are needed in the molecule to achieve stability. In the same vein, it is not the orbitals in the isolated atom that matter, but which orbitals the molecule requires for minimum energy.

The requirements for the various types of hybridization are summarized in Fig. 9.24 on the following page.

Number of Effective Pairs	Arrangement of Pairs	Hybridization Required
2	Linear	$sp$
3	Trigonal planar	$sp^2$
4	Tetrahedral	$sp^3$
5	Trigonal bipyramidal	$dsp^3$
6	Octahedral	$d^2sp^3$

**FIGURE 9.24**

The relationship of the number of effective pairs, their spatial arrangement, and the hybrid orbital set required.

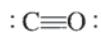
**Sample Exercise 9.5****The Localized Electron Model V**

For each of the following molecules or ions, predict the hybridization of each atom, and describe the molecular structure.

- a. CO    b.  $\text{BF}_4^-$     c.  $\text{XeF}_2$

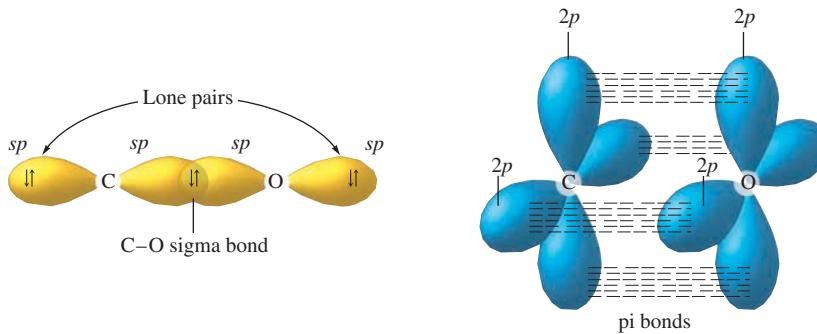
**Solution**

- a. The CO molecule has 10 valence electrons, and its Lewis structure is

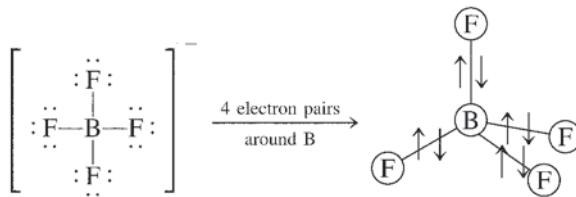


Each atom has two effective pairs, which means that both are  $sp$  hybridized. The triple bond consists of a  $\sigma$  bond produced by overlap of an  $sp$  orbital from each atom and

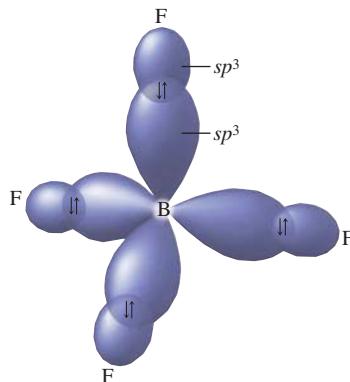
two  $\pi$  bonds produced by overlap of  $2p$  orbitals from each atom. The lone pairs are in  $sp$  orbitals. Since the CO molecule has only two atoms, it must be linear.



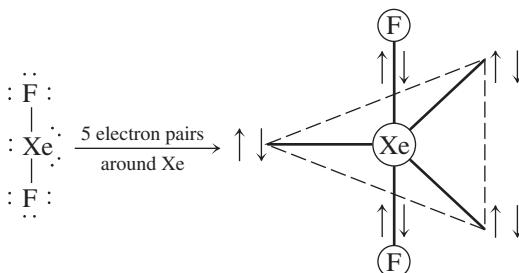
- b. The  $\text{BF}_4^-$  ion has 32 valence electrons. The Lewis structure shows four pairs of electrons around the boron atom, which means a tetrahedral arrangement:



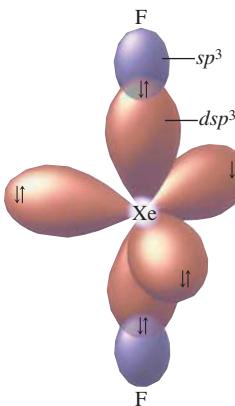
This requires  $sp^3$  hybridization of the boron atom. Each fluorine atom also has four electron pairs and can be assumed to be  $sp^3$  hybridized (only one  $sp^3$  orbital is shown for each fluorine atom). The  $\text{BF}_4^-$  ion's molecular structure is tetrahedral.



- c. The  $\text{XeF}_2$  molecule has 22 valence electrons. The Lewis structure shows five electron pairs on the xenon atom, which requires a trigonal bipyramidal arrangement:



Note that the lone pairs are placed in the plane where they are 120 degrees apart. To accommodate five pairs at the vertices of a trigonal bipyramidal requires that the xenon atom adopt a set of five  $dsp^3$  orbitals. Each fluorine atom has four electron pairs and can be assumed to be  $sp^3$  hybridized. The  $XeF_2$  molecule has a linear arrangement of atoms.



*See Exercises 9.27 and 9.28.*

## 9.2 The Molecular Orbital Model



### Visualization: Bonding in $H_2$

Molecular orbital theory parallels the atomic theory discussed in Chapter 7.

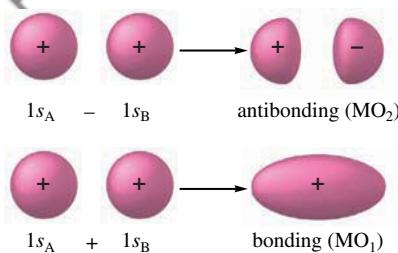
We have seen that the localized electron model is of great value in interpreting the structure and bonding of molecules. However, there are some problems with this model. For example, it incorrectly assumes that electrons are localized, and so the concept of resonance must be added. Also, the model does not deal effectively with molecules containing unpaired electrons. And finally, the model gives no direct information about bond energies.

Another model often used to describe bonding is the **molecular orbital model**. To introduce the assumptions, methods, and results of this model, we will consider the simplest of all molecules,  $H_2$ , which consists of two protons and two electrons. A very stable molecule,  $H_2$  is lower in energy than the separated hydrogen atoms by 432 kJ/mol.

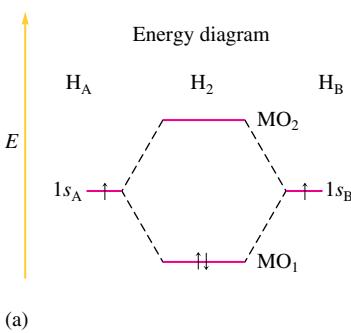
Since the hydrogen molecule consists of protons and electrons, the same components found in separated hydrogen atoms, it seems reasonable to use a theory similar to the atomic theory discussed in Chapter 7, which assumes that the electrons in an atom exist in orbitals of a given energy. Can we apply this same type of model to the hydrogen molecule? Yes. In fact, describing the  $H_2$  molecule in terms of quantum mechanics is quite straightforward.

However, even though it is formulated rather easily, this problem cannot be solved exactly. The difficulty is the same as that in dealing with polyelectronic atoms—the electron correlation problem. Since we do not know the details of the electron movements, we cannot deal with the electron–electron interactions in a specific way. We need to make approximations that allow a solution of the problem but do not destroy the model's physical integrity. The success of these approximations can only be measured by comparing predictions based on theory with experimental observations. In this case we will see that the simplified model works very well.

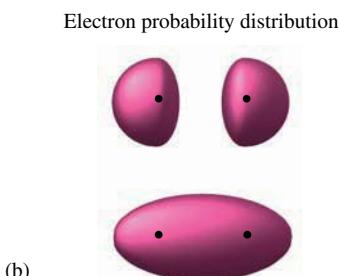
Just as atomic orbitals are solutions to the quantum mechanical treatment of atoms, **molecular orbitals (MOs)** are solutions to the molecular problem. Molecular orbitals

**FIGURE 9.25**

The combination of hydrogen 1s atomic orbitals to form MOs. The phases of the orbitals are shown by signs inside the boundary surfaces. When the orbitals are added, the matching phases produce constructive interference, which give enhanced electron probability between the nuclei. This results in a bonding molecular orbital. When one orbital is subtracted from the other, destructive interference occurs between the opposite phases, leading to a node between the nuclei. This is an antibonding MO.



(a)

**FIGURE 9.26**

(a) The MO energy-level diagram for the  $\text{H}_2$  molecule. (b) The shapes of the MOs are obtained by squaring the wave functions for  $\text{MO}_1$  and  $\text{MO}_2$ . The positions of the nuclei are indicated by •.

have many of the same characteristics as atomic orbitals. Two of the most important are that they can hold two electrons with opposite spins and that the square of the molecular orbital wave function indicates electron probability.

We will now describe the bonding in the hydrogen molecule using this model. The first step is to obtain the hydrogen molecule's orbitals, a process that is greatly simplified if we assume that the molecular orbitals can be constructed from the hydrogen 1s atomic orbitals.

When the quantum mechanical equations for the hydrogen molecule are solved, two molecular orbitals result, which can be represented as

$$\begin{aligned}\text{MO}_1 &= 1s_A + 1s_B \\ \text{MO}_2 &= 1s_A - 1s_B\end{aligned}$$

where  $1s_A$  and  $1s_B$  represent the 1s orbitals from the two separated hydrogen atoms. This process is shown schematically in Fig. 9.25.

The orbital properties of most interest are size, shape (described by the electron probability distribution), and energy. These properties for the hydrogen molecular orbitals are represented in Fig. 9.26. From Fig. 9.26 we can note several important points:

1. The electron probability of both molecular orbitals is centered along the line passing through the two nuclei. For  $\text{MO}_1$  the greatest electron probability is *between* the nuclei, and for  $\text{MO}_2$  it is on *either side* of the nuclei. This type of electron distribution is described as  **$\sigma$  (sigma)**, as in the localized electron model. Accordingly, we refer to  $\text{MO}_1$  and  $\text{MO}_2$  as  **$\sigma$  (sigma) molecular orbitals**.
2. In the molecule only the molecular orbitals are available for occupation by electrons. The 1s atomic orbitals of the hydrogen atoms no longer exist, because the  $\text{H}_2$  molecule—a new entity—has its own set of new orbitals.
3.  $\text{MO}_1$  is lower in energy than the 1s orbitals of free hydrogen atoms, while  $\text{MO}_2$  is higher in energy than the 1s orbitals. This fact has very important implications for the stability of the  $\text{H}_2$  molecule, since if the two electrons (one from each hydrogen atom) occupy the lower-energy  $\text{MO}_1$ , they will have lower energy than they do in the two separate hydrogen atoms. This situation favors molecule formation, because nature tends to seek the lowest energy state. That is, the driving force for molecule formation is that the molecular orbital available to the two electrons has lower energy than the atomic orbitals these electrons occupy in the separated atoms. This situation is favorable to bonding, or *probonding*.

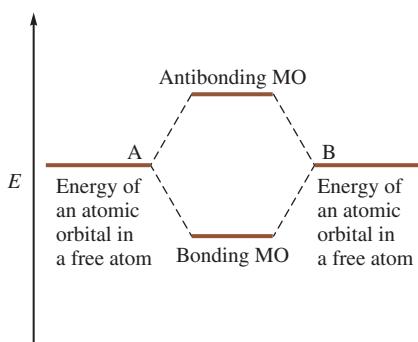
On the other hand, if the two electrons were forced to occupy the higher-energy  $\text{MO}_2$ , they would be definitely *antibonding*. In this case, these electrons would have lower energy in the separated atoms than in the molecule, and the separated state would be favored. Of course, since the lower-energy  $\text{MO}_1$  is available, the two electrons occupy that MO and the molecule is stable.

We have seen that the molecular orbitals of the hydrogen molecule fall into two classes: bonding and antibonding. A **bonding molecular orbital** is *lower in energy than the atomic orbitals of which it is composed*. Electrons in this type of orbital will favor the molecule; that is, they will favor bonding. An **antibonding molecular orbital** is *higher in energy than the atomic orbitals of which it is composed*. Electrons in this type of orbital will favor the separated atoms (they are antibonding). Figure 9.27 illustrates these ideas.

4. Figure 9.26 shows that for the bonding molecular orbital in the  $\text{H}_2$  molecule the electrons have the greatest probability of being between the nuclei. This is exactly what we would expect, since the electrons can lower their energies by being simultaneously attracted by both nuclei. On the other hand, the electron distribution for the

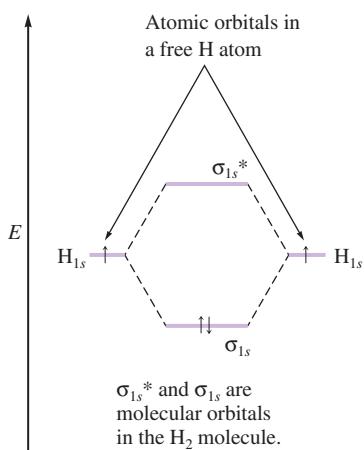


Bonding will result if the molecule has lower energy than the separated atoms.



**FIGURE 9.27**

Bonding and antibonding molecular orbitals (MOs).



**FIGURE 9.28**

A molecular orbital energy-level diagram for the  $\text{H}_2$  molecule.

Although the model predicts that  $\text{H}_2^-$  should be stable, this ion has never been observed, again emphasizing the perils of simple models.

antibonding molecular orbital is such that the electrons are mainly outside the space between the nuclei. This type of distribution is not expected to provide any bonding force. In fact, it causes the electrons to be higher in energy than in the separated atoms. Thus the molecular orbital model produces electron distributions and energies that agree with our basic ideas of bonding. This fact reassures us that the model is physically reasonable.

- The labels on molecular orbitals indicate their symmetry (shape), the parent atomic orbitals, and whether they are bonding or antibonding. Antibonding character is indicated by an asterisk. For the  $\text{H}_2$  molecule, both MOs have  $\sigma$  symmetry, and both are constructed from hydrogen  $1s$  atomic orbitals. The molecular orbitals for  $\text{H}_2$  are therefore labeled as follows:

$$\begin{aligned} \text{MO}_1 &= \sigma_{1s} \\ \text{MO}_2 &= \sigma_{1s}^* \end{aligned}$$

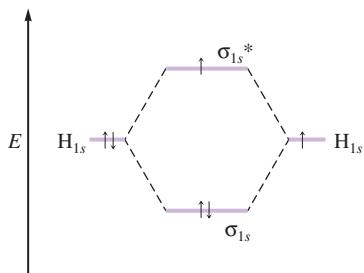
- Molecular electron configurations can be written in much the same way as atomic (electron) configurations. Since the  $\text{H}_2$  molecule has two electrons in the  $\sigma_{1s}$  molecular orbital, the electron configuration is  $\sigma_{1s}^2$ .
- Each molecular orbital can hold two electrons, but the spins must be opposite.
- Orbitals are conserved. The number of molecular orbitals will always be the same as the number of atomic orbitals used to construct them.

Many of the above points are summarized in Fig. 9.28.

Now suppose we could form the  $\text{H}_2^-$  ion from a hydride ion ( $\text{H}^-$ ) and a hydrogen atom. Would this species be stable? Since the  $\text{H}^-$  ion has the configuration  $1s^2$  and the H atom has a  $1s^1$  configuration, we will use  $1s$  atomic orbitals to construct the MO diagram for the  $\text{H}_2^-$  ion, as shown in Fig. 9.29. The electron configuration for  $\text{H}_2^-$  is  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ .

The key idea is that the  $\text{H}_2^-$  ion will be stable if it has a lower energy than its separated parts. From Fig. 9.29 we see that in going from the separated  $\text{H}^-$  ion and H atom to the  $\text{H}_2^-$  ion, the model predicts that two electrons are lowered in energy and one electron is raised in energy. In other words, two electrons are bonding and one electron is antibonding. Since more electrons favor bonding,  $\text{H}_2^-$  is predicted to be a stable entity—a bond has formed. But how would we expect the bond strengths in the molecules of  $\text{H}_2$  and  $\text{H}_2^-$  to compare?

In the formation of the  $\text{H}_2$  molecule, two electrons are lowered in energy and no electrons are raised in energy compared with the parent atoms. When  $\text{H}_2^-$  is formed, two electrons are lowered in energy and one is raised, producing a net lowering of the energy of only one electron. Thus the model predicts that  $\text{H}_2$  is twice as stable as  $\text{H}_2^-$  with respect to their separated components. In other words, the bond in the  $\text{H}_2$  molecule is predicted to be about twice as strong as the bond in the  $\text{H}_2^-$  ion.



**FIGURE 9.29**

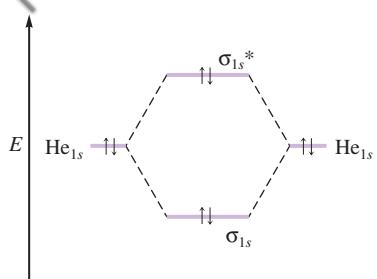
The molecular orbital energy-level diagram for the  $\text{H}_2^-$  ion.

## Bond Order

To indicate bond strength, we use the concept of bond order. **Bond order** is the difference between the number of bonding electrons and the number of antibonding electrons divided by 2.

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

We divide by 2 because, from the localized electron model, we are used to thinking of bonds in terms of pairs of electrons.

**FIGURE 9.30**

The molecular orbital energy-level diagram for the  $\text{He}_2$  molecule.

Since the  $\text{H}_2$  molecule has two bonding electrons and no antibonding electrons, the bond order is

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

The  $\text{H}_2^-$  ion has two bonding electrons and one antibonding electron; the bond order is

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

Bond order is an indication of bond strength because it reflects the difference between the number of bonding electrons and the number of antibonding electrons. *Larger bond order means greater bond strength.*

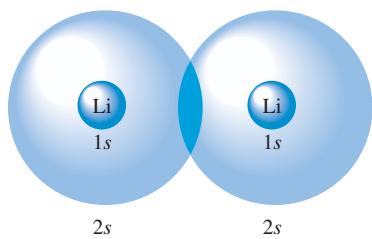
We will now apply the molecular orbital model to the helium molecule ( $\text{He}_2$ ). Does this model predict that this molecule will be stable? Since the He atom has a  $1s^2$  configuration,  $1s$  orbitals are used to construct the molecular orbitals, and the molecule will have four electrons. From the diagram shown in Fig. 9.30 it is apparent that two electrons are raised in energy and two are lowered in energy. Thus the bond order is zero:

$$\frac{2 - 2}{2} = 0$$

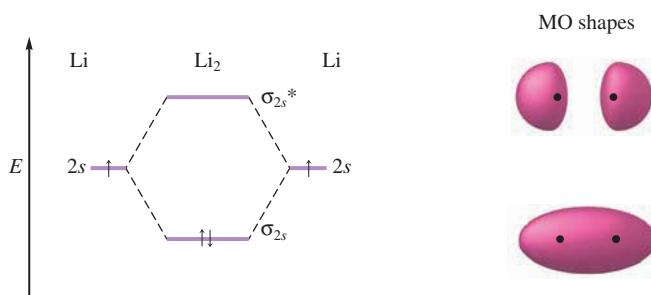
This implies that the  $\text{He}_2$  molecule is *not* stable with respect to the two free He atoms, which agrees with the observation that helium gas consists of individual He atoms.

## 9.3 Bonding in Homonuclear Diatomic Molecules

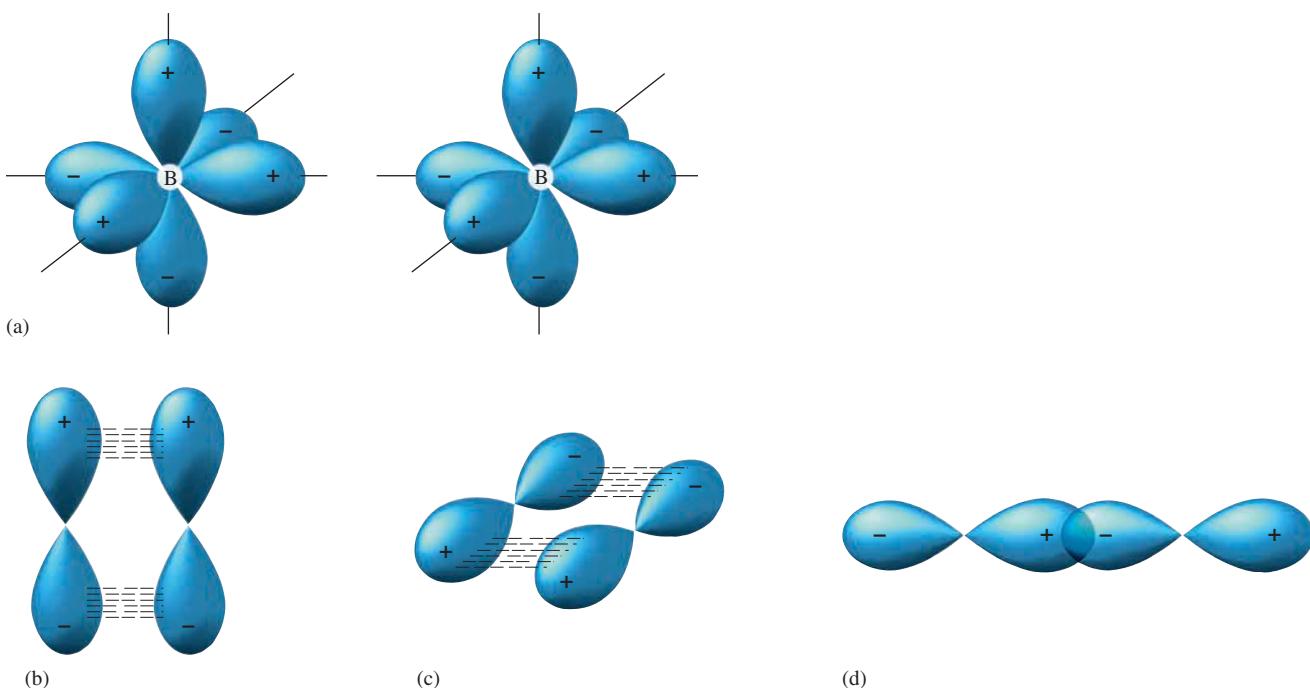
In this section we consider *homonuclear diatomic molecules* (those composed of two identical atoms) of elements in Period 2 of the periodic table. Since the lithium atom has a  $1s^22s^1$  electron configuration, it would seem that we should use the Li  $1s$  and  $2s$  orbitals to form the molecular orbitals of the  $\text{Li}_2$  molecule. However, the  $1s$  orbitals on the lithium atoms are much smaller than the  $2s$  orbitals and therefore do not overlap in space to any appreciable extent (see Fig. 9.31). Thus the two electrons in each  $1s$  orbital can be assumed to be localized and not to participate in the bonding. *To participate in molecular orbitals, atomic orbitals must overlap in space.* This means that only the valence orbitals of the atoms contribute significantly to the molecular orbitals of a particular molecule.

**FIGURE 9.31**

The relative sizes of the lithium  $1s$  and  $2s$  atomic orbitals.

**FIGURE 9.32**

The molecular orbital energy-level diagram for the  $\text{Li}_2$  molecule.



**FIGURE 9.33**

(a) The three mutually perpendicular  $2p$  orbitals on two adjacent boron atoms. The signs indicate the orbital phases. Two pairs of parallel  $p$  orbitals can overlap, as shown in (b) and (c), and the third pair can overlap head-on, as shown in (d).

The molecular orbital diagram of the  $\text{Li}_2$  molecule and the shapes of its bonding and antibonding MOs are shown in Fig. 9.32. The electron configuration for  $\text{Li}_2$  (valence electrons only) is  $\sigma_{s,2}^2$ , and the bond order is

$$\frac{2 - 0}{2} = 1$$

The  $\text{Li}_2$  is a stable molecule (has lower energy than two separated lithium atoms). However, this does not mean that  $\text{Li}_2$  is the most stable form of elemental lithium. In fact, at normal temperature and pressure, lithium exists as a solid containing many lithium atoms bound to each other.

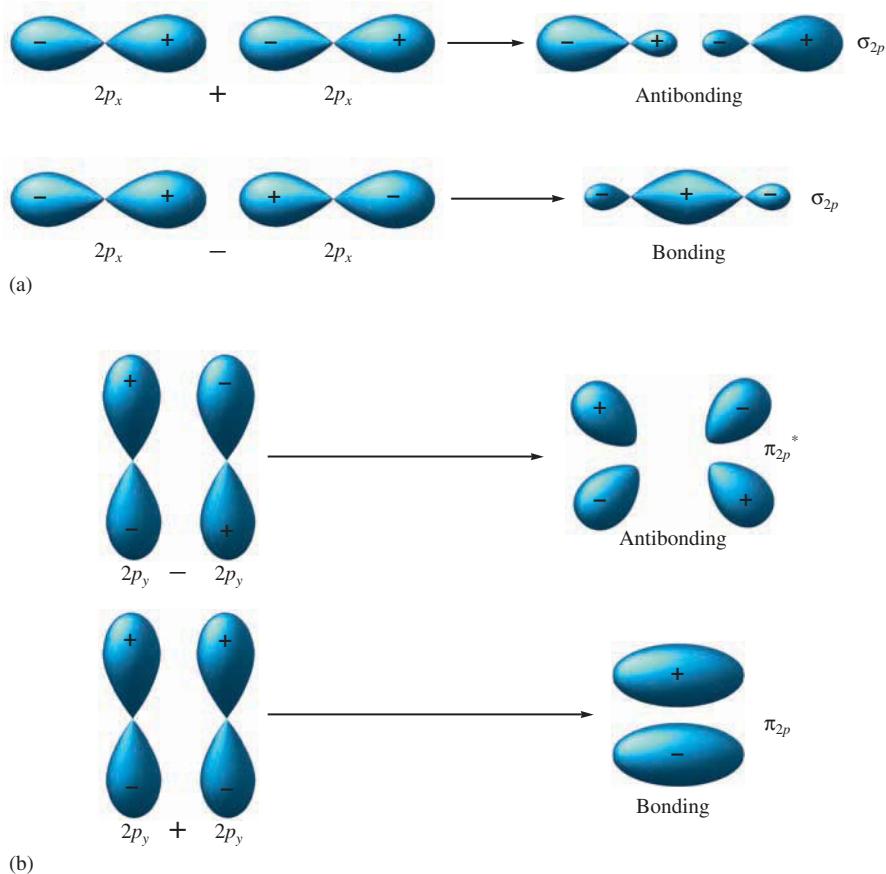
For the beryllium molecule ( $\text{Be}_2$ ) the bonding and antibonding orbitals both contain two electrons. In this case the bond order is  $(2 - 2)/2 = 0$ , and since  $\text{Be}_2$  is not more stable than two separated Be atoms, no molecule forms. However, beryllium metal contains many beryllium atoms bonded to each other and is stable for reasons we will discuss in Chapter 10.

Since the boron atom has a  $1s^22s^22p^1$  configuration, we describe the  $B_2$  molecule by considering how  $p$  atomic orbitals combine to form molecular orbitals. Recall that  $p$  orbitals have two lobes and that they occur in sets of three mutually perpendicular orbitals [see Fig. 9.33(a)]. When two B atoms approach each other, two pairs of  $p$  orbitals can overlap in a parallel fashion [Fig. 9.33(b) and (c)] and one pair can overlap head-on [Fig. 9.33(d)].

First, let's consider the molecular orbitals from the head-on overlap, as shown in Fig. 9.34(a). Note that the electrons in the bonding MO are, as expected, concentrated between the nuclei, and the electrons in the antibonding MO are concentrated outside the area between the two nuclei. Also, both these MOs are  $\sigma$  molecular orbitals. The



## Visualization: Pi Bonding and Antibonding Orbitals

**FIGURE 9.34**

(a) The two  $p$  orbitals on the boron atoms that overlap head-on combine to form  $\sigma$  bonding and antibonding orbitals. The bonding orbital is formed by reversing the sign of the right orbital so the positive phases of both orbitals match between the nuclei to produce constructive interference. This leads to enhanced electron probability between the nuclei. The antibonding orbital is formed by the direct combination of the orbitals, which gives destructive interference of the positive phase of one orbital with the negative phase of the second orbital. This produces a node between the nuclei, which gives decreased electron probability. (b) When the parallel  $p$  orbitals are combined with the positive and negative phases matched, constructive interference occurs, giving a bonding  $\pi$  orbital. When the orbitals have opposite phases (the signs of one orbital are reversed), destructive interference occurs, resulting in an antibonding  $\pi$  orbital.

$p$  orbitals that overlap in a parallel fashion also produce bonding and antibonding orbitals [Fig. 9.34(b)]. Since the electron probability lies above and below the line between the nuclei, both the orbitals are **pi ( $\pi$ ) molecular orbitals**. They are designated as  $\pi_{2p}$  for the bonding MO and  $\pi_{2p}^*$  for the antibonding MO.

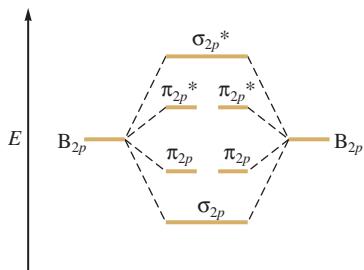
Let's try to make an educated guess about the relative energies of the  $\sigma$  and  $\pi$  molecular orbitals formed from the  $2p$  atomic orbitals. Would we expect the electrons to prefer the  $\sigma$  bonding orbital (where the electron probability is concentrated in the area between the nuclei) or the  $\pi$  bonding orbital? The  $\sigma$  orbital would seem to have the lower energy, since the electrons are closest to the two nuclei. This agrees with the observation that  $\sigma$  interactions are stronger than  $\pi$  interactions.

Figure 9.35 gives the molecular orbital energy-level diagram *expected* when the two sets of  $2p$  orbitals on the boron atoms combine to form molecular orbitals. Note that there are two  $\pi$  bonding orbitals at the same energy (degenerate orbitals) formed from the two pairs of parallel  $p$  orbitals, and there are two degenerate  $\pi$  antibonding orbitals. The energy of the  $\pi_{2p}$  orbitals is expected to be higher than that of the  $\sigma_{2p}$  orbital because  $\sigma$  interactions are generally stronger than  $\pi$  interactions.

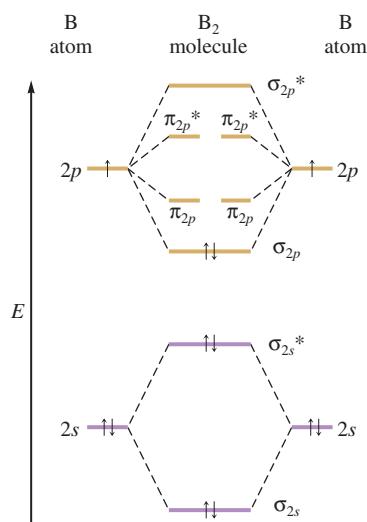
To construct the total molecular orbital diagram for the  $B_2$  molecule, we make the assumption that the  $2s$  and  $2p$  orbitals combine separately (in other words, there is no  $2s-2p$  mixing). The resulting diagram is shown in Fig. 9.36. Note that  $B_2$  has six *valence* electrons. (Remember the  $1s$  orbitals and electrons are assumed not to participate in the bonding.) This diagram predicts the bond order:

$$\frac{4 - 2}{2} = 1$$

Therefore,  $B_2$  should be a stable molecule.

**FIGURE 9.35**

The *expected* molecular orbital energy-level diagram resulting from the combination of the  $2p$  orbitals on two boron atoms.

**FIGURE 9.36**

The expected molecular orbital energy-level diagram for the  $\text{B}_2$  molecule.

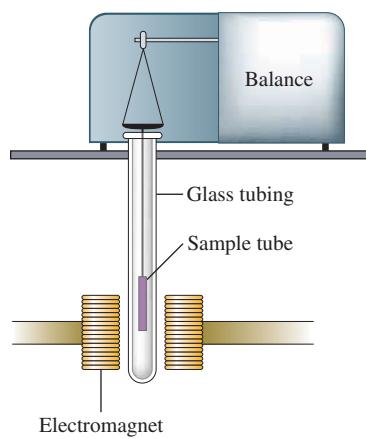
**FIGURE 9.37**

Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.

## Paramagnetism

At this point we need to discuss an additional molecular property—magnetism. Most materials have no magnetism until they are placed in a magnetic field. However, in the presence of such a field, magnetism of two types can be induced. **Paramagnetism** causes the substance to be attracted into the inducing magnetic field. **Diamagnetism** causes the substance to be repelled from the inducing magnetic field. Figure 9.37 illustrates how paramagnetism is measured. The sample is weighed with the electromagnet turned off and then weighed again with the electromagnet turned on. An increase in weight when the field is turned on indicates the sample is paramagnetic. Studies have shown that *paramagnetism is associated with unpaired electrons and diamagnetism is associated with paired electrons*. Any substance that has both paired and unpaired electrons will exhibit a net paramagnetism, since the effect of paramagnetism is much stronger than that of diamagnetism.

The molecular orbital energy-level diagram represented in Fig. 9.36 predicts that the  $\text{B}_2$  molecule will be diamagnetic, since the MOs contain only paired electrons. However, experiments show that  $\text{B}_2$  is actually paramagnetic with two unpaired electrons. Why does the model yield the wrong prediction? This is yet another illustration of how models are developed and used. In general, we try to use the simplest possible model that accounts for all the important observations. In this case, although the simplest model successfully describes the diatomic molecules up to  $\text{B}_2$ , it certainly is suspect if it cannot describe the  $\text{B}_2$  molecule correctly. This means we must either discard the model or find a way to modify it.

Let's consider one assumption that we made. In our treatment of  $\text{B}_2$ , we have assumed that the  $s$  and  $p$  orbitals combine separately to form molecular orbitals. Calculations show that when the  $s$  and  $p$  orbitals are allowed to mix in the same molecular orbital, a different energy-level diagram results for  $\text{B}_2$  (see Fig. 9.38). Note that even though the  $s$  and  $p$  contributions to the MOs are no longer separate, we retain the simple orbital designations. The energies of  $\pi_{2p}$  and  $\sigma_{2p}$  orbitals are reversed by  $p-s$  mixing, and the  $\sigma_{2s}$  and the  $\sigma_{2s}^*$  orbitals are no longer equally spaced relative to the energy of the free  $2s$  orbital.

When the six valence electrons for the  $\text{B}_2$  molecule are placed in the modified energy-level diagram, each of the last two electrons goes into one of the degenerate  $\pi_{2p}$  orbitals. This produces a paramagnetic molecule in agreement with experimental results. Thus, when the model is extended to allow  $p-s$  mixing in molecular orbitals, it predicts the correct magnetism. Note that the bond order is  $(4 - 2)/2 = 1$ , as before.

The remaining diatomic molecules of the elements in Period 2 can be described using similar ideas. For example, the  $\text{C}_2$  and  $\text{N}_2$  molecules use the same set of orbitals as for  $\text{B}_2$  (see Fig. 9.38). Because the importance of  $2s-2p$  mixing decreases across the period, the  $\sigma_{2p}$  and  $\pi_{2p}$  orbitals revert to the order expected in the absence of  $2s-2p$  mixing for the molecules  $\text{O}_2$  and  $\text{F}_2$ , as shown in Fig. 9.39.

Several significant points arise from the orbital diagrams, bond strengths, and bond lengths summarized in Fig. 9.39 for the Period 2 diatomics:

1. There are definite correlations between bond order, bond energy, and bond length. As the bond order predicted by the molecular orbital model increases, the bond energy increases and the bond length decreases. This is a clear indication that the bond order predicted by the model accurately reflects bond strength, and it strongly supports the reasonableness of the MO model.
2. Comparison of the bond energies of the  $\text{B}_2$  and  $\text{F}_2$  molecules indicates that bond order cannot automatically be associated with a particular bond energy. Although both molecules have a bond order of 1, the bond in  $\text{B}_2$  appears to be about twice as strong as the bond in  $\text{F}_2$ . As we will see in our later discussion of the halogens,  $\text{F}_2$  has an unusually weak single bond due to larger than usual electron–electron repulsions (there are 14 valence electrons on the small  $\text{F}_2$  molecule).

3. Note the very large bond energy associated with the  $N_2$  molecule, which the molecular orbital model predicts will have a bond order of 3, a triple bond. The very strong bond in  $N_2$  is the principal reason that many nitrogen-containing compounds are used as high explosives. The reactions involving these explosives give the very stable  $N_2$  molecule as a product, thus releasing large quantities of energy.

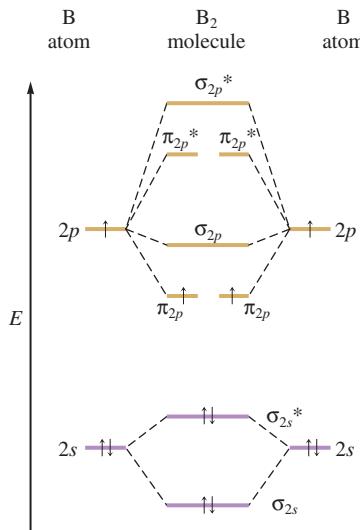


**Visualization: Magnetic Properties of Liquid Nitrogen and Oxygen**

4. The  $O_2$  molecule is known to be paramagnetic. This can be very convincingly demonstrated by pouring liquid oxygen between the poles of a strong magnet, as shown in Fig. 9.40. The oxygen remains there until it evaporates. Significantly, the molecular orbital model correctly predicts oxygen's paramagnetism, while the localized electron model predicts a diamagnetic molecule.

### Sample Exercise 9.6

### The Molecular Orbital Model I



**FIGURE 9.38**

The correct molecular orbital energy-level diagram for the  $B_2$  molecule. When  $p-s$  mixing is allowed, the energies of the  $\sigma_{2p}$  and  $\pi_{2p}$  orbitals are reversed. The two electrons from the B 2p orbitals now occupy separate, degenerate  $\pi_{2p}$  molecular orbitals and thus have parallel spins. Therefore, this diagram explains the observed paramagnetism of  $B_2$ .

For the species  $O_2$ ,  $O_2^+$ , and  $O_2^-$ , give the electron configuration and the bond order for each. Which has the strongest bond?

#### Solution

The  $O_2$  molecule has 12 valence electrons ( $6 + 6$ );  $O_2^+$  has 11 valence electrons ( $6 + 6 - 1$ ); and  $O_2^-$  has 13 valence electrons ( $6 + 6 + 1$ ). We will assume that the ions

	$B_2$	$C_2$	$N_2$	$O_2$	$F_2$
$\sigma_{2p}^*$	—	—	—	$\sigma_{2p}^*$ —	—
$\pi_{2p}^*$	— —	— —	— —	$\pi_{2p}^*$ ↑ ↑	↑ ↑
$\sigma_{2p}$	—	—	↑ ↓	$\pi_{2p}$ ↑ ↑	↑ ↑
$\pi_{2p}$	↑ ↑	↑ ↑	↑ ↑	$\sigma_{2p}$ —	— ↑
$\sigma_{2s}^*$	↑ ↓	↑ ↓	↑ ↓	$\sigma_{2s}^*$ —	— ↑
$\sigma_{2s}$	↑ ↓	↑ ↓	↑ ↓	$\sigma_{2s}$ —	— ↑
Magnetism	Para-magnetic	Dia-magnetic	Dia-magnetic	Para-magnetic	Dia-magnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143



**Visualization: Molecular Orbital Diagram ( $N_2$ )**

**FIGURE 9.39**

The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic molecules  $B_2$  through  $F_2$ . Note that for  $O_2$  and  $F_2$  the  $\sigma_{2p}$  orbital is lower in energy than the  $\pi_{2p}$  orbitals.

**FIGURE 9.40**

When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the  $O_2$  molecule.

can be treated using the same molecular orbital diagram as for the neutral diatomic molecule:

	$O_2$	$O_2^+$	$O_2^-$
$\sigma_{2p}^*$	—	—	—
$\pi_{2p}^*$	↑↑	↑—	↑↑
$\pi_{2p}$	↑↑	↑↑	↑↑
$\sigma_{2p}$	↑↓	↑↓	↑↓
$\sigma_{2s}^*$	↑↓	↑↓	↑↓
$\sigma_{2s}$	↑↓	↑↓	↑↓

The electron configuration for each species can then be taken from the diagram:

$$O_2: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$$

$$O_2^+: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$$

$$O_2^-: (\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$$

The bond orders are:

$$\text{For } O_2: \frac{8 - 4}{2} = 2$$

$$\text{For } O_2^+: \frac{8 - 3}{2} = 2.5$$

$$\text{For } O_2^-: \frac{8 - 5}{2} = 1.5$$

Thus  $O_2^+$  is expected to have the strongest bond of the three species.

*See Exercises 9.39 and 9.40.*

### Sample Exercise 9.7

### The Molecular Orbital Model II

Use the molecular orbital model to predict the bond order and magnetism of each of the following molecules.

- $Ne_2$
- $P_2$

#### Solution

- The valence orbitals for Ne are  $2s$  and  $2p$ . Thus we can use the molecular orbitals we have already constructed for the diatomic molecules of the Period 2 elements. The  $Ne_2$  molecule has 16 valence electrons (8 from each atom). Placing these electrons in the appropriate molecular orbitals produces the following diagram:

$E$	$\sigma_{2p}^*$	↑↓
	$\pi_{2p}^*$	↑↓ ↑↓
	$\pi_{2p}$	↑↓ ↑↓
	$\sigma_{2p}$	↑↓
	$\sigma_{2s}^*$	↑↓
	$\sigma_{2s}$	↑↓

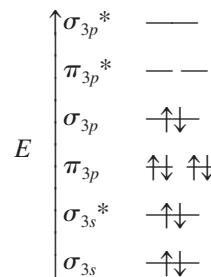
The bond order is  $(8 - 8)/2 = 0$ , and  $Ne_2$  does not exist.

- The  $P_2$  molecule contains phosphorus atoms from the third row of the periodic table. We will assume that the diatomic molecules of the Period 3 elements can be



Visualization: Magnetic Properties of Liquid Nitrogen and Oxygen

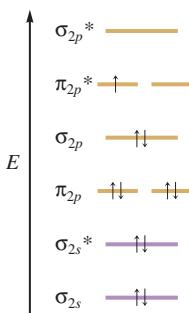
treated in a way very similar to that which we have used so far. Thus we will draw the MO diagram for  $P_2$  analogous to that for  $N_2$ . The only change will be that the molecular orbitals will be formed from  $3s$  and  $3p$  atomic orbitals. The  $P_2$  model has 10 valence electrons (5 from each phosphorus atom). The resulting molecular orbital diagram is



The molecule has a bond order of 3 and is expected to be diamagnetic.

*See Exercises 9.37 through 9.42.*

## 9.4 Bonding in Heteronuclear Diatomic Molecules



**FIGURE 9.41**

The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for  $N_2$ . The bond order is 2.5.

In this section we will deal with selected examples of **heteronuclear** (different atoms) **diatomic molecules**. A special case involves molecules containing atoms adjacent to each other in the periodic table. Since the atoms involved in such a molecule are so similar, we can use the molecular orbital diagram for homonuclear molecules. For example, we can predict the bond order and magnetism of nitric oxide (NO) by placing its 11 valence electrons (5 from nitrogen and 6 from oxygen) in the molecular orbital energy-level diagram shown in Fig. 9.41. The molecule should be paramagnetic and has a bond order of

$$\frac{8 - 3}{2} = 2.5$$

Experimentally, nitric oxide is indeed found to be paramagnetic. Notice that this odd-electron molecule is described very naturally by the MO model. In contrast, the localized electron model, in the simple form used in this text, cannot be used readily to treat such molecules.

### Sample Exercise 9.8

### The Molecular Orbital Model III

Use the molecular orbital model to predict the magnetism and bond order of the  $NO^+$  and  $CN^-$  ions.

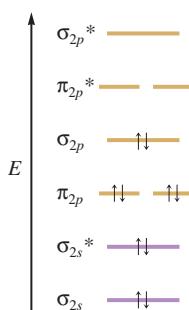
#### Solution

The  $NO^+$  ion has 10 valence electrons ( $5 + 6 - 1$ ). The  $CN^-$  ion also has 10 valence electrons ( $4 + 5 + 1$ ). Both ions are therefore diamagnetic and have a bond order derived from the equation

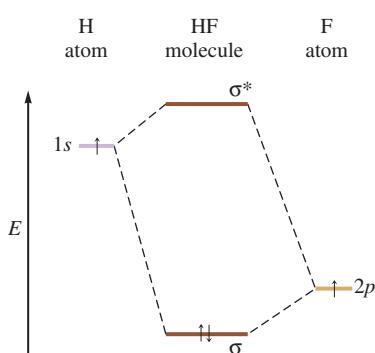
$$\frac{8 - 2}{2} = 3$$

The molecular orbital diagram for these two ions is the same (see Fig. 9.42).

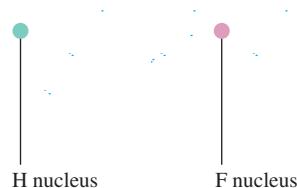
*See Exercises 9.43 and 9.44.*

**FIGURE 9.42**

The molecular orbital energy-level diagram for both the  $\text{NO}^+$  and  $\text{CN}^-$  ions.

**FIGURE 9.43**

A partial molecular orbital energy-level diagram for the HF molecule.

**FIGURE 9.44**

The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

When the two atoms of a diatomic molecule are very different, the energy-level diagram for homonuclear molecules can no longer be used. A new diagram must be devised for each molecule. We will illustrate this case by considering the hydrogen fluoride (HF) molecule. The electron configurations of the hydrogen and fluorine atoms are  $1s^1$  and  $1s^2 2s^2 2p^5$ , respectively. To keep things as simple as possible, we will assume that fluorine uses only one of its  $2p$  orbitals to bond to hydrogen. Thus the molecular orbitals for HF will be composed of fluorine  $2p$  and hydrogen  $1s$  orbitals. Figure 9.43 gives the partial molecular orbital energy-level diagram for HF, focusing only on the orbitals involved in the bonding. We are assuming that fluorine's other valence electrons remain localized on the fluorine. The  $2p$  orbital of fluorine is shown at a lower energy than the  $1s$  orbital of hydrogen on the diagram because fluorine binds its valence electrons more tightly. Thus the  $2p$  electron on a free fluorine atom is at lower energy than the  $1s$  electron on a free hydrogen atom. The diagram predicts that the HF molecule should be stable because both electrons are lowered in energy relative to their energy in the free hydrogen and fluorine atoms, which is the driving force for bond formation.

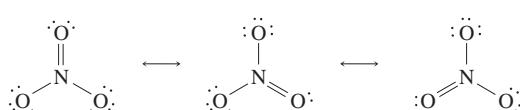
Because the fluorine  $2p$  orbital is lower in energy than the hydrogen  $1s$  orbital, the electrons prefer to be closer to the fluorine atom. That is, the  $\sigma$  molecular orbital containing the bonding electron pair shows greater electron probability close to the fluorine (see Fig. 9.44). The electron pair is not shared equally. This causes the fluorine atom to have a slight excess of negative charge and leaves the hydrogen atom partially positive. This is *exactly* the bond polarity observed for HF. Thus the molecular orbital model accounts in a straightforward way for the different electronegativities of hydrogen and fluorine and the resulting unequal charge distribution.

## 9.5 Combining the Localized Electron and Molecular Orbital Models

One of the main difficulties with the localized electron model is its assumption that electrons are localized. This problem is most apparent with molecules for which several valid Lewis structures can be drawn. It is clear that none of these structures taken alone adequately describes the electronic structure of the molecule. The concept of resonance was invented to solve this problem. However, even with resonance included, the localized electron model does not describe molecules and ions such as  $\text{O}_3$  and  $\text{NO}_3^-$  in a very satisfying way.

It would seem that the ideal bonding model would be one with the simplicity of the localized electron model but with the delocalization characteristic of the molecular orbital model. We can achieve this by combining the two models to describe molecules that require resonance. Note that for species such as  $\text{O}_3$  and  $\text{NO}_3^-$  the double bond changes position in the resonance structures (see Fig. 9.45). Since a double bond involves one  $\sigma$  and one  $\pi$  bond, there is a  $\sigma$  bond between all bound atoms in each resonance structure. It is really the  $\pi$  bond that has different locations in the various resonance structures.

Therefore we conclude that the  $\sigma$  bonds in a molecule can be described as being localized with no apparent problems. It is the  $\pi$  bonding that must be treated as being

**FIGURE 9.45**

The resonance structures for  $\text{O}_3$  and  $\text{NO}_3^-$ . Note that it is the double bond that occupies various positions in the resonance structures.

## Chapter Nine Covalent Bonding: Orbitals

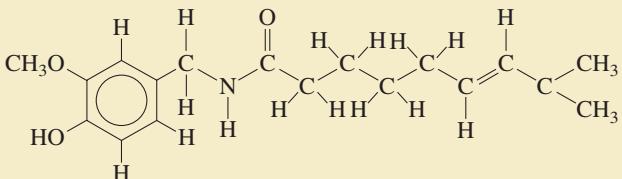


# CHEMICAL IMPACT

## What's Hot?

**O**ne of the best things about New Mexico is the food. Authentic New Mexican cuisine employs liberal amounts of green and red chilies—often called chili peppers. Chilies apparently originated in parts of South America and were spread north by birds. When Columbus came to North America, which he originally thought was India, he observed the natives using chilies for spicing foods. When he took chilies back to Europe, Columbus mistakenly called them peppers and the name stuck.

The spicy payload of chilies is delivered mainly by the chemical capsaicin, which has the following structure:



Capsaicin was isolated as a pure substance by L. T. Thresh in 1846. Since then substituted capsaicins have also been found in chilies. The spicy power of chilies derives mostly from capsaicin and dihydrocapsaicin.

The man best known for explaining the “heat” of chilies is Wilbur Scoville, who defined the Scoville unit for measuring chili power. He arbitrarily established the hotness of pure capsaicin as 16 million. On this scale a typical green or red chili has a rating of about 2500 Scoville units. You may have had an encounter with habanero chilies that left you looking for a firehose to put out the blaze in your mouth—habaneros have a Scoville rating of about 500,000!

Capsaicin has found many uses outside of cooking. It is used in pepper sprays and repellent sprays for many garden pests, although birds are unaffected by capsaicin. Capsaicin also stimulates the body's circulation and causes pain receptors to release endorphins, similar to the effect produced by intense exercise. Instead of jogging you may want to sit on the couch eating chilies. Either way you are going to sweat.

In molecules that require resonance, it is the  $\pi$  bonding that is most clearly delocalized.

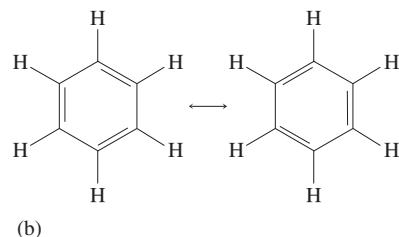
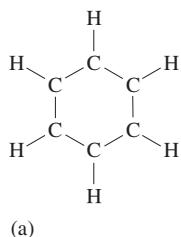
delocalized. Thus, for molecules that require resonance, we will use the localized electron model to describe the  $\sigma$  bonding and the molecular orbital model to describe the  $\pi$  bonding. This allows us to keep the bonding model as simple as possible and yet give a more physically accurate description of such molecules.

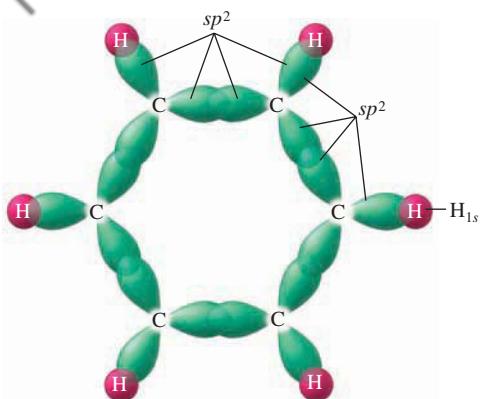
We will illustrate the general method by considering the bonding in benzene, an important industrial chemical that must be handled carefully because it is a known carcinogen. The benzene molecule ( $C_6H_6$ ) consists of a planar hexagon of carbon atoms with one hydrogen atom bound to each carbon atom, as shown in Fig. 9.46(a). In the molecule all six C—C bonds are known to be equivalent. To explain this fact, the localized electron model must invoke resonance [see Fig. 9.46(b)].

A better description of the bonding in benzene results when we use a combination of the models, as described above. In this description it is assumed that the  $\sigma$  bonds of carbon involve  $sp^2$  orbitals, as shown in Fig. 9.47. These  $\sigma$  bonds are all centered in the plane of the molecule.

## FIGURE 9.46

(a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon; all atoms are in the same plane. All the C—C bonds are known to be equivalent. (b) Two of the resonance structures for the benzene molecule. The localized electron model must invoke resonance to account for the six equal C—C bonds.



**FIGURE 9.47**

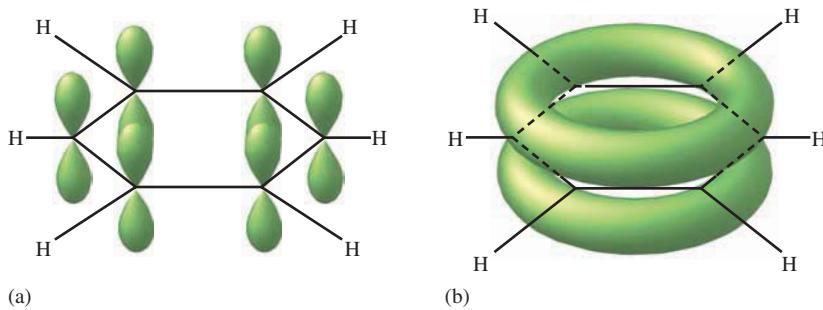
The  $\sigma$  bonding system in the benzene molecule.

Since each carbon atom is  $sp^2$  hybridized, a  $p$  orbital perpendicular to the plane of the ring remains on each carbon atom. These six  $p$  orbitals can be used to form  $\pi$  molecular orbitals, as shown in Fig. 9.48(a). The electrons in the resulting  $\pi$  molecular orbitals are delocalized above and below the plane of the ring, as shown in Fig. 9.48(b). This gives six equivalent C—C bonds, as required by the known structure of the benzene molecule. The benzene structure is often written as



to indicate the **delocalized  $\pi$  bonding** in the molecule.

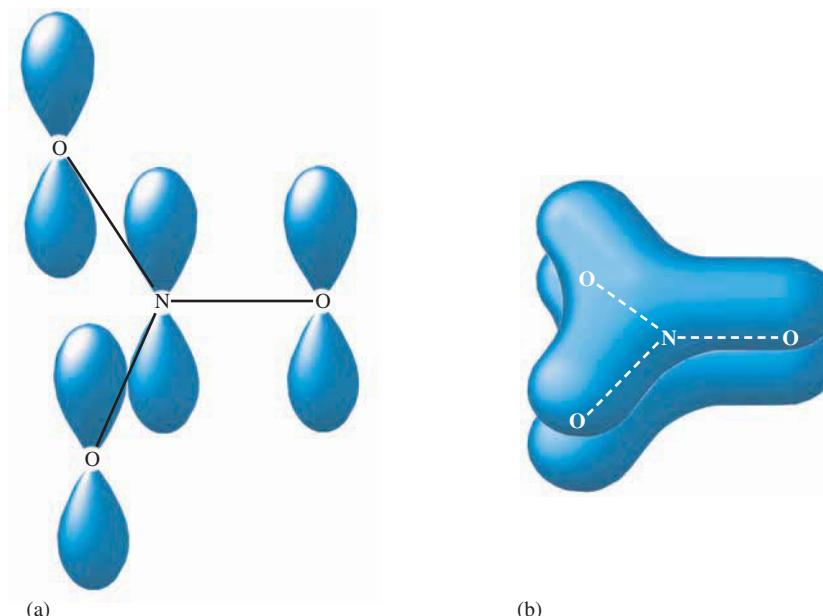
Very similar treatments can be applied to other planar molecules for which resonance is required by the localized electron model. For example, the  $\text{NO}_3^-$  ion can be described using the  $\pi$  molecular orbital system shown in Fig. 9.49. In this molecule each atom is assumed to be  $sp^2$  hybridized, which leaves one  $p$  orbital on each atom perpendicular to the plane of the ion. These  $p$  orbitals can combine to form the  $\pi$  molecular orbital system.

**FIGURE 9.48**

(a) The  $\pi$  molecular orbital system in benzene is formed by combining the six  $p$  orbitals from the six  $sp^2$  hybridized carbon atoms. (b) The electrons in the resulting  $\pi$  molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is represented here.



Visualization: Pi Bonding in the Nitrate Ion

**FIGURE 9.49**

(a) The  $p$  orbitals used to form the  $\pi$  bonding system in the  $\text{NO}_3^-$  ion. (b) A representation of the delocalization of the electrons in the  $\pi$  molecular orbital system of the  $\text{NO}_3^-$  ion.

## Key Terms

### Section 9.1

hybridization  
 $sp^3$  hybridization  
 hybrid orbitals  
 $sp^2$  hybridization  
 sigma ( $\sigma$ ) bond  
 pi ( $\pi$ ) bond  
 $sp$  hybridization  
 $dsp^3$  hybridization  
 $d^2sp^3$  hybridization

### Section 9.2

molecular orbital model  
 molecular orbital (MO)  
 sigma ( $\sigma$ ) molecular orbital  
 bonding molecular orbital  
 antibonding molecular orbital  
 bond order

### Section 9.3

pi ( $\pi$ ) molecular orbital  
 paramagnetism  
 diamagnetism

### Section 9.4

heteronuclear diatomic molecule

### Section 9.5

delocalized  $\pi$  bonding

## For Review

### Two widely used bonding models

- Localized electron model
- Molecular orbital model

### Localized electron model

- Molecule is pictured as a group of atoms sharing electron pairs between atomic orbitals
- Hybrid orbitals, which are combinations of the “native” atomic orbitals, are often required to account for the molecular structure
  - Four electron pairs (tetrahedral arrangement) require  $sp^3$  orbitals
  - Three electron pairs (trigonal planar arrangement) require  $sp^2$  orbitals
  - Two electron pairs (linear arrangement) requires  $sp$  orbitals

### Two types of bonds

- Sigma: electrons are shared in the area centered on a line joining the atoms
- Pi: a shared electron pair occupies the space above and below the line joining the atoms

### Molecular orbital model

- A molecule is assumed to be a new entity consisting of positively charged nuclei and electrons
- The electrons in the molecule are contained in molecular orbitals, which in the simplest form of the model are constructed from the atomic orbitals of the constituent atoms
- The model correctly predicts relative bond strength, magnetism, and bond polarity
- It correctly portrays electrons as being delocalized in polyatomic molecules
- The main disadvantage of the model is that it is difficult to apply qualitatively to polyatomic molecules

### Molecular orbitals are classified in two ways: energy and shape

- Energy
  - A bonding MO is lower in energy than the atomic orbitals from which it is constructed. Electrons in this type of MO are lower in energy in the molecule than in the separated atoms and thus favor molecule formation.
  - An antibonding MO is higher in energy than the atomic orbitals from which it is constructed. Electrons in this type of MO are higher in energy in the molecule than in the separated atoms and thus do not favor molecule formation.
- Shape (symmetry)
  - Sigma ( $\sigma$ ) MOs have their electron probability centered on a line passing through the nuclei
  - Pi ( $\pi$ ) MOs have their electron probability concentrated above and below the line connecting the nuclei

### Bond order is an index of bond strength

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

### Molecules that require the concept of resonance in the localized electron model can be more accurately described by combining the localized electron and molecular orbital models

- The  $\sigma$  bonds are localized
- The  $\pi$  bonds are delocalized

### REVIEW QUESTIONS

1. Why do we hybridize atomic orbitals to explain the bonding in covalent compounds? What type of bonds form from hybrid orbitals, sigma or pi? Explain.
2. What hybridization is required for central atoms that have a tetrahedral arrangement of electron pairs? A trigonal planar arrangement of electron pairs? A linear arrangement of electron pairs? How many unhybridized  $p$  atomic orbitals are present when a central atom exhibits tetrahedral geometry? Trigonal planar geometry? Linear geometry? What are the unhybridized  $p$  atomic orbitals used for?
3. Describe the bonding in  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{CO}$ , and  $\text{HCN}$  using the localized electron model.
4. What hybridization is required for central atoms exhibiting trigonal bipyramidal geometry? Octahedral geometry? Describe the bonding of  $\text{PF}_5$ ,  $\text{SF}_4$ ,  $\text{SF}_6$ , and  $\text{IF}_5$  using the localized electron model.
5. Electrons in  $\sigma$  bonding molecular orbitals are most likely to be found in the region between the two bonded atoms. Why does this arrangement favor bonding? In a  $\sigma$  antibonding orbital, where are the electrons most likely to be found in relation to the nuclei in a bond?
6. Show how  $2s$  orbitals combine to form  $\sigma$  bonding and  $\sigma$  antibonding molecular orbitals. Show how  $2p$  orbitals overlap to form  $\sigma$  bonding,  $\pi$  bonding,  $\pi$  antibonding, and  $\sigma$  antibonding molecular orbitals.
7. What are the relationships among bond order, bond energy, and bond length? Which of these can be measured? Distinguish between the terms *paramagnetic* and *diamagnetic*. What type of experiment can be done to determine if a material is paramagnetic?
8. How does molecular orbital theory explain the following observations?
  - a.  $\text{H}_2$  is stable, while  $\text{He}_2$  is unstable.
  - b.  $\text{B}_2$  and  $\text{O}_2$  are paramagnetic, while  $\text{C}_2$ ,  $\text{N}_2$ , and  $\text{F}_2$  are diamagnetic.
  - c.  $\text{N}_2$  has a very large bond energy associated with it.
  - d.  $\text{NO}^+$  is more stable than  $\text{NO}^-$ .
9. Consider the heteronuclear diatomic molecule HF. Explain in detail how molecular orbital theory is applied to describe the bonding in HF.
10. What is delocalized  $\pi$  bonding and what does it explain? Explain the delocalized  $\pi$  bonding system in  $\text{C}_6\text{H}_6$  (benzene) and  $\text{O}_3$  (ozone).

### Active Learning Questions

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

1. What are molecular orbitals? How do they compare with atomic orbitals? Can you tell by the shape of the bonding and antibonding orbitals which is lower in energy? Explain.
2. Explain the difference between the  $\sigma$  and  $\pi$  MOs for homonuclear diatomic molecules. How are bonding and antibonding orbitals different? Why are there two  $\pi$  MOs and one  $\sigma$  MO? Why are the  $\pi$  MOs degenerate?
3. Compare Figs. 9.36 and 9.38. Why are they different? Because  $\text{B}_2$  is known to be paramagnetic, the  $\pi_{2p}$  and  $\sigma_{2p}$  molecular orbitals must be switched from the first prediction. What is the rationale

for this? Why might one expect the  $\sigma_{2p}$  to be lower in energy than the  $\pi_{2p}$ ? Why can't we use diatomic oxygen to help us decide whether the  $\sigma_{2p}$  or  $\pi_{2p}$  is lower in energy?

4. Which of the following would you expect to be more favorable energetically? Explain.
  - a. An  $\text{H}_2$  molecule in which enough energy is added to excite one electron from the bonding to the antibonding MO
  - b. Two separate H atoms
5. Draw the Lewis structure for HCN. Indicate the hybrid orbitals, and draw a picture showing all the bonds between the atoms, labeling each bond as  $\sigma$  or  $\pi$ .
6. Which is the more correct statement: "The methane molecule ( $\text{CH}_4$ ) is a tetrahedral molecule because it is  $sp^3$  hybridized" or "The methane molecule ( $\text{CH}_4$ ) is  $sp^3$  hybridized because it is a tetrahedral molecule"? What, if anything, is the difference between these two statements?

## 418 Chapter Nine Covalent Bonding: Orbitals

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

### Questions

7. In the hybrid orbital model, compare and contrast  $\sigma$  bonds versus  $\pi$  bonds. What orbitals form the  $\sigma$  bonds and what orbitals form the  $\pi$  bonds? Assume the  $z$ -axis is the internuclear axis.
8. In the molecular orbital model, compare and contrast  $\sigma$  versus  $\pi$  bonds. What orbitals form the  $\sigma$  bonds and what orbitals form the  $\pi$  bonds? Assume the  $z$ -axis is the internuclear axis.
9. Why are  $d$  orbitals sometimes used to form hybrid orbitals? Which period of elements does not use  $d$  orbitals for hybridization? If necessary, which  $d$  orbitals ( $3d$ ,  $4d$ ,  $5d$ , or  $6d$ ) would sulfur use to form hybrid orbitals requiring  $d$  atomic orbitals? Answer the same question for arsenic and for iodine.
10. The atoms in a single bond can rotate about the internuclear axis without breaking the bond. The atoms in a double and triple bond cannot rotate about the internuclear axis unless the bond is broken. Why?
11. Compare and contrast bonding versus antibonding molecular orbitals.
12. What modification to the molecular orbital model was made from the experimental evidence that  $B_2$  is paramagnetic?
13. Why does the molecular orbital model do a better job in explaining the bonding in  $NO^-$  and  $NO$  than the hybrid orbital model?
14. The three NO bonds in  $NO_3^-$  are all equivalent in length and strength. How is this explained even though any valid Lewis structure for  $NO_3^-$  has one double bond and two single bonds to nitrogen?

### Exercises

In this section similar exercises are paired.

#### The Localized Electron Model and Hybrid Orbitals

15. Use the localized electron model to describe the bonding in  $H_2O$ .
16. Use the localized electron model to describe the bonding in  $CCl_4$ .
17. Use the localized electron model to describe the bonding in  $H_2CO$  (carbon is the central atom).
18. Use the localized electron model to describe the bonding in  $C_2H_2$  (exists as  $HCCH$ ).
19. The space-filling models of ethane and ethanol are shown below.



Ethane  
( $C_2H_6$ )



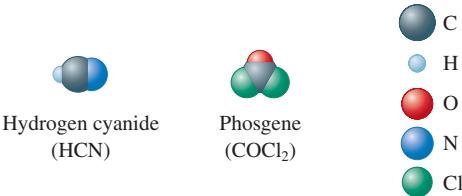
Ethanol  
( $C_2H_5OH$ )



C  
H  
O

Use the localized electron model to describe the bonding in ethane and ethanol.

20. The space-filling models of hydrogen cyanide and phosgene are shown below.

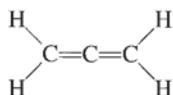


Use the localized electron model to describe the bonding in hydrogen cyanide and phosgene.

21. Give the expected hybridization of the central atom for the molecules or ions in Exercises 67 and 73 from Chapter 8.
22. Give the expected hybridization of the central atom for the molecules or ions in Exercises 68 and 74 from Chapter 8.
23. Give the expected hybridization of the central atom for the molecules or ions in Exercise 71 from Chapter 8.
24. Give the expected hybridization of the central atom for the molecules in Exercise 72 from Chapter 8.
25. Give the expected hybridization of the central atom for the molecules in Exercises 91 and 92 from Chapter 8.
26. Give the expected hybridization of the central atom for the molecules in Exercises 93 and 94 from Chapter 8.
27. For each of the following molecules, write the Lewis structure(s), predict the molecular structure (including bond angles), give the expected hybrid orbitals on the central atom, and predict the overall polarity.
  - a.  $CF_4$
  - e.  $BeH_2$
  - i.  $KrF_4$
  - b.  $NF_3$
  - f.  $TeF_4$
  - j.  $SeF_6$
  - c.  $OF_2$
  - g.  $AsF_5$
  - k.  $IF_5$
  - d.  $BF_3$
  - h.  $KrF_2$
  - l.  $IF_3$
28. For each of the following molecules or ions that contain sulfur, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybrid orbitals for sulfur.
  - a.  $SO_2$
  - b.  $SO_3$
  - c.  $S_2O_3^{2-}$
  - d.  $S_2O_8^{2-}$
  - e.  $SO_3^{2-}$
  - f.  $SO_4^{2-}$
  - g.  $SF_2$
  - h.  $SF_4$
  - i.  $SF_6$
  - j.  $F_3S-SF$
  - k.  $SF_5^+$

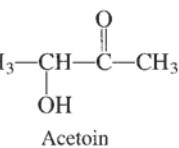
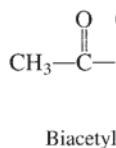
29. Why must all six atoms in  $C_2H_4$  be in the same plane?

30. The allene molecule has the following Lewis structure:



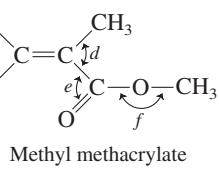
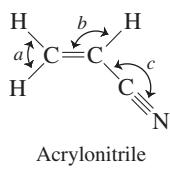
Are all four hydrogen atoms in the same plane? If not, what is their spatial relationship? Explain.

31. Biacetyl and acetoin are added to margarine to make it taste more like butter.



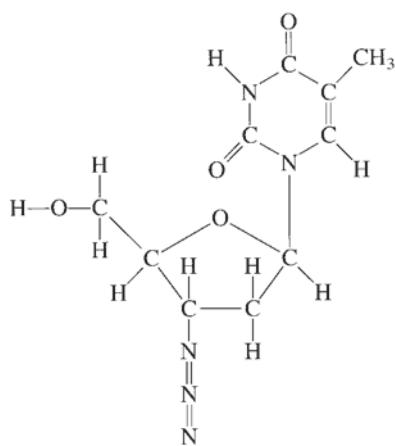
Complete the Lewis structures, predict values for all C—C—O bond angles, and give the hybridization of the carbon atoms in these two compounds. Are the four carbons and two oxygens in biacetyl in the same plane? How many  $\sigma$  bonds and how many  $\pi$  bonds are there in biacetyl and acetoin?

32. Many important compounds in the chemical industry are derivatives of ethylene ( $C_2H_4$ ). Two of them are acrylonitrile and methyl methacrylate.



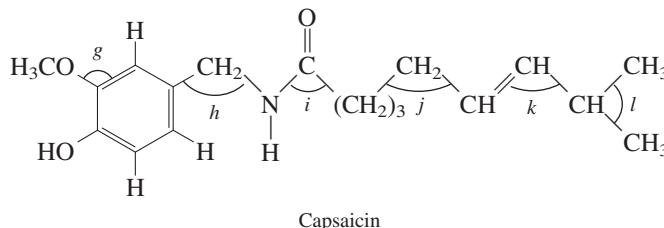
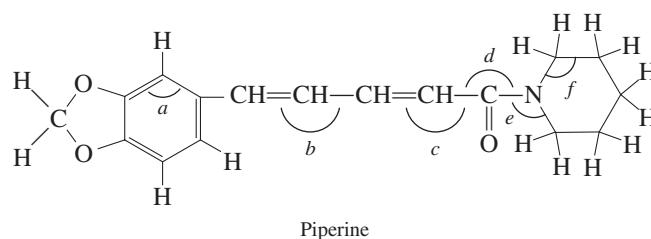
Complete the Lewis structures, showing all lone pairs. Give approximate values for bond angles *a* through *f*. Give the hybridization of all carbon atoms. In acrylonitrile, how many of the atoms in the molecule lie in the same plane? How many  $\sigma$  bonds and how many  $\pi$  bonds are there in methyl methacrylate and acrylonitrile?

33. One of the first drugs to be approved for use in treatment of acquired immune deficiency syndrome (AIDS) was azidothymidine (AZT). Complete the Lewis structure for AZT.



- How many carbon atoms are  $sp^3$  hybridized?
- How many carbon atoms are  $sp^2$  hybridized?
- Which atom is  $sp$  hybridized?
- How many  $\sigma$  bonds are in the molecule?
- How many  $\pi$  bonds are in the molecule?
- What is the N—N—N bond angle in the azide ( $-\text{N}_3^-$ ) group?
- What is the H—O—C bond angle in the side group attached to the five-membered ring?
- What is the hybridization of the oxygen atom in the  $-\text{CH}_2\text{OH}$  group?

34. Hot and spicy foods contain molecules that stimulate pain-detecting nerve endings. Two such molecules are piperine and capsaicin:



Piperine is the active compound in white and black pepper, and capsaicin is the active compound in chili peppers. The ring structures in piperine and capsaicin are shorthand notation. Each point where lines meet represents a carbon atom.

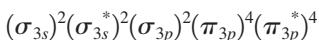
- Complete the Lewis structure for piperine and capsaicin showing all lone pairs of electrons.
- How many carbon atoms are  $sp$ ,  $sp^2$ , and  $sp^3$  hybridized in each molecule?
- Which hybrid orbitals are used by the nitrogen atoms in each molecule?
- Give approximate values for the bond angles marked *a* through *l* in the above structures.

### The Molecular Orbital Model

- Which of the following are predicted by the molecular orbital model to be stable diatomic species?
  - $\text{H}_2^+$ ,  $\text{H}_2$ ,  $\text{H}_2^-$ ,  $\text{H}_2^{2-}$
  - $\text{He}_2^{2+}$ ,  $\text{He}_2^+$ ,  $\text{He}_2$
- Which of the following are predicted by the molecular orbital model to be stable diatomic species?
  - $\text{N}_2^{2-}$ ,  $\text{O}_2^{2-}$ ,  $\text{F}_2^{2-}$
  - $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{Ne}_2$
- Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?
  - $\text{Li}_2$
  - $\text{C}_2$
  - $\text{S}_2$

## 420 Chapter Nine Covalent Bonding: Orbitals

**38.** Consider the following electron configuration:



Give four species that, in theory, would have this electron configuration

**39.** Using molecular orbital theory, explain why the removal of one electron in O<sub>2</sub> strengthens bonding, while the removal of one electron in N<sub>2</sub> weakens bonding.

**40.** Using the molecular orbital model to describe the bonding in F<sub>2</sub><sup>+</sup>, F<sub>2</sub>, and F<sub>2</sub><sup>-</sup>, predict the bond orders and the relative bond lengths for these three species. How many unpaired electrons are present in each species?

**41.** Which charge(s) for the N<sub>2</sub> molecule would give a bond order of 2.5?

**42.** A Lewis structure obeying the octet rule can be drawn for O<sub>2</sub> as follows:



Use the molecular orbital energy-level diagram for O<sub>2</sub> to show that the above Lewis structure corresponds to an excited state.

**43.** Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic? Place the species in order of increasing bond length and bond energy.

- a. CO    b. CO<sup>+</sup>    c. CO<sup>2+</sup>

**44.** Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic? Place the species in order of increasing bond length and bond energy.

- a. NO<sup>+</sup>    b. NO    c. NO<sup>-</sup>

**45.** In which of the following diatomic molecules would the bond strength be expected to weaken as an electron is removed to form the positive charged ion?

- a. H<sub>2</sub>    c. C<sub>2</sub><sup>2-</sup>  
b. B<sub>2</sub>    d. OF

**46.** In terms of the molecular orbital model, which species in each of the following two pairs will most likely be the one to gain an electron? Explain.

- CN or NO  
O<sub>2</sub><sup>2+</sup> or N<sub>2</sub><sup>2+</sup>

**47.** Show how two 2p atomic orbitals can combine to form a  $\sigma$  or a  $\pi$  molecular orbital.

**48.** Show how a hydrogen 1s atomic orbital and a fluorine 2p atomic orbital overlap to form bonding and antibonding molecular orbitals in the hydrogen fluoride molecule. Are these molecular orbitals  $\sigma$  or  $\pi$  molecular orbitals?

**49.** Use Figs. 9.43 and 9.44 to answer the following questions.

- a. Would the bonding molecular orbital in HF place greater electron density near the H or the F atom? Why?
- b. Would the bonding molecular orbital have greater fluorine 2p character, greater hydrogen 1s character, or an equal contribution from both? Why?

**c.** Answer the previous two questions for the antibonding molecular orbital in HF.

**50.** The diatomic molecule OH exists in the gas phase. The bond length and bond energy have been measured to be 97.06 pm and 424.7 kJ/mol, respectively. Assume that the OH molecule is analogous to the HF molecule discussed in the chapter and that molecular orbitals result from the overlap of a lower-energy  $p_z$  orbital from oxygen with the higher-energy 1s orbital of hydrogen (the O—H bond lies along the z-axis).

- a. Which of the two molecular orbitals will have the greater hydrogen 1s character?
- b. Can the  $2p_x$  orbital of oxygen form molecular orbitals with the 1s orbital of hydrogen? Explain.
- c. Knowing that only the 2p orbitals of oxygen will interact significantly with the 1s orbital of hydrogen, complete the molecular orbital energy-level diagram for OH. Place the correct number of electrons in the energy levels.
- d. Estimate the bond order for OH.
- e. Predict whether the bond order of OH<sup>+</sup> will be greater than, less than, or the same as that of OH. Explain.

**51.** Describe the bonding in the O<sub>3</sub> molecule and the NO<sub>2</sub><sup>-</sup> ion using the localized electron model. How would the molecular orbital model describe the  $\pi$  bonding in these two species?

**52.** Describe the bonding in the CO<sub>3</sub><sup>2-</sup> ion using the localized electron model. How would the molecular orbital model describe the  $\pi$  bonding in this species?

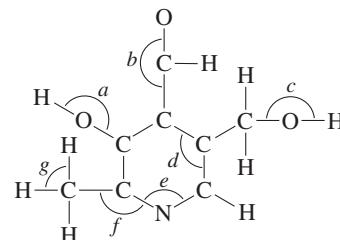
### Additional Exercises

**53.** Draw the Lewis structures, predict the molecular structures, and describe the bonding (in terms of the hybrid orbitals for the central atom) for the following.

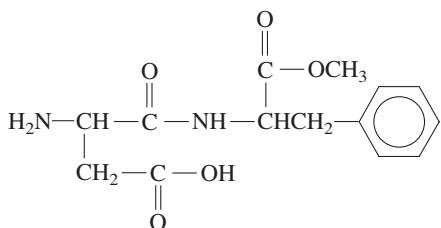
- a. XeO<sub>3</sub>    d. XeOF<sub>2</sub>
- b. XeO<sub>4</sub>    e. XeO<sub>3</sub>F<sub>2</sub>
- c. XeOF<sub>4</sub>

**54.** FClO<sub>2</sub> and F<sub>3</sub>ClO can both gain a fluoride ion to form stable anions. F<sub>3</sub>ClO and F<sub>3</sub>ClO<sub>2</sub> will both lose a fluoride ion to form stable cations. Draw the Lewis structures and describe the hybrid orbitals used by chlorine in these ions.

**55.** Vitamin B<sub>6</sub> is an organic compound whose deficiency in the human body can cause apathy, irritability, and an increased susceptibility to infections. Below is an incomplete Lewis structure for vitamin B<sub>6</sub>. Complete the Lewis structure and answer the following questions. Hint: Vitamin B<sub>6</sub> can be classified as an organic compound (a compound based on carbon atoms). The majority of Lewis structures for simple organic compounds have all atoms with a formal charge of zero. Therefore, add lone pairs and multiple bonds to the structure below to give each atom a formal charge of zero.

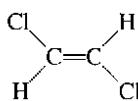


- a. How many  $\sigma$  bonds and  $\pi$  bonds exist in vitamin B<sub>6</sub>?  
 b. Give approximate values for the bond angles marked *a* through *g* in the structure.  
 c. How many carbon atoms are  $sp^2$  hybridized?  
 d. How many carbon, oxygen, and nitrogen atoms are  $sp^3$  hybridized?  
 e. Does vitamin B<sub>6</sub> exhibit delocalized  $\pi$  bonding? Explain.
- 56.** Aspartame is an artificial sweetener marketed under the name Nutra-Sweet. A partial Lewis structure for aspartame is shown below.

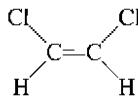


Note that the six-sided ring is shorthand notation for a benzene ring ( $-C_6H_5$ ). Benzene is discussed in Section 9.5. Complete the Lewis structure for aspartame. How many C and N atoms exhibit  $sp^2$  hybridization? How many C and O atoms exhibit  $sp^3$  hybridization? How many  $\sigma$  and  $\pi$  bonds are in aspartame? Aspartame is an organic compound and the Lewis structure follows the guidelines outlined in Exercise 55.

- 57.** Using bond energies from Table 8.4, estimate the barrier to rotation about a carbon–carbon double bond. To do this, consider what must happen to go from



to



in terms of making and breaking chemical bonds; that is, what must happen in terms of the  $\pi$  bond?

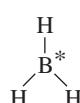
- 58.** The three most stable oxides of carbon are carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), and carbon suboxide (C<sub>3</sub>O<sub>2</sub>). The space-filling models for these three compounds are



For each oxide, draw the Lewis structure, predict the molecular structure, and describe the bonding (in terms of the hybrid orbitals for the carbon atoms).

- 59.** Complete the Lewis structures of the following molecules. Predict the molecular structure, polarity, bond angles, and hybrid orbitals used by the atoms marked by asterisks for each molecule.

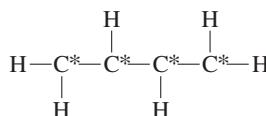
- a. BH<sub>3</sub>



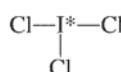
- b. N<sub>2</sub>F<sub>2</sub>



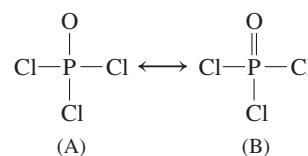
- c. C<sub>4</sub>H<sub>6</sub>



- d. ICl<sub>3</sub>



- 60.** Complete the following resonance structures for POCl<sub>3</sub>.



- a. Would you predict the same molecular structure from each resonance structure?  
 b. What is the hybridization of P in each structure?  
 c. What orbitals can the P atom use to form the  $\pi$  bond in structure B?  
 d. Which resonance structure would be favored on the basis of formal charges?

- 61.** The N<sub>2</sub>O molecule is linear and polar.

- a. On the basis of this experimental evidence, which arrangement, NNO or NON, is correct? Explain your answer.  
 b. On the basis of your answer to part a, write the Lewis structure of N<sub>2</sub>O (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.  
 c. How would the multiple bonding in :N≡N— $\ddot{\text{O}}$ : be described in terms of orbitals?

- 62.** Describe the bonding in NO<sup>+</sup>, NO<sup>-</sup>, and NO using both the localized electron and molecular orbital models. Account for any discrepancies between the two models.

- 63.** Describe the bonding in the first excited state of N<sub>2</sub> (the one closest in energy to the ground state) using the molecular orbital model. What differences do you expect in the properties of the molecule in the ground state as compared to the first excited state? (An excited state of a molecule corresponds to an electron arrangement other than that giving the lowest possible energy.)

- 64.** Acetylene (C<sub>2</sub>H<sub>2</sub>) can be produced from the reaction of calcium carbide (CaC<sub>2</sub>) with water. Use both the localized electron and molecular orbital models to describe the bonding in the acetylide anion (C<sub>2</sub><sup>2-</sup>).

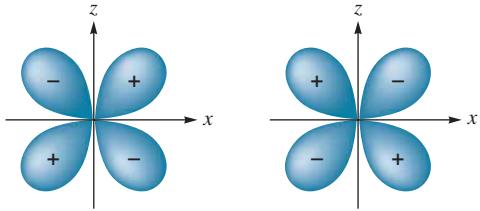
- 65.** Using an MO energy-level diagram, would you expect F<sub>2</sub> to have a lower or higher first ionization energy than atomic fluorine? Why?

- 66.** Show how a  $d_{xz}$  atomic orbital and a  $p_z$  atomic orbital combine to form a bonding molecular orbital. Assume the  $x$ -axis is the

## 422 Chapter Nine Covalent Bonding: Orbitals

internuclear axis. Is a  $\sigma$  or a  $\pi$  molecular orbital formed? Explain.

67. What type of molecular orbital would result from the in phase combination of two  $d_{xz}$  atomic orbitals shown below? Assume the  $x$ -axis is the internuclear axis.

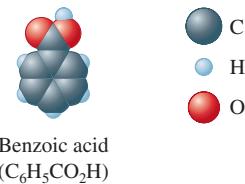


68. Consider three molecules: A, B, and C. Molecule A has a hybridization of  $sp^3$ . Molecule B has two more effective pairs (electron pairs around the central atom) than molecule A. Molecule C consists of two  $\sigma$  bonds and two  $\pi$  bonds. Give the molecular structure, hybridization, bond angles, and an example for each molecule.

### Challenge Problems

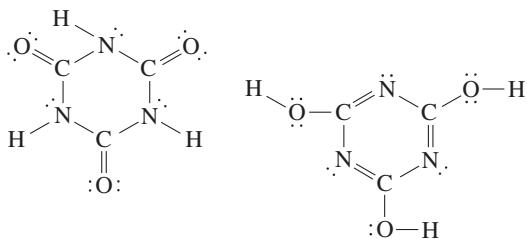
69. Consider your Lewis structure for the computer-generated model of caffeine shown in Exercise 130 of Chapter 8. How many C and N atoms are  $sp^2$  hybridized in your Lewis structure for caffeine? How many C and N atoms are  $sp^3$  hybridized?  $sp$  hybridized? How many  $\sigma$  and  $\pi$  bonds are in your Lewis structure?

70. The space-filling model for benzoic acid is shown below.



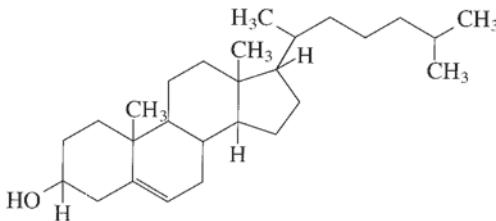
Describe the bonding in benzoic acid using the localized electron model combined with the molecular orbital model.

71. Two structures can be drawn by cyanuric acid:



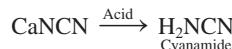
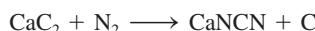
- a. Are these two structures the same molecule? Explain.  
b. Give the hybridization of the carbon and nitrogen atoms in each structure.  
c. Use bond energies (Table 8.4) to predict which form is more stable; that is, which contains the strongest bonds?

72. Cholesterol ( $C_{27}H_{46}O$ ) has the following structure:

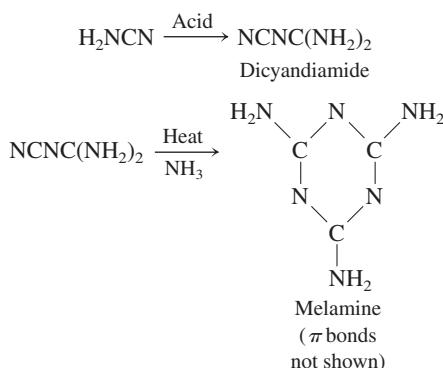


In such shorthand structures, each point where lines meet represents a carbon atom and most H atoms are not shown. Draw the complete structure showing all carbon and hydrogen atoms. (There will be four bonds to each carbon atom.) Indicate which carbon atoms use  $sp^2$  or  $sp^3$  hybrid orbitals. Are all carbon atoms in the same plane, as implied by the structure?

73. Cyanamide ( $H_2NCN$ ), an important industrial chemical, is produced by the following steps:



Calcium cyanamide ( $CaNCN$ ) is used as a direct-application fertilizer, weed killer, and cotton defoliant. It is also used to make cyanamide, dicyandiamide, and melamine plastics:

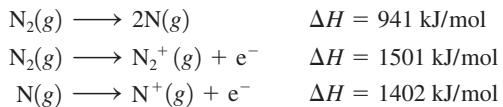


- a. Write Lewis structures for  $NCN^{2-}$ ,  $H_2NCN$ , dicyandiamide, and melamine, including resonance structures where appropriate.  
b. Give the hybridization of the C and N atoms in each species.  
c. How many  $\sigma$  bonds and how many  $\pi$  bonds are in each species?  
d. Is the ring in melamine planar?  
e. There are three different C—N bond distances in dicyandiamide,  $NCNC(NH_2)_2$ , and the molecule is nonlinear. Of all the resonance structures you drew for this molecule, predict which should be the most important.

74. In Exercise 75 in Chapter 8, the Lewis structures for benzene ( $C_6H_6$ ) were drawn. Using one of the Lewis structures, estimate  $\Delta H_f^\circ$  for  $C_6H_6(g)$  using bond energies and given that the standard enthalpy of formation of  $C(g)$  is 717 kJ/mol. The experimental  $\Delta H_f^\circ$  value of  $C_6H_6(g)$  is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated  $\Delta H_f^\circ$  value for  $C_6H_6(g)$ .

**75.** A flask containing gaseous N<sub>2</sub> is irradiated with 25-nm light.

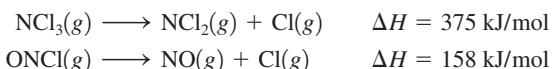
- a. Using the following information, indicate what species can form in the flask during irradiation.



- b. What range of wavelengths will produce atomic nitrogen in the flask but will not produce any ions?
- c. Explain why the first ionization energy of N<sub>2</sub> (1501 kJ/mol) is greater than the first ionization energy of atomic nitrogen (1402 kJ/mol).

**76.** As compared with CO and O<sub>2</sub>, CS and S<sub>2</sub> are very unstable molecules. Give an explanation based on the relative abilities of the sulfur and oxygen atoms to form  $\pi$  bonds.

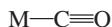
**77.** Values of measured bond energies may vary greatly depending on the molecule studied. Consider the following reactions:



Rationalize the difference in the values of  $\Delta H$  for these reactions, even though each reaction appears to involve only the breaking of one N—Cl bond. (*Hint:* Consider the bond order of the NO bond in ONCl and in NO.)

**78.** Use the MO model to explain the bonding in BeH<sub>2</sub>. When constructing the MO energy-level diagram, assume that the Be's 1s electrons are not involved in bond formation.

**79.** Carbon monoxide (CO) forms bonds to a variety of metals and metal ions. Its ability to bond to iron in hemoglobin is the reason that CO is so toxic. The bond carbon monoxide forms to metals is through the carbon atom:



- a. On the basis of electronegativities, would you expect the carbon atom or the oxygen atom to form bonds to metals?
- b. Assign formal charges to the atoms in CO. Which atom would you expect to bond to a metal on this basis?
- c. In the MO model, bonding MOs place more electron density near the more electronegative atom. (See the HF molecule, Figs. 9.43 and 9.44.) Antibonding MOs place more electron density near the less electronegative atom in the diatomic molecule. Use the MO model to predict which atom of carbon monoxide should form bonds to metals.

**80.** Arrange the following from lowest to highest ionization energy: O, O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>+</sup>. Explain your answer.

**81.** Use the MO model to determine which of the following has the smallest ionization energy: N<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub><sup>2-</sup>, N<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>+</sup>. Explain your answer.

**82.** Given that the ionization energy of F<sub>2</sub><sup>-</sup> is 290 kJ, do the following:

- a. Calculate the bond energy of F<sub>2</sub><sup>-</sup>. You will need to look up the bond energy of F<sub>2</sub> and ionization energy of F<sup>-</sup>.
- b. Explain the difference in bond energy between F<sub>2</sub><sup>-</sup> and F<sub>2</sub> using MO theory.

## Integrative Problems

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

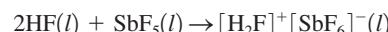
**83.** As the head engineer of your starship in charge of the warp drive, you notice that the supply of dilithium is critically low. While searching for a replacement fuel, you discover some diboron, B<sub>2</sub>.

- a. What is the bond order in Li<sub>2</sub> and B<sub>2</sub>?
- b. How many electrons must be removed from B<sub>2</sub> to make it isoelectronic with Li<sub>2</sub> so that it might be used in the warp drive?
- c. The reaction to make B<sub>2</sub> isoelectronic with Li<sub>2</sub> is generalized (where  $n$  = number of electrons determined in part b) as follows:



How much energy is needed to ionize 1.5 kg of B<sub>2</sub> to the desired isoelectronic species?

**84.** An unusual category of acids known as superacids, which are defined as any acid stronger than 100% sulfuric acid, can be prepared by seemingly simple reactions similar to the one below. In this example, the reaction of anhydrous HF with SbF<sub>5</sub> produces the superacid [H<sub>2</sub>F]<sup>+[SbF<sub>6</sub>]<sup>-</sup>(l)</sup>



- a. What are the molecular structures of all species in this reaction? What are the hybridizations of the central atoms in each species?

- b. What mass of [H<sub>2</sub>F]<sup>+[SbF<sub>6</sub>]<sup>-</sup> can be prepared when 2.93 mL of anhydrous HF (density = 0.975 g/mL) and 10.0 mL of SbF<sub>5</sub> (density = 3.10 g/mL) are allowed to react?</sup>

**85.** Determine the molecular structure and hybridization of the central atom X in the polyatomic ion XY<sub>3</sub><sup>+</sup> given the following information: A neutral atom of X contains 36 electrons, and the element Y makes an anion with a 1<sup>-</sup> charge, which has the electron configuration 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving by visiting the Online Study Center at [college.hmc.com/PIC/zumdahl7e](http://college.hmc.com/PIC/zumdahl7e).

# 10 Liquids and Solids

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- London Dispersion Forces

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### 10.3 An Introduction to Structures and Types of Solids

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### 10.6 Molecular Solids

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### 10.8 Vapor Pressure and Changes of State

- Vapor Pressure
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### 10.9 Phase Diagrams

- Applications of the Phase Diagram for Water
- The Phase Diagram for Carbon Dioxide



Karst formation in Phang Nga Bay, Thailand at sunset. The Karst is limestone that has eroded into these formations rising out of the sea.

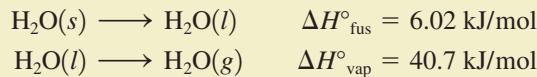
# Y

You have only to think about water to appreciate how different the three states of matter are. Flying, swimming, and ice skating are all done in contact with water in its various forms. Clearly, the arrangements of the water molecules must be significantly different in its gas, liquid, and solid forms.

In Chapter 5 we saw that a gas can be pictured as a substance whose component particles are far apart, are in rapid random motion, and exert relatively small forces on each other. The kinetic molecular model was constructed to account for the ideal behavior that most gases approach at high temperatures and low pressures.

Solids are obviously very different from gases. A gas has low density and high compressibility and completely fills its container. Solids have much greater densities, are compressible only to a very slight extent, and are rigid—a solid maintains its shape irrespective of its container. These properties indicate that the components of a solid are close together and exert large attractive forces on each other.

The properties of liquids lie somewhere between those of solids and gases but not midway between, as can be seen from some of the properties of the three states of water. For example, compare the enthalpy change for the melting of ice at 0°C (the heat of fusion) with that for vaporizing liquid water at 100°C (the heat of vaporization):



These values show a much greater change in structure in going from the liquid to the gaseous state than in going from the solid to the liquid state. This suggests that there are extensive attractive forces among the molecules in liquid water, similar to but not as strong as those in the solid state.

The relative similarity of the liquid and solid states also can be seen in the densities of the three states of water. As shown in Table 10.1, the densities for liquid and solid water are quite close.\* Compressibilities also can be used to explore the relationship among water's states. At 25°C, the density of liquid water changes from 0.99707 g/cm<sup>3</sup> at a pressure of 1 atm to 1.046 g/cm<sup>3</sup> at 1065 atm. Given the large change in pressure, this is a very small variation in the density. Ice also shows little variation in density with increased pressure. On the other hand, at 400°C, the density of gaseous water changes from  $3.26 \times 10^{-4}$  g/cm<sup>3</sup> at 1 atm pressure to 0.157 g/cm<sup>3</sup> at 242 atm—a huge variation.

The conclusion is clear. The liquid and solid states show many similarities and are strikingly different from the gaseous state, as shown schematically in Fig. 10.1. We must bear this in mind as we develop models for the structures of solids and liquids.

We will proceed in our study of liquids and solids by first considering the properties and structures of liquids and solids. Then we will consider the changes in state that occur between solid and liquid, liquid and gas, and solid and gas.



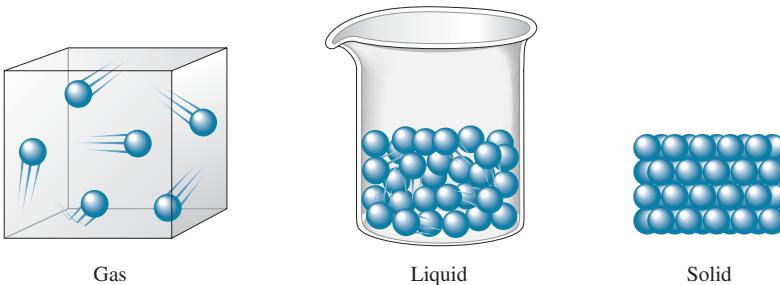
**Visualization: Intermolecular Forces: London Dispersion Forces**

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\*Although the densities of solid and liquid water are quite similar, as is typical for most substances, water is quite unusual in that the density of its solid state is slightly less than that of its liquid state. For most substances, the density of the solid state is slightly greater than that of the liquid state.

**TABLE 10.1 Densities of the Three States of Water**

State	Density (g/cm <sup>3</sup> )
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	$3.26 \times 10^{-4}$

**FIGURE 10.1**  
Schematic representations of the three states of matter.

Intermolecular forces were introduced in Chapter 5 to explain nonideal gas behavior.

Remember that temperature is a measure of the random motions of the particles in a substance.

Dipole–dipole forces are forces that act between polar molecules.



Visualization: Intermolecular Forces: Dipole–Dipole Forces



Visualization: Intermolecular Forces: Hydrogen Bonding Forces

## 10.1 Intermolecular Forces

In Chapters 8 and 9 we saw that atoms can form stable units called *molecules* by sharing electrons. This is called *intramolecular* (within the molecule) *bonding*. In this chapter we consider the properties of the **condensed states** of matter (liquids and solids) and the forces that cause the aggregation of the components of a substance to form a liquid or a solid. These forces may involve covalent or ionic bonding, or they may involve weaker interactions usually called **intermolecular forces** (because they occur between, rather than within, molecules).

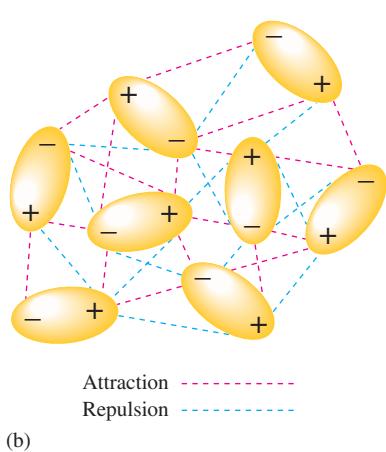
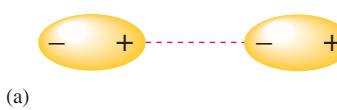
It is important to recognize that when a substance such as water changes from solid to liquid to gas, the *molecules remain intact*. The changes in states are due to changes in the forces *among* the molecules rather than in those *within* the molecules. In ice, as we will see later in this chapter, the molecules are virtually locked in place, although they can vibrate about their positions. If energy is added, the motions of the molecules increase, and they eventually achieve the greater movement and disorder characteristic of liquid water. The ice has melted. As more energy is added, the gaseous state is eventually reached, with the individual molecules far apart and interacting relatively little. However, the gas still consists of water molecules. It would take much energy to overcome the covalent bonds and decompose the water molecules into their component atoms. This can be seen by comparing the energy needed to vaporize 1 mole of liquid water (40.7 kJ) with that needed to break the O—H bonds in 1 mole of water molecules (934 kJ).

### Dipole–Dipole Forces

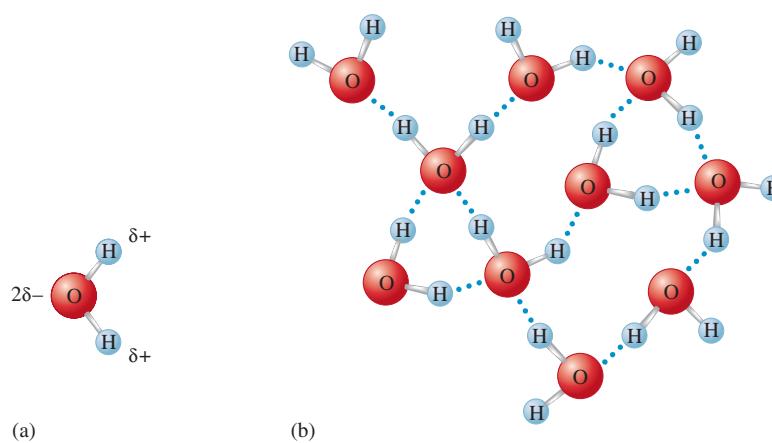
As we saw in Section 8.3, molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge. That is, they exhibit a dipole moment. Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other, as shown in Fig. 10.2(a). This is called a **dipole–dipole attraction**. In a condensed state such as a liquid, where many molecules are in close proximity, the dipoles find the best compromise between attraction and repulsion. That is, the molecules orient themselves to maximize the  $\text{+---}\text{-}$  interactions and to minimize  $\text{+---+}$  and  $\text{-----}$  interactions, as represented in Fig. 10.2(b).

Dipole–dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they rapidly become weaker as the distance between the dipoles increases. At low pressures in the gas phase, where the molecules are far apart, these forces are relatively unimportant.

Particularly strong dipole–dipole forces, however, are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine. Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom. Because dipole–dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding**. Figure 10.3 shows hydrogen bonding among water

**FIGURE 10.2**

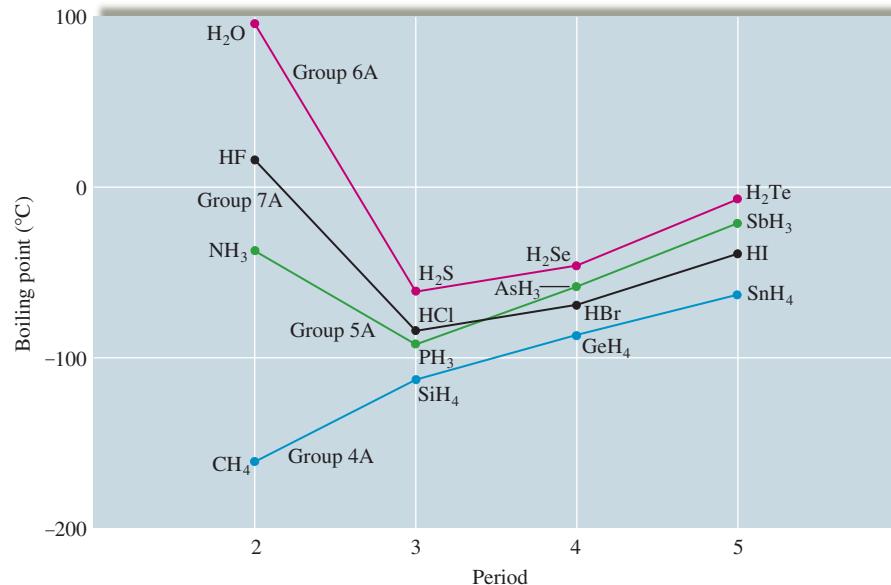
(a) The electrostatic interaction of two polar molecules. (b) The interaction of many dipoles in a condensed state.

**FIGURE 10.3**

(a) The polar water molecule. (b) Hydrogen bonding among water molecules. Note that the small size of the hydrogen atom allows for close interactions.

molecules, which occurs between the partially positive H atoms and the lone pairs on adjacent water molecules.

Hydrogen bonding has a very important effect on physical properties. For example, the boiling points for the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A are given in Fig. 10.4. Note that the nonpolar tetrahedral hydrides of Group 4A show a steady increase in boiling point with molar mass (that is, in going down the group), whereas, for the other groups, the lightest member has an unexpectedly high boiling point. Why? The answer lies in the especially large hydrogen bonding interactions that exist among the smallest molecules with the most polar X—H bonds. These unusually strong hydrogen bonding forces are due primarily to two factors. One factor is the relatively large electronegativity values of the lightest elements in each group, which leads to especially polar X—H bonds. The second factor is the small size of the first element of each group, which allows for the close approach of the dipoles, further strengthening the intermolecular forces. Because the interactions among the molecules containing the lightest elements in Groups 5A and 6A are so strong, an unusually large quantity of energy must be supplied

**FIGURE 10.4**

The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.

Boiling point will be defined precisely in Section 10.8.

to overcome these interactions and separate the molecules to produce the gaseous state. These molecules will remain together in the liquid state even at high temperatures—hence the very high boiling points.

Hydrogen bonding is also important in organic molecules (molecules with a carbon chain backbone). For example, the alcohols methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) have much higher boiling points than would be expected from their molar masses because of the polar O—H bonds in these molecules, which produce hydrogen bonding.

### London Dispersion Forces

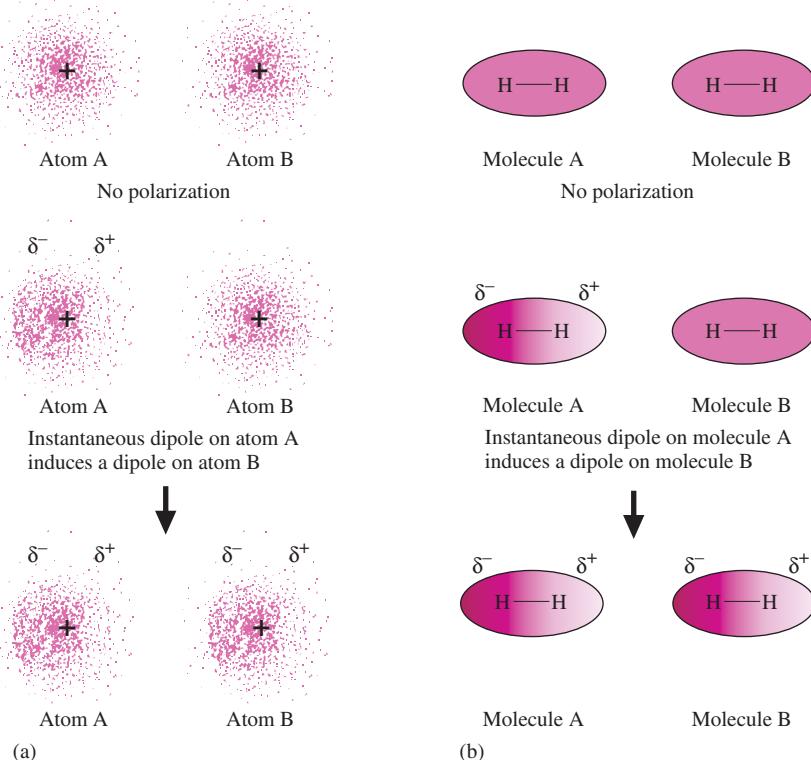
Even molecules without dipole moments must exert forces on each other. We know this because all substances—even the noble gases—exist in the liquid and solid states under certain conditions. The forces that exist among noble gas atoms and nonpolar molecules are called **London dispersion forces**. To understand the origin of these forces, let's consider a pair of noble gas atoms. Although we usually assume that the electrons of an atom are uniformly distributed about the nucleus, this is apparently not true at every instant. As the electrons move about the nucleus, a momentary nonsymmetrical electron distribution can develop that produces a temporary dipolar arrangement of charge. The formation of this temporary dipole can, in turn, affect the electron distribution of a neighboring atom. That is, this *instantaneous dipole* that occurs accidentally in a given atom can then *induce* a similar dipole in a neighboring atom, as represented in Fig. 10.5(a). This phenomenon leads to an interatomic attraction that is relatively weak and short-lived but that can be very significant especially for large atoms (see below). For these interactions to become strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This explains, for instance, why the noble gas elements have such low freezing points (see Table 10.2).

Note from Table 10.2 that the freezing point rises going down the group. The principal cause for this trend is that as the atomic number increases, the number of electrons increases, and there is an increased chance of the occurrence of momentary dipole interactions. We describe this phenomenon using the term *polarizability*, which indicates the

**TABLE 10.2 The Freezing Points of the Group 8A Elements**

Element	Freezing Point (°C)
Helium*	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9

\*Helium is the only element that will not freeze by lowering its temperature at 1 atm. Pressure must be applied to freeze helium.



**FIGURE 10.5**

(a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as  $\text{H}_2$  also can develop instantaneous and induced dipoles.

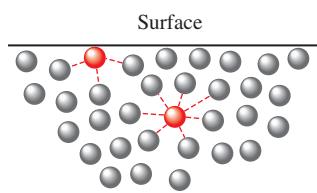
The dispersion forces in molecules with large atoms are quite significant and are often actually more important than dipole-dipole forces.

For a given volume, a sphere has a smaller surface area than any other shape.

**Surface tension:** The resistance of a liquid to an increase in its surface area.

The composition of glass is discussed in Section 10.5.

**Viscosity:** A measure of a liquid's resistance to flow.



**FIGURE 10.6**

A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

ease with which the electron “cloud” of an atom can be distorted to give a dipolar charge distribution. Thus we say that large atoms with many electrons exhibit a higher polarizability than small atoms. This means that the importance of London dispersion forces increases greatly as the size of the atom increases.

These same ideas also apply to nonpolar molecules such as H<sub>2</sub>, CH<sub>4</sub>, CCl<sub>4</sub>, and CO<sub>2</sub> [see Fig. 10.5(b)]. Since none of these molecules has a permanent dipole moment, their principal means of attracting each other is through London dispersion forces.

## 10.2 The Liquid State

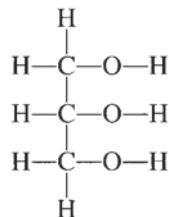
Liquids and liquid solutions are vital to our lives. Of course, water is the most important liquid. Besides being essential to life, water provides a medium for food preparation, for transportation, for cooling in many types of machines and industrial processes, for recreation, for cleaning, and for a myriad of other uses.

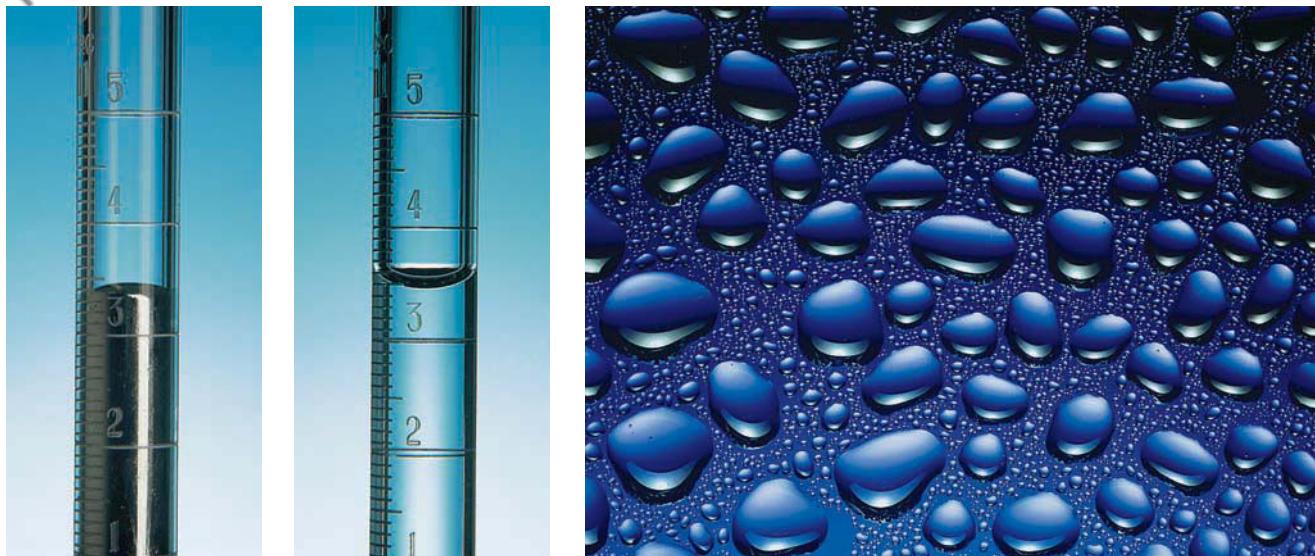
Liquids exhibit many characteristics that help us understand their nature. We have already mentioned their low compressibility, lack of rigidity, and high density compared with gases. Many of the properties of liquids give us direct information about the forces that exist among the particles. For example, when a liquid is poured onto a solid surface, it tends to bead as droplets, a phenomenon that depends on the intermolecular forces. Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject to attractions only from the side and from below (Fig. 10.6). The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a sphere.

To increase a liquid’s surface area, molecules must move from the interior of the liquid to the surface. This requires energy, since some intermolecular forces must be overcome. The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid. As we would expect, liquids with relatively large intermolecular forces, such as those with polar molecules, tend to have relatively high surface tensions.

Polar liquids typically exhibit **capillary action**, the spontaneous rising of a liquid in a narrow tube. Two different types of forces are responsible for this property: *cohesive forces*, the intermolecular forces among the molecules of the liquid, and *adhesive forces*, the forces between the liquid molecules and their container. We have already seen how cohesive forces operate among polar molecules. Adhesive forces occur when a container is made of a substance that has polar bonds. For example, a glass surface contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water. This ability of water to “wet” glass makes it creep up the walls of the tube where the water surface touches the glass. This, however, tends to increase the surface area of the water, which is opposed by the cohesive forces that try to minimize the surface. Thus, because water has both strong cohesive (intermolecular) forces and strong adhesive forces to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter) to a height where the weight of the column of water just balances the water’s tendency to be attracted to the glass surface. The concave shape of the meniscus (see Fig. 10.7) shows that water’s adhesive forces toward the glass are stronger than its cohesive forces. A nonpolar liquid such as mercury (see Fig. 10.7) shows a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.

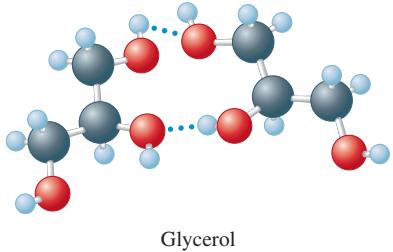
Another property of liquids strongly dependent on intermolecular forces is **viscosity**, a measure of a liquid’s resistance to flow. As might be expected, liquids with large intermolecular forces tend to be highly viscous. For example, glycerol, whose structure is



**FIGURE 10.7**

Nonpolar liquid mercury forms a convex meniscus in a glass tube, whereas polar water forms a concave meniscus.

Beads of water on a waxed car finish. The nonpolar component of the wax causes the water to form approximately spherical droplets.



has an unusually high viscosity due mainly to its high capacity to form hydrogen bonds using its O—H groups (see margin).

Molecular complexity also leads to higher viscosity because very large molecules can become entangled with each other. For example, gasoline, a nonviscous liquid, contains hydrocarbon molecules of the type  $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$ , where  $n$  varies from about 3 to 8. However, grease, which is very viscous, contains much larger hydrocarbon molecules in which  $n$  varies from 20 to 25.

### Structural Model for Liquids

In many respects, the development of a structural model for liquids presents greater challenges than the development of such a model for the other two states of matter. In the gaseous state the particles are so far apart and are moving so rapidly that intermolecular forces are negligible under most circumstances. This means that we can use a relatively simple model for gases. In the solid state, although the intermolecular forces are large, the molecular motions are minimal, and fairly simple models are again possible. The liquid state, however, has both strong intermolecular forces *and* significant molecular motions. Such a situation precludes the use of really simple models for liquids. Recent advances in *spectroscopy*, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids. As a result, our models of liquids are becoming more accurate. As a starting point, a typical liquid might best be viewed as containing a large number of regions where the arrangements of the components are similar to those found in the solid, but with more disorder, and a smaller number of regions where holes are present. The situation is highly dynamic, with rapid fluctuations occurring in both types of regions.

## 10.3 An Introduction to Structures and Types of Solids

There are many ways to classify solids, but the broadest categories are **crystalline solids**, those with a highly regular arrangement of their components, and **amorphous solids**, those with considerable disorder in their structures.

**FIGURE 10.8**

Two crystalline solids: pyrite (left), amethyst (right).

The regular arrangement of the components of a crystalline solid at the microscopic level produces the beautiful, characteristic shapes of crystals, such as those shown in Fig. 10.8. The positions of the components in a crystalline solid are usually represented by a **lattice**, a three-dimensional system of points designating the positions of the components (atoms, ions, or molecules) that make up the substance. The *smallest repeating unit* of the lattice is called the **unit cell**. Thus a particular lattice can be generated by repeating the unit cell in all three dimensions to form the extended structure. Three common unit cells and their lattices are shown in Fig. 10.9. Note from Fig. 10.9 that the extended structure in each case can be viewed as a series of repeating unit cells that share common faces in the interior of the solid.

Although we will concentrate on crystalline solids in this book, there are many important noncrystalline (amorphous) materials. An example is common glass, which is best pictured as a solution in which the components are “frozen in place” before they can achieve an ordered arrangement. Although glass is a solid (it has a rigid shape), a great deal of disorder exists in its structure.

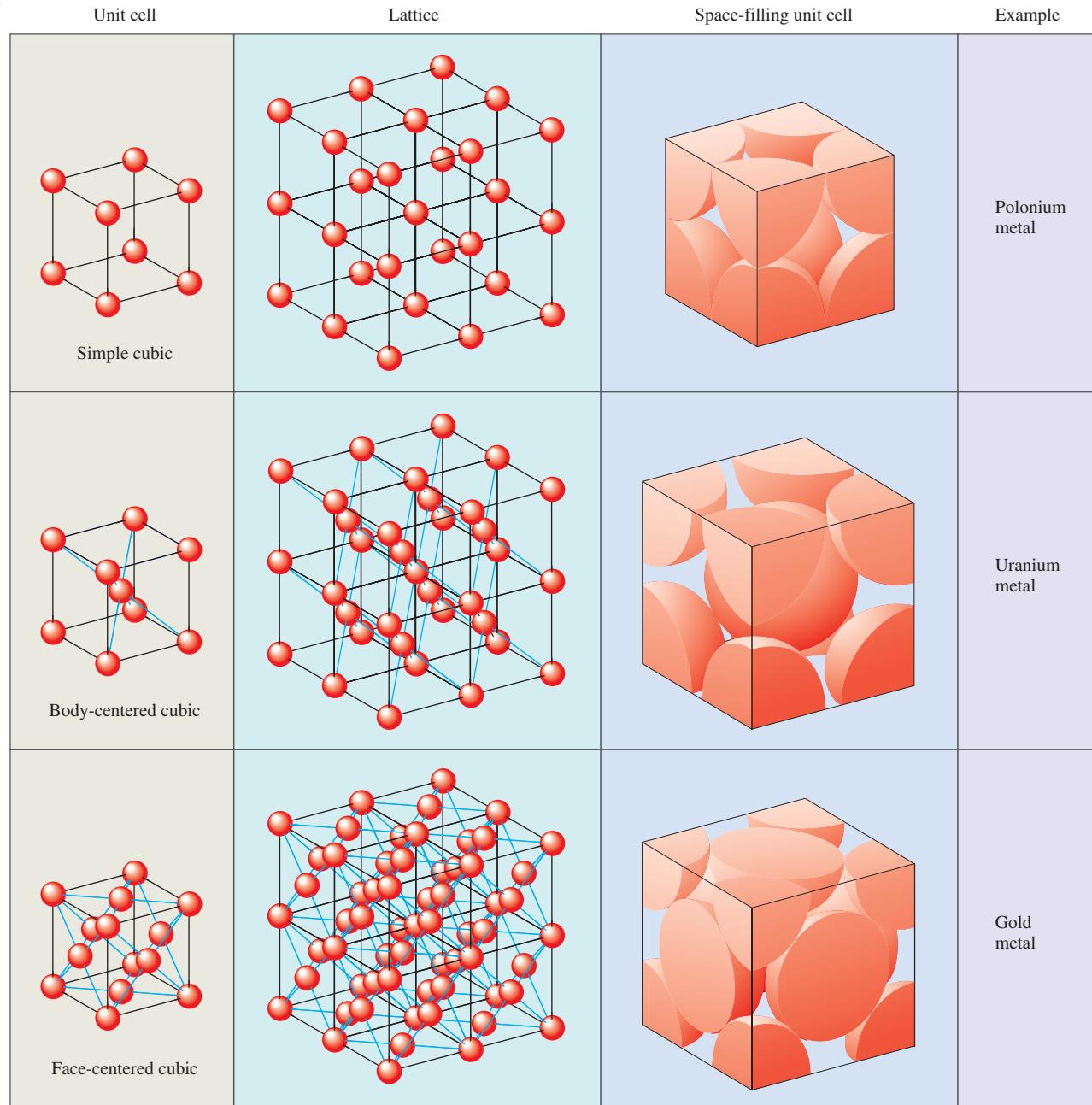
### X-Ray Analysis of Solids

The structures of crystalline solids are most commonly determined by **X-ray diffraction**. Diffraction occurs when beams of light are scattered from a regular array of points in which the spacings between the components are comparable with the wavelength of the light. Diffraction is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase.

When X rays of a single wavelength are directed at a crystal, a diffraction pattern is obtained, as we saw in Fig. 7.5. The light and dark areas on the photographic plate occur because the waves scattered from various atoms may reinforce or cancel each other (see Fig. 10.10). The key to whether the waves reinforce or cancel is the difference in distance traveled by the waves after they strike the atoms. The waves are in phase before they are reflected, so if the difference in distance traveled is an *integral number of wavelengths*, the waves will still be in phase.

Since the distance traveled depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacings. The exact relationship can be worked out using the diagram in Fig. 10.11, which shows two in-phase waves being reflected by atoms in two different layers in a crystal. The extra distance traveled by the lower wave is the sum of the distances  $xy$  and  $yz$ , and the waves will be in phase after reflection if

$$xy + yz = n\lambda \quad (10.1)$$

**FIGURE 10.9**

Three cubic unit cells and the corresponding lattices. Note that only parts of spheres on the corners and faces of the unit cells reside inside the unit cell, as shown by the “cutoff” versions.

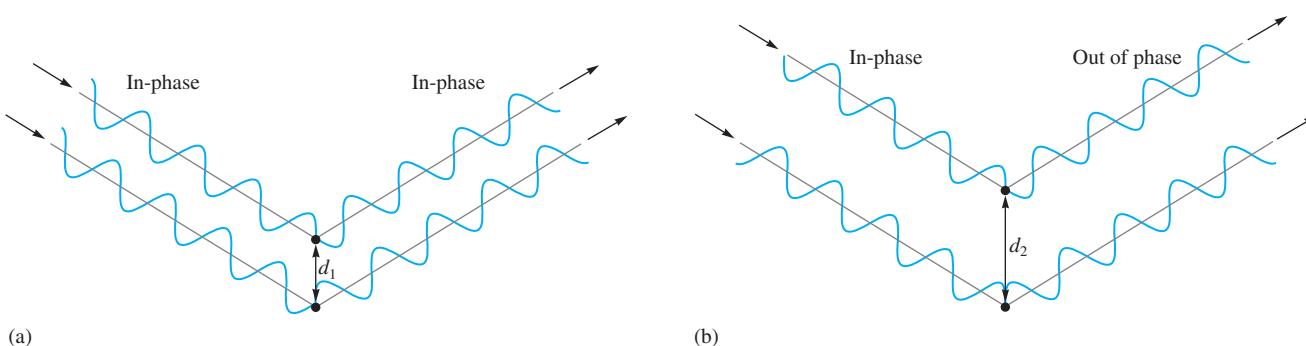
where  $n$  is an integer and  $\lambda$  is the wavelength of the X rays. Using trigonometry (see Fig. 10.11), we can show that

$$xy + yz = 2d \sin \theta \quad (10.2)$$

where  $d$  is the distance between the atoms and  $\theta$  is the angle of incidence and reflection. Combining Equation (10.1) and Equation (10.2) gives

$$n\lambda = 2d \sin \theta \quad (10.3)$$

Equation (10.3) is called the *Bragg equation* after William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1972), who shared the Nobel Prize in physics in 1915 for their pioneering work in X-ray crystallography.

**FIGURE 10.10**

X rays scattered from two different atoms may reinforce (constructive interference) or cancel (destructive interference) one another. (a) Both the incident rays and the reflected rays are also in phase. In this case,  $d_1$  is such that the difference in the distances traveled by the two rays is a whole number of wavelengths. (b) The incident rays are in phase but the reflected rays are exactly out of phase. In this case  $d_2$  is such that the difference in distances traveled by the two rays is an odd number of half wavelengths.

A diffractometer is a computer-controlled instrument used for carrying out the X-ray analysis of crystals. It rotates the crystal with respect to the X-ray beam and collects the data produced by the scattering of the X rays from the various planes of atoms in the crystal. The results are then analyzed by computer.

The techniques for crystal structure analysis have reached a level of sophistication that allows the determination of very complex structures, such as those important in biological systems. For example, the structures of several enzymes have been determined, thus enabling biochemists to understand how they perform their functions. We will explore this topic further in Chapter 12. Using X-ray diffraction, we can gather data on bond lengths and angles and in so doing can test the predictions of our models of molecular geometry.

### Sample Exercise 10.1



Graduate student Maria Zhuravlera operating an X-ray diffractometer at Michigan State University.

### Using the Bragg Equation

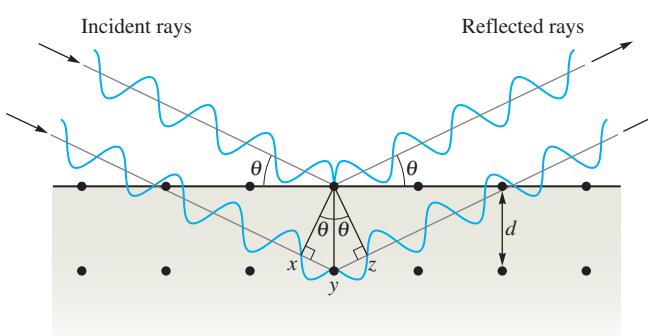
X rays of wavelength  $1.54 \text{ \AA}$  were used to analyze an aluminum crystal. A reflection was produced at  $\theta = 19.3$  degrees. Assuming  $n = 1$ , calculate the distance  $d$  between the planes of atoms producing this reflection.

#### Solution

To determine the distance between the planes, we use Equation (10.3) with  $n = 1$ ,  $\lambda = 1.54 \text{ \AA}$ , and  $\theta = 19.3$  degrees. Since  $2d \sin \theta = n\lambda$ ,

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(1.54 \text{ \AA})}{(2)(0.3305)} = 2.33 \text{ \AA} = 233 \text{ pm}$$

*See Exercises 10.41 through 10.44.*

**FIGURE 10.11**

Reflection of X rays of wavelength  $\lambda$  from a pair of atoms in two different layers of a crystal. The lower wave travels an extra distance equal to the sum of  $xy$  and  $yz$ . If this distance is an integral number of wavelengths ( $n = 1, 2, 3, \dots$ ), the waves will reinforce each other when they exit the crystal.



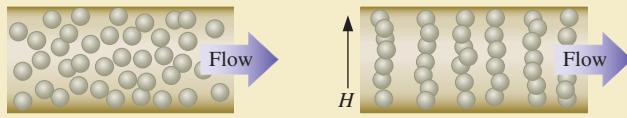
## CHEMICAL IMPACT

### Smart Fluids

Matter seems to be getting smarter these days. Increasingly, we have discovered materials that can remember their initial shape after being deformed or can sense and respond to their environment. In particular, valuable new materials have been formulated whose properties can be changed instantly by applying a magnetic or electric field.

One example of such a substance is a fluid whose flow characteristics (rheology) can be changed from free flowing to almost solid in about 0.01 second by the application of an electromagnetic field. This “magnetorheological” (MR) fluid was developed by Lord Corporation. Working in collaboration with Delphi Corporation, the company is applying the fluid in suspension control of General Motors automobiles such as Cadillacs and Corvettes. The so-called Magneride system has sensors that monitor the road surface and provide information about what suspension damping is needed. In response, a message is instantly sent to an electromagnetic coil in the shock absorbers, which adjusts the viscosity of the MR fluid to provide continuously variable damping. The result: an amazingly smooth ride and unerring road-holding ability.

The MR fluid is composed of a synthetic oil in which particles of an iron-containing compound are suspended. When

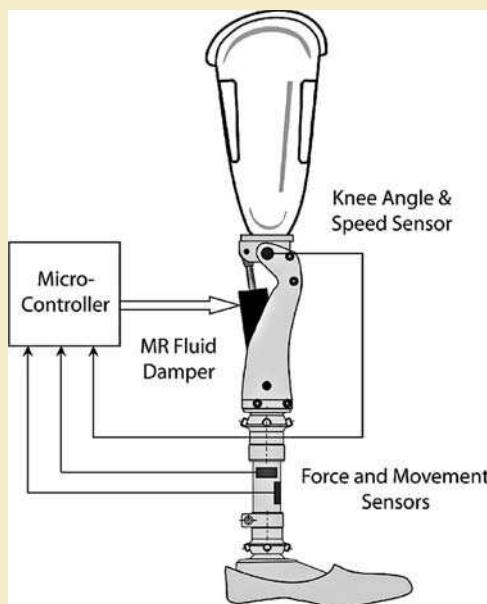


**Magnetic field off**  
Magnetic particles  
flow randomly

**Magnetic field on**  
Applied field ( $H$ )  
creates structure that  
increases viscosity

the magnetic field is turned off, these particles flow freely in all directions (see the figure above). When the field is turned on, the particles aggregate into chains that line up perpendicular to the flow of the fluid, thereby increasing its viscosity in proportion to the strength of the applied field.

Many other applications of MR fluids besides auto suspensions are under development. For example, this technology is being used in a prosthesis (see below) for above-the-knee amputees, which gives them a more natural gait and improves stair climbing. One very large-scale application is in Japan's National Museum of Emerging Science and Innovation, where an MR fluid is being used in dampers to protect the building against earthquake damage. Large MR-fluid dampers are also being used for stabilizing bridges such as the Dong Ting Lake Bridge in China's Hunan province to steady it in high winds.



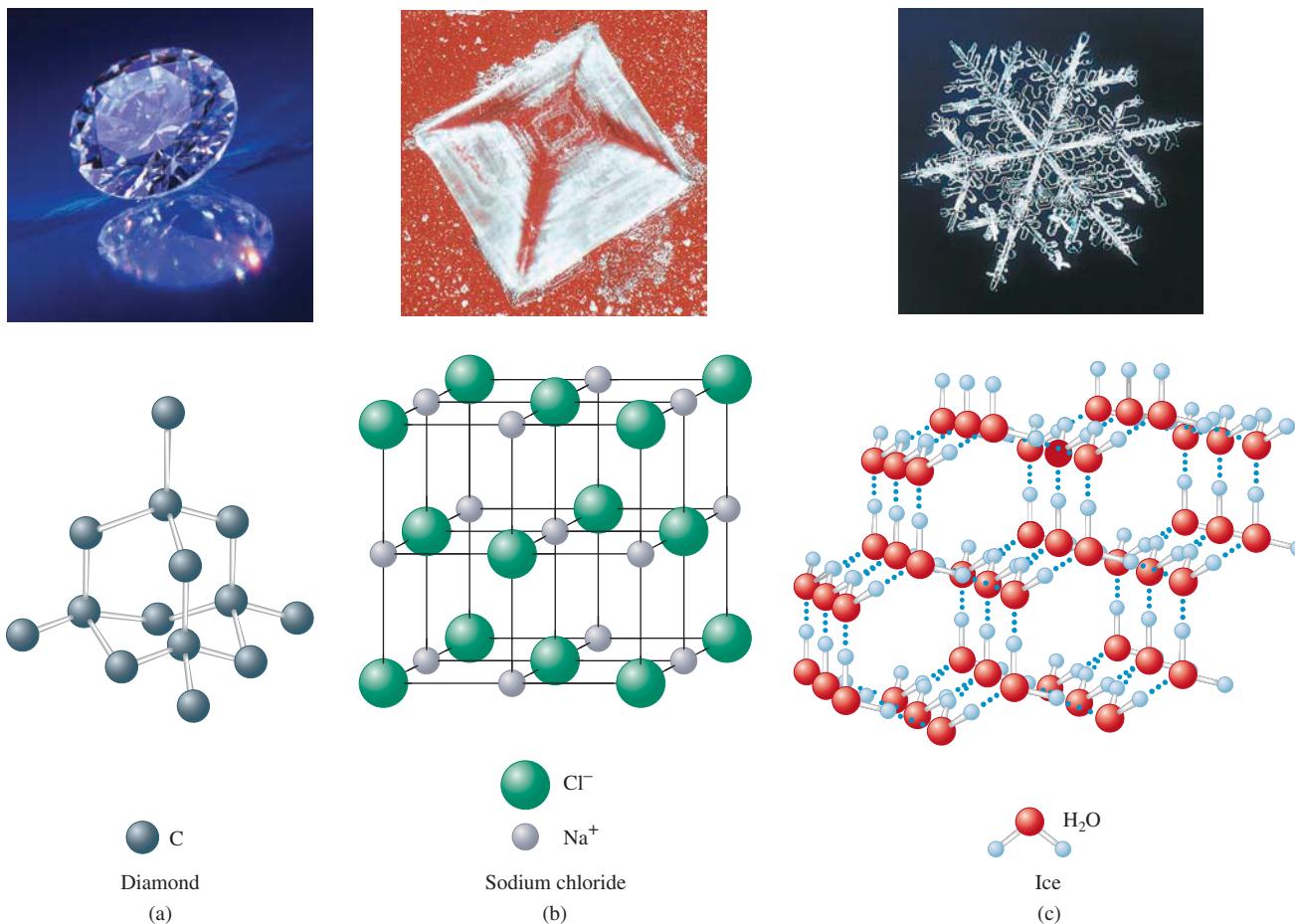
This High Intelligence Prosthetic for the knee uses an MR fluid damper to provide motion that closely duplicates the natural movement of the knee joint.

## Types of Crystalline Solids

There are many different types of crystalline solids. For example, although both sugar and salt dissolve readily in water, the properties of the resulting solutions are quite different. The salt solution readily conducts an electric current, whereas the sugar solution does not. This behavior arises from the nature of the components in these two solids. Common salt ( $\text{NaCl}$ ) is an ionic solid; it contains  $\text{Na}^+$  and  $\text{Cl}^-$  ions. When solid sodium chloride dissolves in the polar water, sodium and chloride ions are distributed throughout the resulting solution and are free to conduct electric current. Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when the solid dissolves. No ions are present, and the resulting solution does not conduct electricity. These examples illustrate two important types of solids: **ionic solids**, represented by sodium chloride, and **molecular solids**, represented by sucrose. Ionic solids have ions at the points of the lattice that describes the structure of the solid. A molecular solid, on the other hand, has discrete covalently bonded molecules at each of its lattice points. Ice is a molecular solid that has an  $\text{H}_2\text{O}$  molecule at each point (see Fig. 10.12).

Buckminsterfullerene,  $\text{C}_{60}$ , is a particular member of the fullerene family.

A third type of solid is represented by elements such as carbon (which exists in the forms graphite, diamond, and the fullerenes), boron, silicon, and all metals. These substances all have atoms at the lattice points that describe the structure of the solid. Therefore, we call solids of this type **atomic solids**. Examples of these three types of solids are shown in Fig. 10.12.



**FIGURE 10.12**

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. (b) An ionic solid. (c) A molecular solid. The dotted lines show the hydrogen bonding interactions among the polar water molecules.

**TABLE 10.3 Classification of Solids**

	Atomic Solids				
	<b>Metallic</b>	<b>Network</b>	<b>Group 8A</b>	<b>Molecular Solids</b>	<b>Ionic Solids</b>
<b>Components That Occupy the Lattice Points:</b>	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
<b>Bonding:</b>	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

To summarize, we find it convenient to classify solids according to what type of component occupies the lattice points. This leads to the classifications *atomic solids* (atoms at the lattice points), *molecular solids* (discrete, relatively small molecules at the lattice points), and *ionic solids* (ions at the lattice points). In addition, atomic solids are placed into the following subgroups based on the bonding that exists among the atoms in the solid: *metallic solids*, *network solids*, and *Group 8A solids*. In metallic solids, a special type of delocalized nondirectional covalent bonding occurs. In network solids, the atoms bond to each other with strong directional covalent bonds that lead to giant molecules, or networks, of atoms. In the Group 8A solids, the noble gas elements are attracted to each other with London dispersion forces. The classification of solids is summarized in Table 10.3.

The markedly different bonding present in the various atomic solids leads to dramatically different properties for the resulting solids. For example, although argon, copper, and diamond all are atomic solids, they have strikingly different properties. Argon (a Group 8A solid) has a very low melting point ( $-189^{\circ}\text{C}$ ), whereas diamond (a network solid) and copper (a metallic solid) melt at high temperatures (about 3500 and  $1083^{\circ}\text{C}$ , respectively). Copper is an excellent conductor of electricity, whereas argon and diamond are both insulators. Copper can be easily changed in shape; it is both malleable (can be formed into thin sheets) and ductile (can be pulled into a wire). Diamond, on the other hand, is the hardest natural substance known. We will explore the structure and bonding of atomic solids in the next two sections.

## 10.4 Structure and Bonding in Metals

Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. As we will see, these properties can be traced to the nondirectional covalent bonding found in metallic crystals.

A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions. We can model such a structure by packing uniform, hard spheres in a manner that most efficiently uses the available space. Such an arrangement is called **closest packing**. The spheres are packed in layers, as shown in Fig. 10.13, in which each sphere is surrounded by six others. In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation (or dimple) formed by three spheres in the first layer. In the third layer the spheres can occupy the dimples of the second layer in two possible ways: They can occupy positions so that each sphere in the third layer lies directly over a sphere in the first layer (the *aba* arrangement; Fig. 10.13a), or they can occupy positions so that no sphere in the third layer lies over one in the first layer (the *abc* arrangement; Fig. 10.13b).

The *aba* arrangement has the *hexagonal* unit cell shown in Fig. 10.14, and the resulting structure is called the **hexagonal closest packed (hcp) structure**. The *abc* arrangement has a *face-centered cubic* unit cell, as shown in Fig. 10.15, and the resulting structure is

The internal forces in a solid determine the properties of the solid.

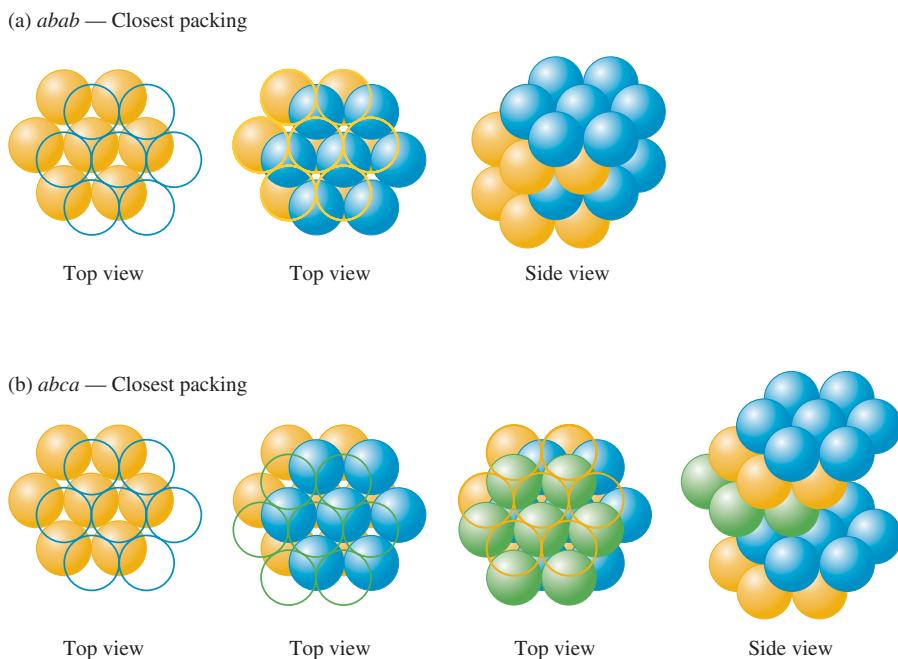
The closest packing model for metallic crystals assumes that metal atoms are uniform, hard spheres.



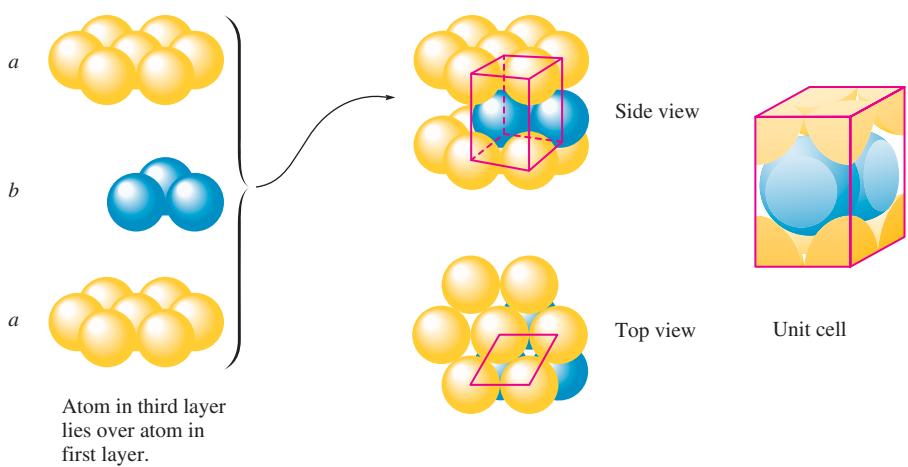
Visualization: Electron Sea Model

**FIGURE 10.13**

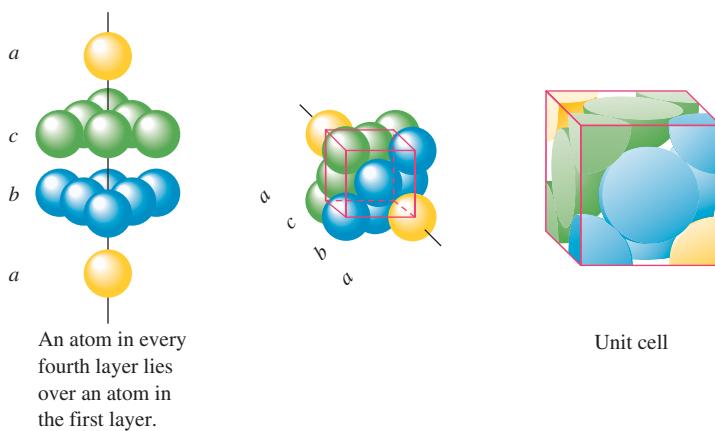
The closest packing arrangement of uniform spheres. In each layer a given sphere is surrounded by six others, creating six dimples, only three of which can be occupied in the next layer. (a) *aba* packing: The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer so that the spheres in the third layer lie directly over those in the first layer (*aba*). (b) *abc* packing: The spheres in the third layer occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer (*abc*). The fourth layer is like the first.

**FIGURE 10.14**

When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (*aba*), the unit cell is the hexagonal prism illustrated here in red.

**FIGURE 10.15**

When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown.





## CHEMICAL IMPACT

### Seething Surfaces

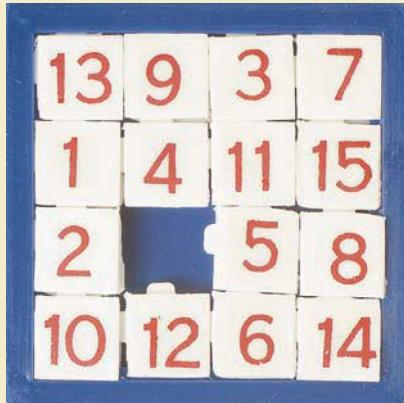
When we picture a solid, we think of the particles as being packed closely together with relatively little motion. The particles are thought to vibrate randomly about their positions but stay in nearly the same place. Recent research, however, indicates surface particles are a great deal more mobile than was previously thought. Independent teams of scientists from the University of Leiden in the Netherlands and Sandia National Laboratory in New Mexico have found a surprising amount of atom-swapping occurring on the surface of a copper crystal.

The Dutch scientist Raoul van Gastel and his colleagues used a scanning tunneling microscope (STM) to study the surface of a copper crystal containing indium atom impurities. They noted that a given patch of surface would stay the same for several scans and then, suddenly, the indium atoms would appear at different places. Surprisingly, the indium atoms seemed to make “long jumps,” moving as many as five atom positions between scans. The most likely explanation for these movements is a “hole” created by a copper atom escaping the surface. This hole moves around as other atoms shift to fill it in succession (see accompanying figure). The best analogy to the movement of the hole is the toy slide puzzle with 15 numbered pieces and one missing

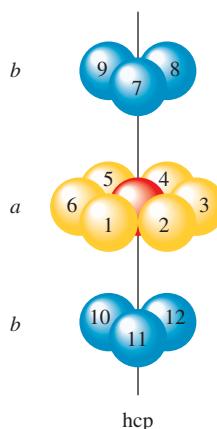
piece in a  $4 \times 4$  array. The object of the game is to slide a piece into the hole and then repeat the process until the numbers appear in order.

The hole on the copper surface moves very fast—up to 100 million times per second—shuffling copper atoms and allowing the indium atoms to change positions. Van Gastel believes that all of the observed motion results from just a few fast-moving holes. In fact, he suggests that just one in 6 billion copper atoms is missing at a given time, analogous to one person in the entire earth’s population. Its absence causes a given atom on the surface to move every 30 or 40 seconds. Brian Swartzentruber of Sandia National Laboratories came to similar conclusions using an STM to track the movement of palladium atoms on a copper surface.

These results have important implications. For example, metal surfaces are often used to speed up particular reactions. The motions on the metal surface could significantly influence the way that reactants interact with the surface. Also, a lot of effort is now being expended to construct tiny “machines” (called nanoscale devices) by assembling individual atoms on a solid surface. These devices could be literally torn apart by excess surface motions.



A toy slide puzzle.

**FIGURE 10.16**

The indicated sphere has 12 nearest neighbors.

called the **cubic closest packed (ccp) structure**. Note that in the hcp structure the spheres in every other layer occupy the same vertical position (*ababab* . . .), whereas in the ccp structure the spheres in every fourth layer occupy the same vertical position (*abcabcabc* . . .). A characteristic of both structures is that each sphere has 12 equivalent nearest neighbors: 6 in the same layer, 3 in the layer above, and 3 in the layer below (that form the dimples). This is illustrated for the hcp structure in Fig. 10.16.

Knowing the *net* number of spheres (atoms) in a particular unit cell is important for many applications involving solids. To illustrate how to find the net number of spheres in a unit cell, we will consider a face-centered cubic unit cell (Fig. 10.17). Note that this unit cell is defined by the *centers* of the spheres on the cube's corners. Thus 8 cubes share a given sphere, so  $\frac{1}{8}$  of this sphere lies inside each unit cell. Since a cube has 8 corners, there are  $8 \times \frac{1}{8}$  pieces, or enough to put together 1 whole sphere. The spheres at the center of each face are shared by 2 unit cells, so  $\frac{1}{2}$  of each lies inside a particular unit cell. Since the cube has 6 faces, we have  $6 \times \frac{1}{2}$  pieces, or enough to construct 3 whole spheres. Thus the net number of spheres in a face-centered cubic unit cell is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

### Sample Exercise 10.2

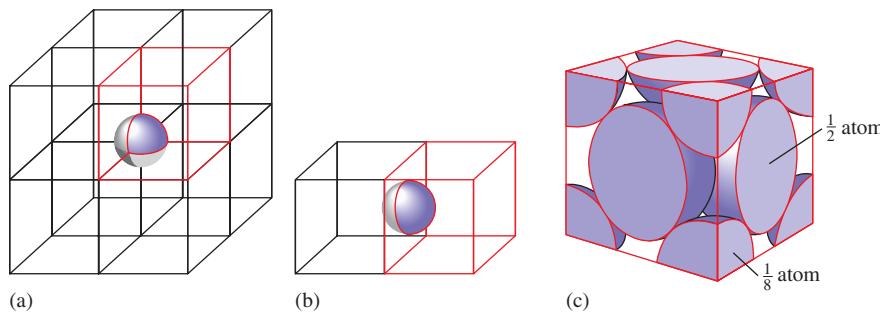
### Calculating the Density of a Closest Packed Solid

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 144 pm. Calculate the density of solid silver.

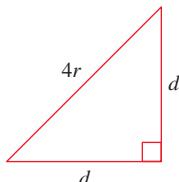
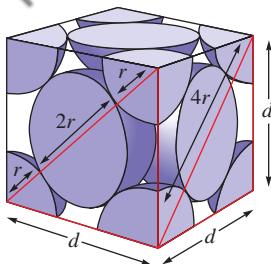
#### *Solution*

Density is mass per unit volume. Thus we need to know how many silver atoms occupy a given volume in the crystal. The structure is cubic closest packed, which means the unit cell is face-centered cubic, as shown in the accompanying figure.

We must find the volume of this unit cell for silver and the net number of atoms it contains. Note that in this structure the atoms touch along the diagonals for each

**FIGURE 10.17**

The net number of spheres in a face-centered cubic unit cell. (a) Note that the sphere on a corner of the colored cell is shared with 7 other unit cells (a total of 8). Thus  $\frac{1}{8}$  of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these  $\frac{1}{8}$  pieces, or 1 net sphere. (b) The sphere on the center of each face is shared by 2 unit cells, and thus each unit cell has  $\frac{1}{2}$  of each of these types of spheres. There are 6 of these  $\frac{1}{2}$  spheres to give 3 net spheres. (c) Thus the face-centered cubic unit cell contains 4 net spheres (all of the pieces can be assembled to give 4 spheres).



face and not along the edges of the cube. Thus the length of the diagonal is  $r + 2r + r$ , or  $4r$ . We use this fact to find the length of the edge of the cube by the Pythagorean theorem:

$$\begin{aligned}d^2 + d^2 &= (4r)^2 \\2d^2 &= 16r^2 \\d^2 &= 8r^2 \\d &= \sqrt{8r^2} = r\sqrt{8}\end{aligned}$$

Since  $r = 144$  pm for a silver atom,

$$d = (144 \text{ pm})(\sqrt{8}) = 407 \text{ pm}$$

The volume of the unit cell is  $d^3$ , which is  $(407 \text{ pm})^3$ , or  $6.74 \times 10^7 \text{ pm}^3$ . We convert this to cubic centimeters as follows:

$$6.74 \times 10^7 \text{ pm}^3 \times \left(\frac{1.00 \times 10^{-10} \text{ cm}}{\text{pm}}\right)^3 = 6.74 \times 10^{-23} \text{ cm}^3$$

Since we know that the net number of atoms in the face-centered cubic unit cell is 4, we have 4 silver atoms contained in a volume of  $6.74 \times 10^{-23} \text{ cm}^3$ . The density is therefore

$$\begin{aligned}\text{Density} &= \frac{\text{mass}}{\text{volume}} = \frac{(4 \text{ atoms})(107.9 \text{ g/mol})(1 \text{ mol}/6.022 \times 10^{23} \text{ atoms})}{6.74 \times 10^{-23} \text{ cm}^3} \\&= 10.6 \text{ g/cm}^3\end{aligned}$$

*See Exercises 10.45 through 10.48.*



Crystalline silver contains cubic closest packed silver atoms.

Examples of metals that form cubic closest packed solids are aluminum, iron, copper, cobalt, and nickel. Magnesium and zinc are hexagonal closest packed. Calcium and certain other metals can crystallize in either of these structures. Some metals, however, assume structures that are not closest packed. For example, the alkali metals have structures characterized by a *body-centered cubic (bcc) unit cell* (see Fig. 10.9), where the spheres touch along the body diagonal of the cube. In this structure, each sphere has 8 nearest neighbors (count the number of atoms around the atom at the center of the unit cell), as compared with 12 in the closest packed structures. Why a particular metal adopts the structure it does is not well understood.

## Bonding Models for Metals

**Malleable:** Can be pounded into thin sheets.

**Ductile:** Can be drawn to form a wire.

Any successful bonding model for metals must account for the typical physical properties of metals: malleability, ductility, and the efficient and uniform conduction of heat and electricity in all directions. Although the shapes of most pure metals can be changed relatively easily, most metals are durable and have high melting points. These facts indicate that the bonding in most metals is both *strong* and *nondirectional*. That is, although it is difficult to separate metal atoms, it is relatively easy to move them, provided the atoms stay in contact with each other.

The simplest picture that explains these observations is the *electron sea model*, which envisions a regular array of metal cations in a “sea” of valence electrons (see Fig. 10.18). The mobile electrons can conduct heat and electricity, and the metal ions can be easily moved around as the metal is hammered into a sheet or pulled into a wire.



# CHEMICAL IMPACT

# **Closest Packing of M & Ms**

**A**lthough we usually think of scientists as dealing with esoteric and often toxic materials, sometimes they surprise us. For example, scientists at several prestigious universities have lately shown a lot of interest in M & M candies.

To appreciate the scientists' interest in M & Ms, we must consider the importance of packing atoms, molecules, or microcrystals in understanding the structures of solids. The most efficient use of space is the closest packing of uniform spheres, where 74% of the space is occupied by the spheres and 26% of space is left unoccupied. Although the structures of most pure metals can be explained in terms of closest packing, most other substances—such as many alloys and ceramics—consist of random arrays of microscopic particles. For this reason, it is of interest to study how such objects pack in a random way.

When uniform spheres, such as marbles, are poured into a large container, the resulting random packing of the spheres results in only 64% of the space being occupied by the spheres. Thus it was very surprising when Princeton University chemist Salvatore Torquato and his colleagues at Cornell and North Carolina Central Universities discovered that, when the ellipsoidal-shaped M & Ms are poured into a large container, the candies occupy 73.5% of the available space. In other words, the randomly packed M & Ms occupy space with almost the same efficiency as closest packed spheres do.

Why do randomly packed ellipsoids occupy space so much more efficiently than randomly packed spheres? The

scientists speculate that because the ellipsoids can tip and rotate in ways that spheres cannot, they can pack more closely to their neighbors.

According to Torquato, these results are important because they will help us better understand the properties of disordered materials ranging from powders to glassy solids. He also says that M & Ms make ideal test objects because they are inexpensive and uniform and “you can eat the experiment afterward.”



A related model that gives a more detailed view of the electron energies and motions is the **band model**, or **molecular orbital (MO) model**, for metals. In this model, the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (Fig. 10.19).

Recall that in the MO model for the gaseous  $\text{Li}_2$  molecule (Section 9.3), two widely spaced molecular orbital energy levels (bonding and antibonding) result when two identical atomic orbitals interact. However, when many metal atoms interact,

## FIGURE 10.18

The electron sea model for metals postulates a regular array of cations in a "sea" of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.

