

CHAPTER 1

1.1 (a) Pure element: i (b) mixture of elements: v, vi (c) pure compound: iv (d) mixture of an element and a compound: ii, iii 1.3 This kind of separation based on solubility differences is called *extraction*. The insoluble grounds are then separated from the coffee solution by *filtration*. 1.5 (a) The aluminum sphere is lightest, then nickel, then silver. (b) The platinum sphere is largest, then gold, then lead. 1.7 (a) 7.5 cm; two significant figures (sig figs) (b) 72 mi/hr (inner scale, two significant figures) or 115 km/hr (outer scale, three significant figures) 1.9 Arrange the conversion factor so that the given unit cancels and the desired unit is in the correct position. 1.11 (a) Heterogeneous mixture (b) homogeneous mixture (heterogeneous if there are undissolved particles) (c) pure substance (d) pure substance. 1.13 (a) S (b) Au (c) K (d) Cl (e) Cu (f) uranium (g) nickel (h) sodium (i) aluminum (j) silicon 1.15 C is a compound; it contains both carbon and oxygen. A is a compound; it contains at least carbon and oxygen. B is not defined by the data given; it is probably also a compound because few elements exist as white solids. 1.17 Physical properties: silvery white; lustrous; melting point = 649 °C; boiling point = 1105 °C; density at 20 °C = 1.738 g/cm³; pounded into sheets; drawn into wires; good conductor. Chemical properties: burns in air; reacts with Cl₂. 1.19 (a) Chemical (b) physical (c) physical (d) chemical (e) chemical 1.21 (a) Add water to dissolve the sugar; filter this mixture, collecting the sand on the filter paper and the sugar water in the flask. Evaporate water from the flask to recover solid sugar. (b) Allow the mixture to settle so that there are two distinct layers. Carefully pour off most of the top oil layer. After the layers reform, use a dropper to remove any remaining oil. Vinegar is in the original vessel and oil is in a second container. 1.23 (a) 1 × 10⁻¹ (b) 1 × 10⁻² (c) 1 × 10⁻¹⁵ (d) 1 × 10⁻⁶ (e) 1 × 10⁶ (f) 1 × 10³ (g) 1 × 10⁻⁹ (h) 1 × 10⁻³ (i) 1 × 10⁻¹² 1.25 (a) 22 °C (b) 422.1 °F (c) 506 K (d) 107 °C (e) 1644 K (f) -459.67 °F 1.27 (a) 1.62 g/mL. Tetrachloroethylene, 1.62 g/mL, is more dense than water, 1.00 g/mL; tetrachloroethylene will sink rather than float on water. (b) 11.7 g 1.29 (a) Calculated density = 0.86 g/mL. The substance is probably toluene, density = 0.866 g/mL. (b) 40.4 mL ethylene glycol (c) 1.11 × 10³ g nickel 1.31 28 Pg 1.33 Exact: (c), (d), and (f) 1.35 (a) 3 (b) 2 (c) 5 (d) 3 (e) 5 (f) 1 1.37 (a) 1.025 × 10² (b) 6.570 × 10⁵ (c) 8.543 × 10⁻³ (d) 2.579 × 10⁻⁴ (e) -3.572 × 10⁻² 1.39 (a) 17.00 (b) 812.0 (c) 8.23 × 10³ (d) 8.69 × 10⁻² 1.41 5 significant figures

1.43 (a) $\frac{1 \times 10^{-3} \text{ m}}{1 \text{ mm}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}}$ (b) $\frac{1 \times 10^{-3} \text{ g}}{1 \text{ mg}} \times \frac{1 \text{ kg}}{1000 \text{ g}}$

(c) $\frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ cm}}{1 \times 10^{-2} \text{ m}} \times \frac{1 \text{ in.}}{2.54 \text{ cm}} \times \frac{1 \text{ ft}}{12 \text{ in.}}$ (d) $\frac{(2.54)^3 \text{ cm}^3}{1^3 \text{ in.}^3}$

1.45 (a) 54.7 km/hr (b) 1.3 × 10³ gal (c) 46.0 m (d) 0.984 in/hr 1.47 (a) 4.32 × 10⁵ s (b) 88.5 m (c) \$0.499/L (d) 46.6 km/hr (e) 1.420 L/s (f) 707.9 cm³ 1.49 (a) 1.2 × 10² L (b) 5 × 10² mg (c) 19.9 mi/gal (2 × 10¹ mi/gal for 1 significant figure) (d) 26 mL/g (3 × 10¹ mL/g for 1 significant figure) 1.51 64 kg air 1.53 14-in. shoe < 57-cm string < 1.1-m pipe 1.55 \$6 × 10⁴ 1.59 8.47 g O; the law of constant composition 1.62 (a) Volume (b) area (c) volume (d) density (e) time (f) length (g) temperature 1.65 (a) 1.13 × 10⁵ quarters (b) 6.41 × 10⁵ g (c) \$2.83 × 10⁴ (d) 4.13 × 10⁸ stacks 1.68 The most dense liquid, Hg, will sink; the least dense, cyclohexane, will float; H₂O will be in the middle. 1.71 density of solid = 1.63 g/mL 1.74 (a) Density of peat = 0.13 g/cm³, density of soil = 2.5 g/cm³. It is not correct to say that peat is “lighter” than topsoil. Volumes must be specified in order to compare masses. (b) Buy 16 bags of peat (more than 15 are needed). (Results to 1 significant figure are not meaningful.) 1.77 The inner diameter of the tube is 1.13 cm. 1.79 The separation

is successful if two distinct spots are seen on the paper. To quantify the characteristics of the separation, calculate a reference value for each spot: distance traveled by spot/distance traveled by solvent. If the values for the two spots are fairly different, the separation is successful.

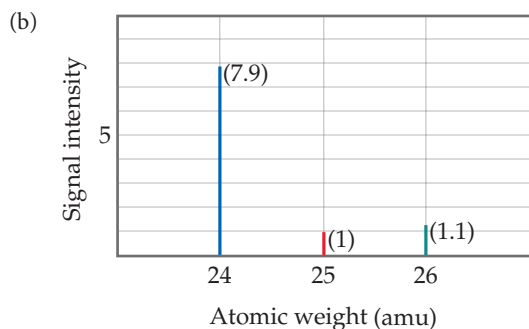
CHAPTER 2

2.1 (a) The path of the charged particle bends because the particle is repelled by the negatively charged plate and attracted to the positively charged plate. (b) (-) (c) increase (d) decrease 2.4 The particle is an ion. ${}_{16}^{32}\text{S}^{2-}$ 2.6 Formula: IF₅; name: iodine pentafluoride; the compound is molecular. 2.9 Postulate 4 of the atomic theory states that the relative number and kinds of atoms in a compound are constant, regardless of the source. Therefore, 1.0 g of pure water should always contain the same relative amounts of hydrogen and oxygen, no matter where or how the sample is obtained. 2.11 (a) 0.5711 g O/1 g N; 1.142 g O/1 g N; 2.284 g O/1 g N; 2.855 g O/1 g N (b) The numbers in part (a) obey the law of multiple proportions. Multiple proportions arise because atoms are the indivisible entities combining, as stated in Dalton's atomic theory. 2.13 (1) Electric and magnetic fields deflected the rays in the same way they would deflect negatively charged particles. (2) A metal plate exposed to cathode rays acquired a negative charge. 2.15 (a) Most of the volume of an atom is empty space in which electrons move. Most alpha particles passed through this space. (b) The few alpha particles that hit the massive, positively charged gold nuclei were strongly repelled and deflected back in the direction they came from. (c) Because the Be nuclei have a smaller volume and a smaller positive charge than the Au nuclei, fewer alpha particles will be scattered and fewer will be strongly back scattered. 2.17 (a) 0.135 nm; 1.35 × 10² or 135 pm (b) 3.70 × 10⁶ Au atoms (c) 1.03 × 10⁻²³ cm³ 2.19 (a) Proton, neutron, electron (b) proton = 1+, neutron = 0, electron = 1- (c) The neutron is most massive. (The neutron and proton have very similar masses.) (d) The electron is least massive. 2.21 (a) Atomic number is the number of protons in the nucleus of an atom. Mass number is the total number of nuclear particles, protons plus neutrons, in an atom. (b) mass number 2.23 (a) ${}^{40}\text{Ar}$: 18 p, 22 n, 18 e (b) ${}^{65}\text{Zn}$: 30 p, 35 n, 30 e (c) ${}^{70}\text{Ga}$: 31 p, 39 n, 31 e (d) ${}^{80}\text{Br}$: 35 p, 45 n, 35 e (e) ${}^{184}\text{W}$: 74 p, 110 n, 74 e (f) ${}^{243}\text{Am}$: 95 p, 148 n, 95e

2.25

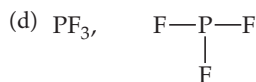
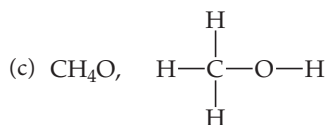
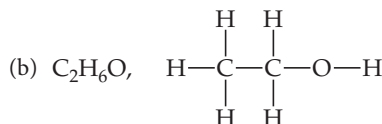
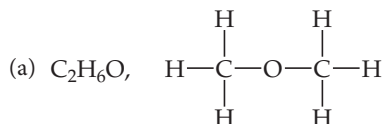
Symbol	${}^{52}\text{Cr}$	${}^{55}\text{Mn}$	${}^{112}\text{Cd}$	${}^{222}\text{Rn}$	${}^{207}\text{Pb}$
Protons	24	25	48	86	82
Neutrons	28	30	64	136	125
Electrons	24	25	48	86	82
Mass no.	52	55	112	222	207

2.27 (a) ${}^{196}\text{Pt}$ (b) ${}^{84}\text{Kr}$ (c) ${}^{75}\text{As}$ (d) ${}^{24}\text{Mg}$ 2.29 (a) ${}^{12}\text{C}$ (b) Atomic weights are average atomic masses, the sum of the mass of each naturally occurring isotope of an element times its fractional abundance. Each B atom will have the mass of one of the naturally occurring isotopes, while the “atomic weight” is an average value. 2.31 63.55 amu 2.33 (a) In Thomson's cathode-ray experiments and in mass spectrometry, a stream of charged particles is passed through the poles of a magnet. The charged particles are deflected by the magnetic field according to their mass and charge. (b) The x-axis label is atomic weight, and the y-axis label is signal intensity. (c) Uncharged particles are not deflected in a magnetic field. The effect of the magnetic field on charged moving particles is the basis of their separation by mass. 2.35 (a) average atomic mass = 24.31 amu



2.37 (a) Cr, 24 (metal) (b) He, 2 (nonmetal) (c) P, 15 (nonmetal) (d) Zn, 30 (metal) (e) Mg, 12 (metal) (f) Br, 35 (nonmetal) (g) As, 33 (metalloid) 2.39 (a) K, alkali metals (metal) (b) I, halogens (nonmetal) (c) Mg, alkaline earth metals (metal) (d) Ar, noble gases (nonmetal) (e) S, chalcogens (nonmetal) 2.41 An empirical formula shows the simplest mole ratio of elements in a compound. A molecular formula shows the exact number and kinds of atoms in a molecule. A structural formula shows which atoms are attached to which. 2.43 (a) AlBr_3 (b) C_4H_5 (c) $\text{C}_2\text{H}_4\text{O}$ (d) P_2O_5 (e) $\text{C}_3\text{H}_2\text{Cl}$ (f) BNH_2 2.45 (a) 6 (b) 6 (c) 12

2.47



2.49

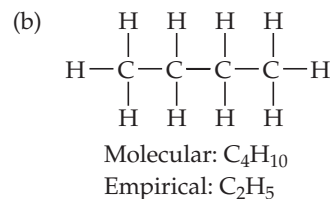
Symbol	$^{59}\text{Co}^{3+}$	$^{80}\text{Se}^{2-}$	$^{192}\text{Os}^{2+}$	$^{200}\text{Hg}^{2+}$
Protons	27	34	76	80
Neutrons	32	46	116	120
Electrons	24	36	74	78
Net Charge	3+	2-	2+	2+

2.51 (a) Mg^{2+} (b) Al^{3+} (c) K^+ (d) S^{2-} (e) F^- 2.53 (a) GaF_3 , gallium(III) fluoride (b) LiH , lithium hydride (c) AlI_3 , aluminum iodide (d) K_2S , potassium sulfide 2.55 (a) CaBr_2 (b) K_2CO_3 (c) $\text{Al}(\text{CH}_3\text{COO})_3$ (d) $(\text{NH}_4)_2\text{SO}_4$ (e) $\text{Mg}_3(\text{PO}_4)_2$

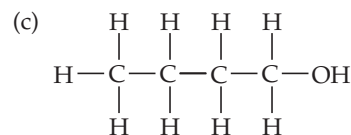
2.57

Ion	K^+	NH_4^+	Mg^{2+}	Fe^{3+}
Cl^-	KCl	NH_4Cl	MgCl_2	FeCl_3
OH^-	KOH	NH_4OH	$\text{Mg}(\text{OH})_2$	$\text{Fe}(\text{OH})_3$
CO_3^{2-}	K_2CO_3	$(\text{NH}_4)_2\text{CO}_3$	MgCO_3	$\text{Fe}_2(\text{CO}_3)_3$
PO_4^{3-}	K_3PO_4	$(\text{NH}_4)_3\text{PO}_4$	$\text{Mg}_3(\text{PO}_4)_2$	FePO_4

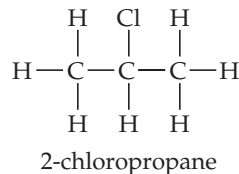
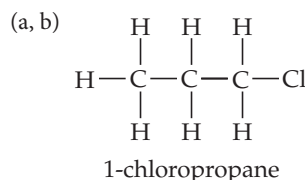
2.59 Molecular: (a) B_2H_6 (b) CH_3OH (f) NOCl (g) NF_3 . Ionic: (c) LiNO_3 (d) Sc_2O_3 (e) CsBr (h) Ag_2SO_4 2.61 (a) ClO_2^- (b) Cl^- (c) ClO_3^- (d) ClO_4^- (e) ClO^- 2.63 (a) calcium, 2+; oxide, 2- (b) sodium, 1+; sulfate, 2- (c) potassium, 1+; perchlorate, 1- (d) iron, 2+, nitrate, 1- (e) chromium, 3+; hydroxide, 1- 2.65 (a) lithium oxide (b) iron(III) chloride (ferric chloride) (c) sodium hypochlorite (d) calcium sulfite (e) copper(II) hydroxide (cupric hydroxide) (f) iron(II) nitrate (ferrous nitrate) (g) calcium acetate (h) chromium(III) carbonate (chromic carbonate) (i) potassium chromate (j) ammonium sulfate 2.67 (a) $\text{Al}(\text{OH})_3$ (b) K_2SO_4 (c) Cu_2O (d) $\text{Zn}(\text{NO}_3)_2$ (e) HgBr_2 (f) $\text{Fe}_2(\text{CO}_3)_3$ (g) NaBrO 2.69 (a) Bromic acid (b) hydrobromic acid (c) phosphoric acid (d) HClO (e) HIO_3 (f) H_2SO_3 2.71 (a) Sulfur hexafluoride (b) iodine pentafluoride (c) xenon trioxide (d) N_2O_4 (e) HCN (f) P_4S_6 2.73 (a) ZnCO_3 , ZnO , CO_2 (b) HF , SiO_2 , SiF_4 , H_2O (c) SO_2 , H_2O , H_2SO_3 (d) PH_3 (e) HClO_4 , Cd , $\text{Cd}(\text{ClO}_4)_2$ (f) VBr_3 2.75 (a) A hydrocarbon is a compound composed of the elements hydrogen and carbon only.



2.77 (a) Functional groups are groups of specific atoms that are constant from one molecule to the next. (b) $-\text{OH}$



2.79



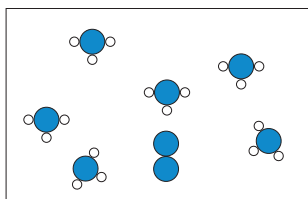
2.82 (a) 2 protons, 1 neutron, 2 electrons (b) tritium, ^3H , is more massive. (c) A precision of 1×10^{-27} g would be required to differentiate between $^3\text{H}^+$ and $^3\text{He}^+$. 2.84 Arrangement A, 4.1×10^{14} atoms/cm² (b) Arrangement B, 4.7×10^{14} atoms/cm² (c) The ratio of atoms going from arrangement B to arrangement A is 1.2 to 1. In three dimensions, arrangement B leads to a greater density for Rb metal. 2.87 (a) ^{16}O , ^{17}O , ^{18}O (b) All isotopes are atoms of the same element, oxygen, with the same atomic number, 8 protons in the nucleus and 8 electrons. We expect their electron arrangements to be the same and their chemical properties to be very similar. Each has a different number of neutrons, a different mass number, and a different atomic mass. 2.90 (a) ^{69}Ga , 31 protons, 38 neutrons; ^{71}Ga , 31 protons, 40 neutrons (b) ^{69}Ga , 60.3%, ^{71}Ga , 39.7%. 2.93 (a) 5 significant figures (b) An electron is 0.05444% of the mass of an ^1H atom. 2.96 Strontium is an alkaline earth metal, similar in chemical properties to calcium and magnesium. Harmful strontium closely mimics essential calcium and magnesium, then behaves badly when the body tries to use it as it uses calcium and

magnesium. **2.98** (a) Nickel(II) oxide, 2+ (b) manganese(IV) oxide, 4+ (c) chromium(III) oxide, 3+ (d) molybdenum(VI) oxide, 6+ **2.101** (a) Perbromate ion (b) selenite ion (c) AsO_4^{3-} (d) HTeO_4^- **2.104** (a) Potassium nitrate (b) sodium carbonate (c) calcium oxide (d) hydrochloric acid (e) magnesium sulfate (f) magnesium hydroxide

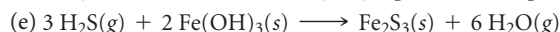
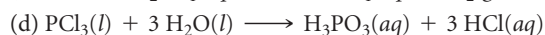
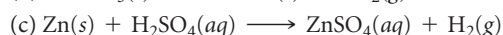
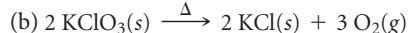
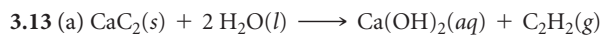
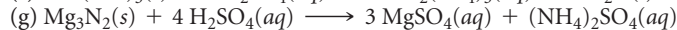
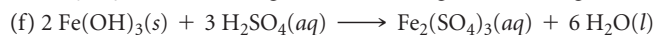
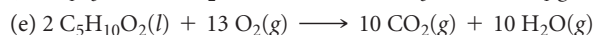
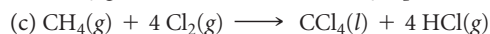
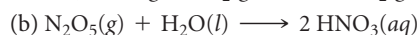
CHAPTER 3

3.1 Equation (a) best fits the diagram. **3.3** (a) NO_2 (b) No, because we have no way of knowing whether the empirical and molecular formulas are the same. NO_2 represents the simplest ratio of atoms in a molecule but not the only possible molecular formula. **3.5** (a) $\text{C}_2\text{H}_5\text{NO}_2$ (b) 75.0 g/mol (c) 225 g glycine (d) Mass %N in glycine is 18.7%.

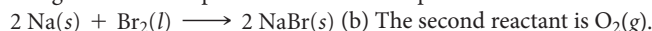
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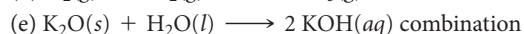
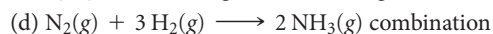
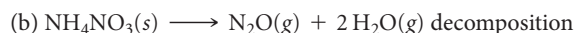
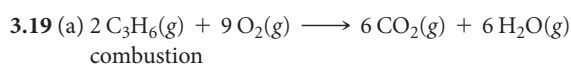
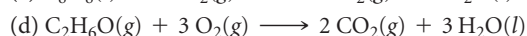
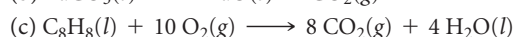
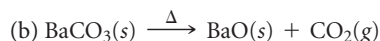
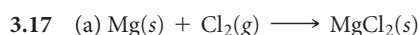
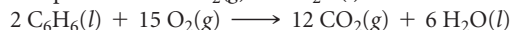
$\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$. Eight N atoms (4 N_2 molecules) require 24 H atoms (12 H_2 molecules) for complete reaction. Only 9 H_2 molecules are available, so H_2 is the limiting reactant. Nine H_2 molecules (18 H atoms) determine that 6 NH_3 molecules are produced. One N_2 molecule is in excess. **3.9** (a) Conservation of mass (b) Subscripts in chemical formulas should not be changed when balancing equations, because changing the subscript changes the identity of the compound (*law of constant composition*). (c) $\text{H}_2\text{O}(l)$, $\text{H}_2\text{O}(g)$, $\text{NaCl}(aq)$, $\text{NaCl}(s)$



3.15 (a) Determine the formula by balancing the positive and negative charges in the ionic product. All ionic compounds are solids.



The products are $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$.



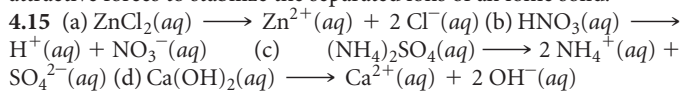
3.21 (a) 63.0 amu (b) 158.0 amu (c) 310.3 amu (d) 60.1 amu (e) 235.7 amu (f) 392.3 amu (g) 137.5 amu **3.23** (a) 16.8% (b) 16.1% (c) 21.1% (d) 28.8% (e) 27.2% (f) 26.5% **3.25** (a) 79.2% (b) 63.2%

(c) 64.6% **3.27** (a) 6.022×10^{23} (b) The formula weight of a substance in amu has the same numerical value as the molar mass expressed in grams. **3.29** 23 g Na contains 1 mol of atoms; 0.5 mol H_2O contains 1.5 mol atoms; 6.0×10^{23} N_2 molecules contain 2 mol of atoms. **3.31** 4.37×10^{25} kg (assuming 160 lb has 3 significant figures). One mole of people weighs 7.31 times as much as Earth. **3.33** (a) 35.9 g $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (b) 0.75766 mol $\text{Zn}(\text{NO}_3)_2$ (c) 6.0×10^{17} $\text{CH}_3\text{CH}_2\text{OH}$ molecules (d) 2.47×10^{23} N atoms **3.35** (a) 0.373 g $(\text{NH}_4)_3\text{PO}_4$ (b) 5.737×10^{-3} mol Cl^- (c) 0.248 g $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ (d) 387 g cholesterol/mol **3.37** (a) Molar mass = 162.3 g (b) 3.08×10^{-5} mol alliin (c) 1.86×10^{19} alliin molecules (d) 3.71×10^{19} S atoms **3.39** (a) 2.500×10^{21} H atoms (b) 2.083×10^{20} $\text{C}_6\text{H}_{12}\text{O}_6$ molecules (c) 3.460×10^{-4} mol $\text{C}_6\text{H}_{12}\text{O}_6$ (d) 0.06227 g $\text{C}_6\text{H}_{12}\text{O}_6$ **3.41** 3.2×10^{-8} mol $\text{C}_2\text{H}_3\text{Cl}/\text{L}$; 1.9×10^{16} molecules/L **3.43** (a) $\text{C}_2\text{H}_6\text{O}$ (b) Fe_2O_3 (c) CH_2O **3.45** (a) CSCl_2 (b) C_3OF_6 (c) Na_3AlF_6 **3.47** 31 g/mol **3.49** (a) C_6H_{12} (b) NH_2Cl **3.51** (a) Empirical formula, CH ; molecular formula, C_8H_8 (b) empirical formula, $\text{C}_4\text{H}_5\text{N}_2\text{O}$; molecular formula, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ (c) empirical formula and molecular formula, $\text{NaC}_5\text{H}_8\text{O}_4\text{N}$ **3.53** (a) C_7H_8 (b) The empirical and molecular formulas are $\text{C}_{10}\text{H}_{20}\text{O}$. **3.55** The molecular formula from the model is $\text{C}_8\text{H}_{16}\text{O}_2$, which corresponds to an empirical formula of $\text{C}_4\text{H}_8\text{O}$. The results from combustion analysis are consistent with this empirical formula. **3.57** $x = 10$; $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ **3.59** If the equation is not balanced, the mole ratios derived from the coefficients will be incorrect and lead to erroneous calculated amounts of products. **3.61** (a) 2.40 mol HF (b) 5.25 g NaF (c) 0.610 g Na_2SiO_3 **3.63** (a) $\text{Al}(\text{OH})_3(s) + 3 \text{HCl}(aq) \longrightarrow \text{AlCl}_3(aq) + 3 \text{H}_2\text{O}(l)$ (b) 0.701 g HCl (c) 0.855 g AlCl_3 ; 0.347 g H_2O (d) Mass of reactants = 0.500 g + 0.701 g = 1.201 g; mass of products = 0.855 g + 0.347 g = 1.202 g. Mass is conserved, within the precision of the data. **3.65** (a) $\text{Al}_2\text{S}_3(s) + 6 \text{H}_2\text{O}(l) \longrightarrow 2 \text{Al}(\text{OH})_3(s) + 3 \text{H}_2\text{S}(g)$ (b) 14.7 g $\text{Al}(\text{OH})_3$ **3.67** (a) 2.25 mol N_2 (b) 15.5 g NaN_3 (c) 548 g NaN_3 **3.69** (a) 5.50×10^{-3} mol Al (b) 1.47 g AlBr_3 **3.71** (a) The limiting reactant determines the maximum number of product moles resulting from a chemical reaction; any other reactant is an excess reactant. (b) The limiting reactant regulates the amount of products because it is completely used up during the reaction; no more product can be made when one of the reactants is unavailable. (c) Combining ratios are molecule and mole ratios. Since different molecules have different masses, comparing initial masses of reactants will not provide a comparison of numbers of molecules or moles. **3.73** (a) 2255 bicycles (b) 50 frames left over, 305 wheels left over (c) the handlebars **3.75** NaOH is the limiting reactant; 0.925 mol Na_2CO_3 can be produced; 0.075 mol CO_2 remains. **3.77** (a) NaHCO_3 is the limiting reactant. (b) 0.524 g CO_2 (c) 0.238 g citric acid remains **3.79** 0.00 g AgNO_3 (limiting reactant), 1.94 g Na_2CO_3 , 4.06 g Ag_2CO_3 , 2.50 g NaNO_3 **3.81** (a) The theoretical yield is 60.3 g $\text{C}_6\text{H}_5\text{Br}$. (b) 70.1% yield **3.83** 28 g S_8 actual yield **3.85** (a) $\text{C}_2\text{H}_4\text{O}_2(l) + 2 \text{O}_2(g) \longrightarrow 2 \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)$ (b) $\text{Ca}(\text{OH})_2(s) \longrightarrow \text{CaO}(s) + \text{H}_2\text{O}(g)$ (c) $\text{Ni}(s) + \text{Cl}_2(g) \longrightarrow \text{NiCl}_2(s)$ **3.89** (a) 8×10^{-20} g Si (b) 2×10^3 Si atoms (with 2 significant figures, 1700 Si atoms) (c) 1×10^3 Ge atoms (with 2 significant figures, 1500 Ge atoms) **3.93** $\text{C}_8\text{H}_8\text{O}_3$ **3.97** (a) 1.19×10^{-5} mol NaI (b) 8.1×10^{-3} g NaI **3.101** 7.5 mol H_2 and 4.5 mol N_2 present initially **3.105** 6.46×10^{24} O atoms **3.107** (a) 88 kg CO_2 (b) 4×10^2 (400) kg CO_2 **3.109** (a) $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$; $\text{SO}_2(g) + \text{CaO}(s) \longrightarrow \text{CaSO}_3(s)$ (b) 7.9×10^7 g CaO (c) 1.7×10^8 g CaSO_3

CHAPTER 4

4.1 Diagram (c) represents Li_2SO_4 **4.3** (a) HCOOH is a weak electrolyte. (b) HNO_3 is a strong electrolyte. (c) $\text{CH}_3\text{CH}_2\text{OH}$ is a non-electrolyte. **4.5** BaCl_2 **4.7** (b) NO_3^- and (c) NH_4^+ will always be spectator ions. **4.9** In a redox reaction, electrons are transferred from the oxidized substance to the reduced substance. In an acid-base reaction, protons are transferred from an acid to a base. **4.11** No. Electrolyte solutions conduct electricity because the dissolved ions carry charge through the solution from one electrode to the other. **4.13** Although H_2O molecules are electrically neutral, there is an unequal distribution of electrons throughout the molecule. The partially

positive ends of H₂O molecules are attracted to anions in the solid, while the partially negative ends are attracted to cations. Thus, both cations and anions in an ionic solid are surrounded and separated (dissolved) by H₂O. We do not expect ionic compounds to be soluble in molecular liquids such as Br₂(l) or Hg(l). There is a symmetrical charge distribution in Hg atoms and Br₂ molecules, so there are no attractive forces to stabilize the separated ions of an ionic solid.



4.17 HCOOH molecules, H⁺ ions, and HCOO⁻ ions;
 $\text{HCOOH}(aq) \rightleftharpoons \text{H}^{+}(aq) + \text{HCOO}^{-}(aq)$ **4.19** (a) Soluble

(b) insoluble (c) soluble (d) soluble (e) soluble **4.21** (a) $\text{Na}_2\text{CO}_3(aq) + 2\text{AgNO}_3(aq) \longrightarrow \text{Ag}_2\text{CO}_3(s) + 2\text{NaNO}_3(aq)$

(b) No precipitate (c) $\text{FeSO}_4(aq) + \text{Pb}(\text{NO}_3)_2(aq) \longrightarrow \text{PbSO}_4(s) + \text{Fe}(\text{NO}_3)_2(aq)$ **4.23** (a) Na⁺, SO₄²⁻ (b) Na⁺, NO₃⁻ (c) NH₄⁺, Cl⁻

4.25 The solution contains Pb²⁺

4.27

Compound	Ba(NO ₃) ₂ Result	NaCl Result
AgNO ₃ (aq)	No ppt	AgCl ppt
CaCl ₂ (aq)	No ppt	No ppt
Al ₂ (SO ₄) ₃ (aq)	BaSO ₄ ppt	No ppt

This sequence of tests would definitely identify the bottle contents.

4.29 LiOH is a strong base, HI is a strong acid, and CH₃OH is a molecular compound and nonelectrolyte. The strong acid HI will have the greatest concentration of solvated protons. **4.31** (a) A monoprotic acid has one ionizable (acidic) H, whereas a diprotic acid has two.

(b) A strong acid is completely ionized in aqueous solution, whereas only a fraction of weak acid molecules are ionized. (c) An acid is an H⁺ donor, and a base is an H⁺ acceptor. **4.33** When each of the strong acids in Table 4.2 dissociates, the anions formed are the same ones that normally form soluble ionic compounds (Table 4.1). The one exception is acetate, CH₃COO⁻, the anion of a weak acid. **4.35** (a) Acid, mixture of ions and molecules (weak electrolyte) (b) none of the above, entirely molecules (nonelectrolyte) (c) salt, entirely ions (strong electrolyte) (d) base, entirely ions (strong electrolyte) **4.37** (a) H₂SO₃, weak electrolyte (b) C₂H₅OH, nonelectrolyte (c) NH₃, weak electrolyte (d) KClO₃, strong electrolyte (e) Cu(NO₃)₂, strong electrolyte

4.39 (a) $2\text{HBr}(aq) + \text{Ca}(\text{OH})_2(aq) \longrightarrow \text{CaBr}_2(aq) + 2\text{H}_2\text{O}(l)$;
 $\text{H}^{+}(aq) + \text{OH}^{-}(aq) \longrightarrow \text{H}_2\text{O}(l)$ (b) $\text{Cu}(\text{OH})_2(s) + 2\text{HClO}_4(aq) \longrightarrow \text{Cu}(\text{ClO}_4)_2(aq) + 2\text{H}_2\text{O}(l)$;
 $\text{Cu}(\text{OH})_2(s) + 2\text{H}^{+}(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{Cu}^{2+}(aq)$ (c) $\text{Al}(\text{OH})_3(s) + 3\text{HNO}_3(aq) \longrightarrow \text{Al}(\text{NO}_3)_3(aq) + 3\text{H}_2\text{O}(l)$;
 $\text{Al}(\text{OH})_3(s) + 3\text{H}^{+}(aq) \longrightarrow 3\text{H}_2\text{O}(l) + \text{Al}^{3+}(aq)$ **4.41** (a) $\text{CdS}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{CdSO}_4(aq) + \text{H}_2\text{S}(g)$;
 $\text{CdS}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{H}_2\text{S}(g) + \text{Cd}^{2+}(aq)$

(b) $\text{MgCO}_3(s) + 2\text{HClO}_4(aq) \longrightarrow \text{Mg}(\text{ClO}_4)_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$;
 $\text{MgCO}_3(s) + 2\text{H}^{+}(aq) \longrightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) + \text{Mg}^{2+}(aq)$

4.43 (a) $\text{MgCO}_3(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$;
 $\text{MgCO}_3(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$;
 $\text{MgO}(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(aq) + \text{H}_2\text{O}(l)$;
 $\text{MgO}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{H}_2\text{O}(l)$;
 $\text{Mg}(\text{OH})_2(s) + 2\text{HCl}(aq) \longrightarrow \text{MgCl}_2(aq) + 2\text{H}_2\text{O}(l)$;
 $\text{Mg}(\text{OH})_2(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{H}_2\text{O}(l)$ (b) Yes. The reaction involving magnesium carbonate, MgCO₃(s), produces CO₂(g), which appears as bubbles. The other two reactions are calm. (c) If excess HCl(aq) is added in each case, the identity of the ions in the clear product solution is the same. The ions are Mg²⁺(aq); Cl⁻(aq); and H⁺(aq). **4.45** (a) In terms of electron transfer, oxidation is the loss of electrons by a substance and reduction is the gain of electrons (LEO says GER). (b) Relative to oxidation numbers, when a substance is oxidized, its oxidation number increases. When a substance is reduced, its oxidation number decreases. **4.47** Metals in region A are most easily oxidized. Nonmetals in region D are least easily oxidized.

4.49 (a) +4 (b) +4 (c) +7 (d) +1 (e) 0 (f) -1

4.51 (a) N₂ → 2 NH₃, N is reduced; 3 H₂ → 2 NH₃, H is oxidized (b) Fe²⁺ → Fe, Fe is reduced; Al → Al³⁺, Al is oxidized (c) Cl₂ → 2 Cl⁻, Cl is reduced; 2 I⁻ → I₂, I is oxidized (d) S²⁻ → SO₄²⁻, S is oxidized; H₂O₂ → H₂O, O is reduced

4.53 (a) $\text{Mn}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{MnSO}_4(aq) + \text{H}_2(g)$;

$\text{Mn}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Mn}^{2+}(aq) + \text{H}_2(g)$

(b) $2\text{Cr}(s) + 6\text{HBr}(aq) \longrightarrow 2\text{CrBr}_3(aq) + 3\text{H}_2(g)$;

$2\text{Cr}(s) + 6\text{H}^{+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 3\text{H}_2(g)$

(c) $\text{Sn}(s) + 2\text{HCl}(aq) \longrightarrow \text{SnCl}_2(aq) + \text{H}_2(g)$;

$\text{Sn}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Sn}^{2+}(aq) + \text{H}_2(g)$

(d) $2\text{Al}(s) + 6\text{HCOOH}(aq) \longrightarrow 2\text{Al}(\text{HCOO})_3(aq) + 3\text{H}_2(g)$;

$2\text{Al}(s) + 6\text{HCOOH}(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 6\text{HCOO}^{-}(aq) + 3\text{H}_2(g)$

4.55 (a) $\text{Fe}(s) + \text{Cu}(\text{NO}_3)_2(aq) \longrightarrow \text{Fe}(\text{NO}_3)_2(aq) + \text{Cu}(s)$

(b) NR (c) $\text{Sn}(s) + 2\text{HBr}(aq) \longrightarrow \text{SnBr}_2(aq) + \text{H}_2(g)$ (d) NR

(e) $2\text{Al}(s) + 3\text{CoSO}_4(aq) \longrightarrow \text{Al}_2(\text{SO}_4)_3(aq) + 3\text{Co}(s)$

4.57 (a) i. $\text{Zn}(s) + \text{Cd}^{2+}(aq) \longrightarrow \text{Cd}(s) + \text{Zn}^{2+}(aq)$;

ii. $\text{Cd}(s) + \text{Ni}^{2+}(aq) \longrightarrow \text{Ni}(s) + \text{Cd}^{2+}(aq)$ (b) Cd is between Zn and Ni on the activity series. (c) Place an iron strip in CdCl₂(aq). If Cd(s) is deposited, Cd is less active than Fe; if there is no reaction, Cd is more active than Fe. Do the same test with Co if Cd is less active than Fe or with Cr if Cd is more active than Fe. **4.59** (a) Intensive; the ratio of amount of solute to total amount of solution is the same, regardless of how much solution is present. (b) The term 0.50 mol HCl defines an amount (~18 g) of the pure substance HCl. The term 0.50 M HCl is a ratio; it indicates that there is 0.50 mol of HCl solute in 1.0 liter of solution. **4.61** (a) 1.17 M ZnCl₂ (b) 0.158 mol HNO₃ (c) 54.2 mL of 6.00 M NaOH **4.63** 16 g Na⁺(aq) **4.65** BAC of 0.08 = 0.02 M CH₃CH₂OH (alcohol) **4.67** (a) 5.21 g KBr (b) 0.06537 M Ca(NO₃)₂ (c) 10.2 mL of 1.50 M Na₃PO₄ **4.69** (a) 0.15 M K₂CrO₄ has the highest K⁺ concentration. (b) 30.0 mL of 0.15 M K₂CrO₄ has more K⁺ ions. **4.71** (a) 0.25 M Na⁺, 0.25 M NO₃⁻ (b) 1.3 × 10⁻² M Mg²⁺, 1.3 × 10⁻² M SO₄²⁻ (c) 0.0150 M C₆H₁₂O₆ (d) 0.111 M Na⁺, 0.111 M Cl⁻, 0.0292 M NH₄⁺, 0.0146 M CO₃²⁻

4.73 (a) 16.9 mL 14.8 M NH₃ (b) 0.296 M NH₃ **4.75** (a) Add 21.4 g C₁₂H₂₂O₁₁ to a 250-mL volumetric flask, dissolve in a small volume of water, and add water to the mark on the neck of the flask. Agitate thoroughly to ensure total mixing. (b) Thoroughly rinse, clean, and fill a 50-mL buret with the 1.50 M C₁₂H₂₂O₁₁. Dispense 23.3 mL of this solution into a 350-mL volumetric container, add water to the mark, and mix thoroughly. **4.77** 1.398 M CH₃COOH **4.79** 0.227 g KCl

4.81 (a) 38.0 mL of 0.115 M HClO₄ (b) 769 mL of 0.128 M HCl (c) 0.408 M AgNO₃ (d) 0.275 g KOH **4.83** 27 g NaHCO₃

4.85 (a) Molar mass of metal hydroxide is 103 g/mol. (b) Rb⁺

4.87 (a) $\text{NiSO}_4(aq) + 2\text{KOH}(aq) \longrightarrow \text{Ni}(\text{OH})_2(s) + \text{K}_2\text{SO}_4(aq)$

(b) Ni(OH)₂ (c) KOH is the limiting reactant. (d) 0.927 g Ni(OH)₂

(e) 0.0667 M Ni²⁺(aq), 0.0667 M K⁺(aq), 0.100 M SO₄²⁻(aq)

4.89 91.40% Mg(OH)₂ **4.92** The precipitate is CdS(s). Na⁺(aq) and NO₃⁻(aq) remain in solution, along with any excess reactant ions. The net ionic equation is Cd²⁺(aq) + S²⁻(aq) → CdS(s). **4.94** (a, b) Expt. 1: NR; Expt. 2: $2\text{Ag}^{+}(aq) + \text{CrO}_4^{2-}(aq) \longrightarrow \text{Ag}_2\text{CrO}_4(s)$ red precipitate; Expt. 3: $2\text{Ca}^{2+}(aq) + \text{CrO}_4^{2-}(aq) \longrightarrow \text{CaCrO}_4(s)$ yellow precipitate; Expt. 4: $2\text{Ag}^{+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \longrightarrow \text{Ag}_2\text{C}_2\text{O}_4(s)$ white precipitate; Expt. 5: $\text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \longrightarrow \text{CaC}_2\text{O}_4(s)$ white precipitate; Expt. 6: $\text{Ag}^{+}(aq) + \text{Cl}^{-}(aq) \longrightarrow \text{AgCl}(s)$ white precipitate. **4.96** $4\text{NH}_3(g) + 5\text{O}_2(g) \longrightarrow 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$. (a) redox reaction (b) N is oxidized, O is reduced. $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$. (a) redox reaction (b) N is oxidized, O is reduced. $3\text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow \text{HNO}_3(aq) + \text{NO}(g)$. (a) redox reaction (b) N is both oxidized and reduced. **4.99** 1.42 M KBr **4.100** (a) 2.2×10^{-9} M Na⁺ (b) 1.3×10^{12} Na⁺ ions

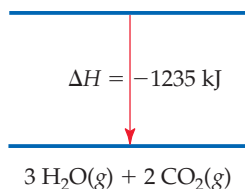
4.103 (a) 1.718 M Sr(OH)₂ (b) $2\text{HNO}_3(aq) + \text{Sr}(\text{OH})_2(s) \longrightarrow \text{Sr}(\text{NO}_3)_2(aq) + 2\text{H}_2\text{O}(l)$ (c) 2.61 M HNO₃ **4.106** (a) The molar-mass of the acid is 136 g/mol. (b) The molecular formula is C₈H₈O₂.

4.109 (a) $\text{Mg}(\text{OH})_2(s) + 2\text{HNO}_3(aq) \longrightarrow \text{Mg}(\text{NO}_3)_2(aq) + 2\text{H}_2\text{O}(l)$ (b) HNO₃ is the limiting reactant. (c) 0.0923 mol Mg(OH)₂, 0 mol HNO₃, and 0.00250 mol Mg(NO₃)₂ are present.

4.112 1.766% Cl⁻ by mass **4.114** 1.5×10^{-5} g Na₃AsO₄ in 1.00 L H₂O

CHAPTER 5

5.1 (a) As the book falls, potential energy decreases and kinetic energy increases. (b) 71 J, assuming no transfer of energy as heat (c) A heavier book falling from the same shelf has greater kinetic energy when it hits the floor. 5.5 (a) No. The distance traveled to the top of a mountain depends on the path taken by the hiker. Distance is a path function, not a state function. (b) Yes. Change in elevation depends only on the location of the base camp and the height of the mountain, not on the path to the top. Change in elevation is a state function, not a path function. 5.8 (a) The sign of w is (+). (b) The internal energy of the system increases during the change; the sign of ΔE is (+). 5.11 (a) $\Delta H_A = \Delta H_B + \Delta H_C$. The diagram and equation both show that the net enthalpy change for a process is independent of path, that ΔH is a state function. (b) $\Delta H_Z = \Delta H_X + \Delta H_Y$. (c) Hess's law states that the enthalpy change for net reaction Z is the sum of the enthalpy changes for steps X and Y, regardless of whether the reaction actually occurs via this path. The diagrams are a visual statement of Hess's law. 5.13 An object can possess energy by virtue of its motion or position. Kinetic energy depends on the mass of the object and its velocity. Potential energy depends on the position of the object relative to the body with which it interacts. 5.15 (a) 1.9×10^5 J (b) 4.6×10^4 cal (c) As the automobile brakes to a stop, its speed (and hence its kinetic energy) drops to zero. The kinetic energy of the automobile is primarily transferred to friction between brakes and wheels and somewhat to deformation of the tire and friction between the tire and road. 5.17 1 Btu = 1054 J 5.19 (a) The *system* is the well-defined part of the universe whose energy changes are being studied. (b) A *closed system* can exchange heat but not mass with its surroundings. (c) Any part of the universe not part of the system is called the surroundings. 5.21 (a) Work is a force applied over a distance. (b) The amount of work done is the magnitude of the force times the distance over which it is applied. $w = F \times d$. 5.23 (a) Gravity; work is done because the force of gravity is opposed and the pencil is lifted. (b) Mechanical force; work is done because the force of the coiled spring is opposed as the spring is compressed over a distance. 5.25 (a) In any chemical or physical change, energy can be neither created nor destroyed; energy is conserved. (b) The *internal energy* (E) of a system is the sum of all the kinetic and potential energies of the system components. (c) Internal energy of a closed system increases when work is done on the system and when heat is transferred to the system. 5.27 (a) $\Delta E = -0.077$ kJ, endothermic (b) $\Delta E = -22.1$ kJ, exothermic (c) $\Delta E = 7.25$ kJ, endothermic 5.29 (a) Since no work is done by the system in case (2), the gas will absorb most of the energy as heat; the case (2) gas will have the higher temperature. (b) In case (2) $w = 0$ and $q = 100$ J. In case (1) energy will be used to do work on the surroundings ($-w$), but some will be absorbed as heat ($+q$). (c) ΔE is greater for case (2) because the entire 100 J increases the internal energy of the system rather than a part of the energy doing work on the surroundings. 5.31 (a) A *state function* is a property that depends only on the physical state (pressure, temperature, etc.) of the system, not on the route used to get to the current state. (b) Internal energy is a state function; heat is not a state function. (c) Volume is a state function. The volume of a system depends only on conditions (pressure, temperature, amount of substance), not the route or method used to establish that volume. 5.33 (a) ΔH is usually easier to measure than ΔE because at constant pressure, $\Delta H = q_p$. The heat flow associated with a process at constant pressure can easily be measured as a change in temperature, while measuring ΔE requires a means to measure both q and w . (b) H is a static quantity that depends only on the specific conditions of the system. q is an energy *change* that, in the general case, does depend on how the change occurs. We can equate change in enthalpy, ΔH , with heat, q_p , only for the specific conditions of constant pressure and exclusively P - V work. (c) The process is endothermic. 5.35 At constant pressure, $\Delta E = \Delta H - P\Delta V$. The values of either P and ΔV or T and Δn must be known to calculate ΔE from ΔH . 5.37 $\Delta E = 1.47$ kJ; $\Delta H = 0.824$ kJ 5.39 (a) $\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{O}_2(g) \longrightarrow 3 \text{H}_2\text{O} + 2 \text{CO}_2(g)$, $\Delta H = -1235$ kJ



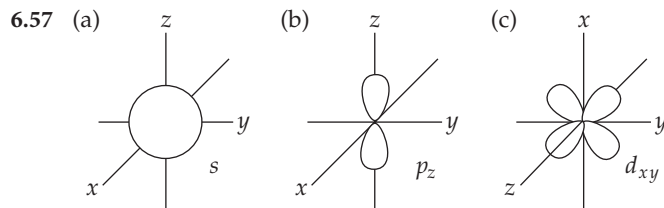
5.41 (a) $\Delta H = -142.3$ kJ/mol $\text{O}_3(g)$ (b) $2 \text{O}_3(g)$ has the higher enthalpy. 5.43 (a) Exothermic (b) -87.9 kJ heat transferred (c) 15.7 g MgO produced (d) 602 kJ heat absorbed 5.45 (a) -29.5 kJ (b) -4.11 kJ (c) 60.6 J 5.47 (a) $\Delta H = 726.5$ kJ (b) $\Delta H = -1453$ kJ (c) The exothermic forward reaction is more likely to be thermodynamically favored. (d) Vaporization is endothermic. If the product were $\text{H}_2\text{O}(g)$, the reaction would be more endothermic and would have a less negative ΔH . 5.49 (a) J/mol \cdot °C or J/mol \cdot K (b) J/g \cdot °C or J/g \cdot K (c) To calculate heat capacity from specific heat, the mass of the particular piece of copper pipe must be known. 5.51 (a) 4.184 J/g \cdot K (b) 75.40 J/mol \cdot °C (c) 774 J/°C (d) 904 kJ 5.53 (a) 2.66×10^3 J (b) It will require more heat to increase the temperature of one mole of octane, $\text{C}_8\text{H}_{18}(l)$, by a certain amount than to increase the temperature of one mole of water, $\text{H}_2\text{O}(l)$, by the same amount. 5.55 $\Delta H = -44.4$ kJ/mol NaOH 5.57 $\Delta H_{\text{rxn}} = -25.5$ kJ/g $\text{C}_6\text{H}_4\text{O}_2$ or -2.75×10^3 kJ/mol $\text{C}_6\text{H}_4\text{O}_2$ 5.59 (a) Heat capacity of the complete calorimeter = 14.4 kJ/°C (b) 7.56 °C 5.61 Hess's law is a consequence of the fact that enthalpy is a state function. Since ΔH is independent of path, we can describe a process by any series of steps that adds up to the overall process. ΔH for the process is the sum of ΔH values for the steps. 5.63 $\Delta H = -1300.0$ kJ 5.65 $\Delta H = -2.49 \times 10^3$ kJ 5.67 (a) *Standard conditions* for enthalpy changes are $P = 1$ atm and some common temperature, usually 298 K. (b) *Enthalpy of formation* is the enthalpy change that occurs when a compound is formed from its component elements. (c) *Standard enthalpy of formation* ΔH_f° is the enthalpy change that accompanies formation of one mole of a substance from elements in their standard states. 5.69 (a) $\frac{1}{2} \text{N}_2(g) + \text{O}_2(g) \longrightarrow \text{NO}_2(g)$, $\Delta H_f^\circ = 33.84$ kJ (b) $\text{S}(s) + 3/2 \text{O}_2(g) \longrightarrow \text{SO}_3(g)$, $\Delta H_f^\circ = -395.2$ kJ (c) $\text{Na}(s) + \frac{1}{2} \text{Br}_2(l) \longrightarrow \text{NaBr}(s)$, $\Delta H_f^\circ = -361.4$ kJ (d) $\text{Pb}(s) + \text{N}_2(g) + 3 \text{O}_2(g) \longrightarrow \text{Pb}(\text{NO}_3)_2(s)$, $\Delta H_f^\circ = -451.9$ kJ 5.71 $\Delta H_{\text{rxn}}^\circ = -847.6$ kJ 5.73 (a) $\Delta H_{\text{rxn}}^\circ = -196.6$ kJ (b) $\Delta H_{\text{rxn}}^\circ = 37.1$ kJ (c) $\Delta H_{\text{rxn}}^\circ = -976.94$ kJ (d) $\Delta H_{\text{rxn}}^\circ = -68.3$ kJ 5.75 $\Delta H_f^\circ = -248$ kJ 5.77 (a) $\text{C}_8\text{H}_{18}(l) + \frac{25}{2} \text{O}_2(g) \longrightarrow 8 \text{CO}_2(g) + 9 \text{H}_2\text{O}(g)$, $\Delta H = -5064.9$ kJ (b) $8 \text{C}(s, \text{graphite}) + 9 \text{H}_2(g) \longrightarrow \text{C}_8\text{H}_{18}(l)$ (c) $\Delta H_f^\circ = -259.5$ kJ 5.79 (a) $\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{O}_2(g) \longrightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(g)$ (b) $\Delta H_{\text{rxn}}^\circ = -1234.8$ kJ (c) 2.11×10^4 kJ/L heat produced (d) 0.071284 g CO_2 /kJ heat emitted 5.81 (a) *Fuel value* is the amount of energy produced when 1 g of a substance (fuel) is combusted. (b) 5 g of fat (c) These products of metabolism are expelled as waste via the alimentary tract, $\text{H}_2\text{O}(l)$ primarily in urine and feces, and $\text{CO}_2(g)$ as gas. 5.83 108 or 1×10^2 Cal/serving (b) Sodium does not contribute to the calorie content of the food because it is not metabolized by the body. 5.85 59.7 Cal 5.87 (a) $\Delta H_{\text{comb}} = -1850$ kJ/mol C_3H_4 , -1926 kJ/mol C_3H_6 , -2044 kJ/mol C_3H_8 (b) $\Delta H_{\text{comb}} = -4.616 \times 10^4$ kJ/kg C_2H_4 , -4.578×10^4 kJ/kg C_3H_6 , -4.635×10^4 kJ/kg C_3H_8 (c) These three substances yield nearly identical quantities of heat per unit mass, but propane is marginally higher than the other two. 5.89 1×10^{12} kg $\text{C}_6\text{H}_{12}\text{O}_6$ /yr 5.91 (a) 469.4 m/s (b) 5.124×10^{-21} J (c) 3.086 kJ/mol 5.93 The spontaneous air bag reaction is probably exothermic, with $-\Delta H$ and thus $-q$. When the bag inflates, work is done by the system, so the sign of w is also negative. 5.97 $\Delta H = 38.95$ kJ; $\Delta E = 36.48$ kJ 5.102 (a) $\Delta H_{\text{rxn}}^\circ = -353.0$ kJ (b) 1.2 g Mg needed 5.106 (a) $\Delta H^\circ = -631.3$ kJ (b) 3 mol of acetylene gas has greater enthalpy. (c) Fuel values are 50 kJ/g $\text{C}_2\text{H}_2(g)$, 42 kJ/g $\text{C}_6\text{H}_6(l)$. 5.109 If all work is used to increase the man's potential energy, the stair climbing uses 58 Cal and will not compensate for the extra order of 245 Cal fries. (More than 58 Cal will be required to climb the stairs because some energy is used to move limbs and some will be lost as heat.)

5.112 (a) 1.479×10^{-18} J/molecule (b) 1×10^{-15} J/photon. The X-ray has approximately 1000 times more energy than is produced by the combustion of 1 molecule of $\text{CH}_4(\text{g})$. **5.114** (a) ΔH° for neutralization of the acids is HNO_3 , -55.8 kJ; HCl , -56.1 kJ; NH_4^+ , -4.1 kJ. (b) $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$ is the net ionic equation for the first two reactions. $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ (c) The ΔH° values for the first two reactions are nearly identical, -55.8 kJ and -56.1 kJ. Since spectator ions do not change during a reaction and these two reactions have the same net ionic equation, it is not surprising that they have the same ΔH° . (d) Strong acids are more likely than weak acids to donate H^+ . Neutralization of the two strong acids is energetically favorable, while the third reaction is barely so. NH_4^+ is likely a weak acid. **5.116** (a) $\Delta H^\circ = -65.7$ kJ (b) ΔH° for the complete molecular equation will be the same as ΔH° for the net ionic equation. Since the overall enthalpy change is the enthalpy of products minus the enthalpy of reactants, the contributions of spectator ions cancel. (c) ΔH_f° for $\text{AgNO}_3(\text{aq})$ is -100.4 kJ/mol.

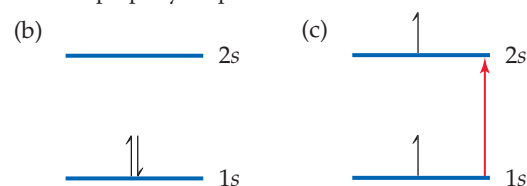
CHAPTER 6

6.2 (a) 0.1 m or 10 cm (b) No. Visible radiation has wavelengths much shorter than 0.1 m. (c) Energy and wavelength are inversely proportional. Photons of the longer 0.1-m radiation have less energy than visible photons. (d) Radiation with $\lambda = 0.1$ m is in the low-energy portion of the microwave region. The appliance is probably a microwave oven. **6.5** (a) Increase (b) decrease (c) the light from the hydrogen discharge tube is a line spectrum, so not all visible wavelengths will be in our "hydrogen discharge rainbow." Starting on the inside, the rainbow will be violet, then blue and blue-green. After a gap, the final band will be red. **6.8** (a) 1 (b) p (c) For the $n = 4$ shell, the lobes in the contour representation would extend farther along the y -axis. **6.11** (a) Meters (b) 1/second (c) meters/second **6.13** (a) True (b) False. Ultraviolet light has shorter wavelengths than visible light. (c) False. X-rays travel at the same speed as microwaves. (d) False. Electromagnetic radiation and sound waves travel at different speeds. **6.15** Wavelength of X-rays $<$ ultraviolet $<$ green light $<$ red light $<$ infrared $<$ radio waves **6.17** (a) $3.0 \times 10^{13} \text{ s}^{-1}$ (b) $5.45 \times 10^{-7} \text{ m} = 545 \text{ nm}$ (c) The radiation in (b) is visible; the radiation in (a) is not. (d) $1.50 \times 10^4 \text{ m}$ **6.19** $5.64 \times 10^{14} \text{ s}^{-1}$; green. **6.21** Quantization means that energy changes can happen only in certain allowed increments. If the human growth quantum is one foot, growth occurs instantaneously in one-foot increments. The child experiences growth spurts of one foot; her height can change only by one-foot increments. **6.23** (a) $4.47 \times 10^{-21} \text{ J}$ (b) $6.17 \times 10^{-19} \text{ J}$ (c) 69.2 nm **6.25** (a) $\lambda = 3.3 \mu\text{m}$, $E = 6.0 \times 10^{-20} \text{ J}$; $\lambda = 0.154 \text{ nm}$, $E = 1.29 \times 10^{-15} \text{ J}$ (b) The 3.3- μm photon is in the infrared region and the 0.154-nm photon is in the X-ray region; the X-ray photon has the greater energy. **6.27** (a) $6.11 \times 10^{-19} \text{ J/photon}$ (b) 368 kJ/mol (c) 1.64×10^{15} photons (d) 368 kJ/mol **6.29** (a) The $\sim 1 \times 10^{-6} \text{ m}$ radiation is in the infrared portion of the spectrum. (b) 8.1×10^{16} photons/s **6.31** (a) $E_{\text{min}} = 7.22 \times 10^{-19} \text{ J}$ (b) $\lambda = 275 \text{ nm}$ (c) $E_{120} = 1.66 \times 10^{-18} \text{ J}$. The excess energy of the 120-nm photon is converted into the kinetic energy of the emitted electron. $E_k = 9.3 \times 10^{-19} \text{ J/electron}$. **6.33** When applied to atoms, the notion of quantized energies means that only certain values of ΔE are allowed. These are represented by the lines in the emission spectra of excited atoms. **6.35** (a) Emitted (b) absorbed (c) emitted **6.37** (a) $E_2 = -5.45 \times 10^{-19} \text{ J}$; $E_6 = -0.606 \times 10^{-19} \text{ J}$; $\Delta E = 4.84 \times 10^{-19} \text{ J}$; $\lambda = 410 \text{ nm}$ (b) visible, violet **6.39** (a) Only lines with $n_f = 2$ represent ΔE values and wavelengths that lie in the visible portion of the spectrum. Lines with $n_f = 1$ have shorter wavelengths and lines with $n_f > 2$ have longer wavelengths than visible radiation. (b) $n_i = 3$, $n_f = 2$; $\lambda = 6.56 \times 10^{-7} \text{ m}$; this is the red line at 656 nm. $n_i = 4$, $n_f = 2$; $\lambda = 4.86 \times 10^{-7} \text{ m}$; this is the blue-green line at 486 nm. $n_i = 5$, $n_f = 2$; $\lambda = 4.34 \times 10^{-7} \text{ m}$; this is the blue-violet line at 434 nm. **6.41** (a) Ultraviolet region (b) $n_i = 6$, $n_f = 1$ **6.43** (a) $\lambda = 5.6 \times 10^{-37} \text{ m}$ (b) $\lambda = 2.65 \times 10^{-34} \text{ m}$ (c) $\lambda = 2.3 \times 10^{-13} \text{ m}$ (d) $\lambda = 1.51 \times 10^{-11} \text{ m}$ **6.45** $4.14 \times 10^3 \text{ m/s}$ **6.47** (a) $\Delta x \geq 4 \times 10^{-27} \text{ m}$ (b) $\Delta x \geq 3 \times 10^{-10} \text{ m}$ **6.49** (a) The uncertainty principle states that there is a limit to how precisely we can simultaneously

know the position and momentum (a quantity related to energy) of an electron. The Bohr model states that electrons move about the nucleus in precisely circular orbits of known radius and energy. This violates the uncertainty principle. (b) De Broglie stated that electrons demonstrate the properties of both particles and waves and that each moving particle has a wave associated with it. A wave function is the mathematical description of the matter wave of an electron. (c) Although we cannot predict the exact location of an electron in an allowed energy state, we can determine the probability of finding an electron at a particular position. This statistical knowledge of electron location is the *probability density* and is a function of Ψ^2 , the square of the wave function Ψ . **6.51** (a) $n = 4$, $l = 3, 2, 1, 0$ (b) $l = 2$, $m_l = -2, -1, 0, 1, 2$ (c) $m_l = 2$, $l \geq 2$ or $l = 2, 3$ or 4 **6.53** (a) $3p$: $n = 3$, $l = 1$ (b) $2s$: $n = 2$, $l = 0$ (c) $4f$: $n = 4$, $l = 3$ (d) $5d$: $n = 5$, $l = 2$ **6.55** (a) impossible, $1p$ (b) possible (c) possible (d) impossible, $2d$



6.59 (a) The hydrogen atom 1s and 2s orbitals have the same overall spherical shape, but the 2s orbital has a larger radial extension and one more node than the 1s orbital. (b) A single 2p orbital is directional in that its electron density is concentrated along one of the three Cartesian axes of the atom. The $d_{x^2-y^2}$ orbital has electron density along both the x - and y -axes, while the p_x orbital has density only along the x -axis. (c) The average distance of an electron from the nucleus in a 3s orbital is greater than for an electron in a 2s orbital. (d) $1s < 2p < 3d < 4f < 6s$ **6.61** (a) In the hydrogen atom, orbitals with the same principal quantum number, n , have the same energy. (b) In a many-electron atom, for a given n value, orbital energy increases with increasing l value: $s < p < d < f$. **6.63** (a) There are two main pieces of experimental evidence for electron "spin." The Stern-Gerlach experiment shows that atoms with a single unpaired electron interact differently with an inhomogeneous magnetic field. Examination of the fine details of emission line spectra of multi-electron atoms reveals that each line is really a close pair of lines. Both observations can be rationalized if electrons have the property of spin.



6.65 (a) 6 (b) 10 (c) 2 (d) 14 **6.67** (a) "Valence electrons" are those involved in chemical bonding. They are part or all of the outer-shell electrons listed after the core. (b) "Core electrons" are inner-shell electrons that have the electron configuration of the nearest noble-gas element. (c) Each box represents an orbital. (d) Each half-arrow in an orbital diagram represents an electron. The direction of the half-arrow represents electron spin. **6.69** (a) Cs, $[\text{Xe}]6s^1$ (b) Ni, $[\text{Ar}]4s^23d^8$ (c) Se, $[\text{Ar}]4s^23d^{10}4p^4$ (d) Cd, $[\text{Kr}]5s^24d^{10}$ (e) U, $[\text{Rn}]5f^36d^17s^2$ (f) Pb, $[\text{Xe}]6s^24f^{14}5d^{10}6p^2$ **6.71** (a) Be, 0 unpaired electrons (b) O, 2 unpaired electrons (c) Cr, 6 unpaired electrons (d) Te, 2 unpaired electrons **6.73** (a) The fifth electron would fill the 2p subshell before the 3s. (b) Either the core is $[\text{He}]$, or the outer electron configuration should be $3s^23p^3$. (c) The 3p subshell would fill before the 3d. **6.75** (a) $\lambda_A = 3.6 \times 10^{-8} \text{ m}$, $\lambda_B = 8.0 \times 10^{-8} \text{ m}$ (b) $\nu_A = 8.4 \times 10^{15} \text{ s}^{-1}$, $\nu_B = 3.7 \times 10^{15} \text{ s}^{-1}$ (c) A, ultraviolet; B, ultraviolet **6.78** 66.7 min **6.82** 1.6×10^7 photons/s, $5.1 \times 10^{-12} \text{ J/s}$ **6.85** (a) The Paschen series lies in the infrared. (b) $n_i = 4$, $\lambda = 1.87 \times 10^{-6} \text{ m}$; $n_i = 5$, $\lambda = 1.28 \times 10^{-6} \text{ m}$; $n_i = 6$, $\lambda = 1.09 \times 10^{-6} \text{ m}$ **6.90** (a) l (b) n and l (c) m_l (d) m_l **6.92** (a) The nodal plane of the p_z orbital is the xy -plane. (b) The two nodal planes of the d_{xy} orbital are the ones where

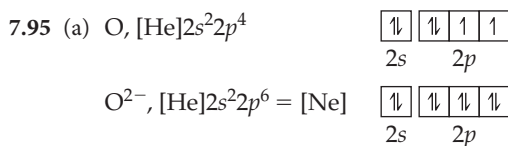
$x = 0$ and $y = 0$. These are the yz - and xz -planes. (c) The two nodal planes of the $d_{x^2-y^2}$ orbital are the ones that bisect the x - and y -axes and contain the z -axis. **6.94** If m_l had three allowed values instead of two, each orbital would hold three electrons instead of two. Assuming that there is no change in the n , l , and m_l values, the number of elements in each of the first four rows would be 1st row, 3 elements; 2nd row, 12 elements; 3rd row, 12 elements; 4th row, 27 elements. **6.97** (a) 1.7×10^{28} photons (b) 34 s. **6.101** (a) Bohr's theory was based on the Rutherford nuclear model of the atom: a dense positive charge at the center and a diffuse negative charge surrounding it. Bohr's theory then specified the nature of the diffuse negative charge. The prevailing theory before the nuclear model was Thomson's plum pudding model: discrete electrons scattered about a diffuse positive charge cloud. Bohr's theory could not have been based on the Thomson model of the atom. (b) De Broglie's hypothesis is that electrons exhibit both particle and wave properties. Thomson's conclusion that electrons have mass is a particle property, while the nature of cathode rays is a wave property. De Broglie's hypothesis actually rationalizes these two seemingly contradictory observations about the properties of electrons.

CHAPTER 7

7.3 (a) The bonding atomic radius of A, r_A , is $d_1/2$; $r_x = d_2 - (d_1/2)$. (b) The length of the X—X bond is $2r_x$ or $2d_2 - d_1$. **7.6** (a) $X + 2F_2 \rightarrow XF_4$ (b) X in the diagram has about the same bonding radius as F, so it is likely to be a nonmetal. **7.7** The number of columns in the various blocks of the periodic chart corresponds to the maximum number of electrons that can occupy the various kinds of atomic orbitals: 2 columns on the left for 2 electrons in s orbitals, 10 columns in the transition metals for 10 electrons in d orbitals, 6 columns on the right for 6 electrons in p orbitals, 14-member rows below for 14 electrons in f orbitals. The order of blocks corresponds to the filling order of atomic orbitals, and the row number corresponds to the principal quantum number of the valence electrons of elements in that row, ns , np , $(n-1)d$, $(n-2)f$. **7.9** In general, elements are discovered according to their ease of isolation in elemental form. **7.11** (a) *Effective nuclear charge*, Z_{eff} , is a representation of the average electrical field experienced by a single electron. It is the average environment created by the nucleus and the other electrons in the molecule, expressed as a net positive charge at the nucleus. (b) Going from left to right across a period, effective nuclear charge increases. **7.13** (a) For both Na and K, $Z_{\text{eff}} = 1$. (b) For both Na and K, $Z_{\text{eff}} = 2.2$. (c) Slater's rules give values closer to the detailed calculations: Na, 2.51; K, 3.49. (d) Both approximations give the same value of Z_{eff} for Na and K; neither accounts for the gradual increase in Z_{eff} moving down a group. (e) Following the trend from detailed calculations, we predict a Z_{eff} value of approximately 4.5. **7.15** The $n = 3$ electrons in Kr experience a greater effective nuclear charge and thus have a greater probability of being closer to the nucleus. **7.17** (a) Atomic radii are determined by measuring distances between atoms in various situations. (b) Bonding radii are calculated from the internuclear separation of two atoms joined by a covalent chemical bond. Nonbonding radii are calculated from the internuclear separation between two gaseous atoms that collide and move apart but do not bond. (c) For a given element, the nonbonding radius is always larger than the bonding radius. (d) If a free atom reacts to become part of a covalent molecule, its radius changes from nonbonding to bonding and the atom gets smaller. **7.19** (a) 1.37 Å (b) The distance between W atoms will decrease. **7.21** From the sum of the atomic radii, $As-I = 2.52$ Å. This is very close to the experimental value of 2.55 Å. **7.23** (a) Decrease (b) increase (c) $O < Si < Ge < I$ **7.25** (a) $Cs > K > Li$ (b) $Pb > Sn > Si$ (c) $N > O > F$ **7.27** (a) False (b) true (c) false **7.29** The red sphere is a metal; its size decreases on reaction, characteristic of the change in radius when a metal atom forms a cation. The blue sphere is a nonmetal; its size increases on reaction, characteristic of the change in radius when a nonmetal atom forms an anion. **7.31** (a) An isoelectronic series is a group of atoms or ions that have the same number of electrons and the same electron configuration. (b) Ga^{3+} : Ar; Zr^{4+} : Kr; Mn^{7+} : Ar; I^- : Xe; Pb^{2+} : Hg. **7.33** (a) Ar (b) Ar (c) There is no neutral atom isoelectronic with Fe^{2+} . Because transition metals fill the s subshell first but

also lose s electrons first when they form ions, many transition metal ions do not have isoelectronic neutral atoms. (d) No isoelectronic neutral atom; same reason as part (c). (e) No isoelectronic neutral atom; same reason as part (c). **7.35** (a) K^+ is smaller. (b) Cl^- , $Z_{\text{eff}} = 7$; K^+ , $Z_{\text{eff}} = 9$ (c) Cl^- : $Z_{\text{eff}} = 5.75$; K^+ , $Z_{\text{eff}} = 7.75$ (d) For isoelectronic ions, as nuclear charge (Z) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases. **7.37** (a) $Se < Se^{2-} < Te^{2-}$ (b) $Co^{3+} < Fe^{3+} < Fe^{2+}$ (c) $Ti^{4+} < Sc^{3+} < Ca$ (d) $Be^{2+} < Na^+ < Ne$ **7.39** $Al(g) \rightarrow Al^+(g) + e^-$; $Al^+(g) \rightarrow Al^{2+}(g) + e^-$; $Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$. The process for the first ionization energy requires the least amount of energy. **7.41** (a) False. Ionization energies are always positive quantities. (b) False. F has a greater first ionization energy than O. (c) True. **7.43** (a) The smaller the atom, the larger its first ionization energy. (b) Of the nonradioactive elements, He has the largest and Cs the smallest first ionization energy. **7.45** (a) Cl (b) Ca (c) K (d) Ge (e) Sn **7.47** (a) Fe^{2+} , $[Ar]3d^6$ (b) Hg^{2+} , $[Xe]4f^{14}5d^{10}$ (c) Mn^{2+} , $[Ar]3d^5$ (d) Pt^{2+} , $[Xe]4f^{14}5d^8$ (e) P^{3-} , $[Ne]3s^23p^6$ **7.49** Ni^{2+} , $[Ar]3d^8$; Pd^{2+} , $[Kr]4d^8$; Pt^{2+} , $[Xe]4f^{14}5d^8$ **7.51** (a) Positive, endothermic, values for ionization energy and electron affinity mean that energy is required to either remove or add electrons. Valence electrons in Ar experience the largest Z_{eff} of any element in the third row, resulting in a large, positive ionization energy. When an electron is added to Ar, the $n = 3$ electrons become core electrons that screen the extra electron so effectively that Ar^- has a higher energy than an Ar atom and a free electron. This results in a large positive electron affinity. (b) kJ/mol **7.53** Electron affinity of Br: $Br(g) + 1e^- \rightarrow Br^-(g)$; $[Ar]4s^23d^{10}4p^5 \rightarrow [Ar]4s^23d^{10}4p^6$; electron affinity of Kr: $Kr(g) + 1e^- \rightarrow Kr^-(g)$; $[Ar]4s^23d^{10}4p^6 \rightarrow [Ar]4s^23d^{10}4p^65s^1$. Br^- adopts the stable electron configuration of Kr; the added electron experiences essentially the same Z_{eff} and stabilization as the other valence electrons and electron affinity is negative. In Kr^- ion, the added electron occupies the higher energy $5s$ orbital. A $5s$ electron is farther from the nucleus, effectively shielded by the spherical Kr core and not stabilized by the nucleus; electron affinity is positive. **7.55** (a) Ionization energy (I_1) of Ne: $Ne(g) \rightarrow Ne^+(g) + 1e^-$; $[He]2s^22p^6 \rightarrow [He]2s^22p^5$; electron affinity (E_1) of F: $F(g) + 1e^- \rightarrow F^-(g)$; $[He]2s^22p^5 \rightarrow [He]2s^22p^6$. (b) I_1 of Ne is positive; E_1 of F is negative. (c) One process is apparently the reverse of the other, with one important difference. Ne has a greater Z and Z_{eff} , so we expect I_1 for Ne to be somewhat greater in magnitude and opposite in sign to E_1 for F. **7.57** The smaller the first ionization energy of an element, the greater the metallic character of that element. **7.59** Agree. When forming ions, all metals form cations. The only nonmetallic element that forms cations is the metalloid Sb, which is likely to have significant metallic character. **7.61** Ionic: SnO_2 , Al_2O_3 , Li_2O , Fe_2O_3 ; molecular: CO_2 , H_2O . Ionic compounds are formed by combining a metal and a nonmetal; molecular compounds are formed by two or more nonmetals. **7.63** (a) An *acidic oxide* dissolved in water produces an acidic solution; a *basic oxide* dissolved in water produces a basic solution. (b) Oxides of nonmetals, such as SO_3 , are acidic; oxides of metals, such as CaO , are basic. **7.65** (a) Dichlorineheptoxide (b) $2Cl_2(g) + 7O_2(g) \rightarrow 2Cl_2O_7(l)$ (c) While most nonmetal oxides we have seen, such as CO_2 or SO_2 , are gases, a boiling point of $81^\circ C$ is expected for a large molecule like Cl_2O_7 . (d) Cl_2O_7 is an acidic oxide, so it will be more reactive to base, OH^- . (e) The oxidation state of Cl in Cl_2O_7 is +7; the corresponding electron configuration for Cl is $[He]2s^22p^6$ or $[Ne]$. **7.67** (a) $BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(aq)$ (b) $FeO(s) + 2HClO_4(aq) \rightarrow Fe(ClO_4)_2(aq) + H_2O(l)$ (c) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ (d) $CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$ **7.69** Yes, the reactivity of a metal correlates with its first ionization energy. Since metals lose electrons when they form ions, the less energy required for this process, the more reactive the metal. However, we usually observe reactivity of metals in the solid state and ionization energy is a gas phase property, so there are differences between the two properties. **7.71** (a) Ca is more reactive because it has a lower ionization energy than Mg. (b) K is more reactive because it has a lower ionization energy than Ca. **7.73** (a) $2K(s) + Cl_2(g) \rightarrow 2KCl(s)$ (b) $SrO(s) + H_2O(l) \rightarrow Sr(OH)_2(aq)$ (c) $4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$ (d) $2Na(s) + S(l) \rightarrow Na_2S(s)$ **7.75** (a) Both classes of reaction are redox

reactions where either hydrogen or the halogen gains electrons and is reduced. The product is an ionic solid, where either hydride ion, H^- , or a halide ion, X^- , is the anion. (b) $\text{Ca}(s) + \text{F}_2(g) \longrightarrow \text{CaF}_2(s)$; $\text{Ca}(s) + \text{H}_2(g) \longrightarrow \text{CaH}_2(s)$. Both products are ionic solids containing Ca^{2+} and the corresponding anion in a 1:2 ratio. **7.77** (a) Br, $[\text{Ar}]4s^24p^5$; Cl, $[\text{Ne}]3s^23p^5$ (b) Br and Cl are in the same group, and both adopt a $1-$ ionic charge. (c) The ionization energy of Br is smaller than that of Cl, because the $4p$ valence electrons in Br are farther from the nucleus and less tightly held than the $3p$ electrons of Cl. (d) Both react slowly with water to form $\text{HX} + \text{HOX}$. (e) The electron affinity of Br is less negative than that of Cl, because the electron added to the $4p$ orbital in Br is farther from the nucleus and less tightly held than the electron added to the $3p$ orbital of Cl. (f) The atomic radius of Br is larger than that of Cl, because the $4p$ valence electrons in Br are farther from the nucleus and less tightly held than the $3p$ electrons of Cl. **7.79** (a) The term *inert* was dropped because it no longer described all the Group 8A elements. (b) In the 1960s, scientists discovered that Xe would react with substances having a strong tendency to remove electrons, such as F_2 . Thus, Xe could not be categorized as an “inert” gas. (c) The group is now called the noble gases. **7.81** (a) $2\text{O}_3(g) \longrightarrow 3\text{O}_2(g)$ (b) $\text{Xe}(g) + \text{F}_2(g) \longrightarrow \text{XeF}_2(g)$; $\text{Xe}(g) + 2\text{F}_2(g) \longrightarrow \text{XeF}_4(s)$; $\text{Xe}(g) + 3\text{F}_2(g) \longrightarrow \text{XeF}_6(s)$ (c) $\text{S}(s) + (\text{d}) 2\text{F}_2(g) + 2\text{H}_2\text{O}(l) \longrightarrow 4\text{HF}(aq) + \text{O}_2(g)$ **7.83** Up to $Z = 82$, there are three instances where atomic weights are reversed relative to atomic numbers: Ar and K; Co and Ni; Te and I. In each case the most abundant isotope of the element with the larger atomic number has one more proton but fewer neutrons than the element with the smaller atomic number. The smaller number of neutrons causes the element with the larger Z to have a smaller than expected atomic weight. **7.85** (a) $5+$ (b) $4.8+$ (c) Shielding is greater for $3p$ electrons, owing to penetration by $3s$ electrons, so Z_{eff} for $3p$ electrons is less than that for $3s$ electrons. (d) The first electron lost is a $3p$ electron because it has a smaller Z_{eff} and experiences less attraction for the nucleus than a $3s$ electron does. **7.88** (a) The estimated distances are a bit longer than the measured distances. This probably shows a systematic bias in either the estimated radii or in the method of obtaining the measured values. (b) The principal quantum number of the outer electrons and thus the average distance of these electrons from the nucleus increase from P($n = 3$) to As($n = 4$) to Sb($n = 5$). This causes the systematic increase in M–H distance. **7.92** (a) $2\text{Sr}(s) + \text{O}_2(g) \longrightarrow 2\text{SrO}(s)$ (b) Based on ionic radii, the length of the side of the cube is 5.16 \AA . (c) There are four SrO units in the cube.

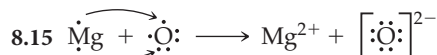
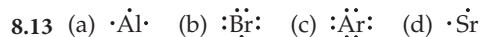


(b) O^{3-} , $[\text{Ne}]3s^1$. The third electron would be added to the $3s$ orbital, which is farther from the nucleus and more strongly shielded by the $[\text{Ne}]$ core. The overall attraction of this $3s$ electron for the oxygen nucleus is not large enough for O^{3-} to be a stable particle. **7.98** (a) For both H and the alkali metals, the added electron will complete an ns subshell, so shielding and repulsion effects will be similar. For the halogens, the electron is added to an np subshell, so the energy change is likely to be quite different. (b) True. The electron configuration of H is $1s^1$. The single $1s$ electron experiences no repulsion from other electrons and feels the full unshielded nuclear charge. The outer electrons of all other elements that form compounds are shielded by a spherical inner core of electrons and are less strongly attracted to the nucleus, resulting in larger bonding atomic radii. (c) Both H and the halogens have large ionization energies. The relatively large effective nuclear charge experienced by np electrons of the halogens is similar to the unshielded nuclear charge experienced by the H $1s$ electron. For the alkali metals, the ns electron being removed is effectively shielded by the core electrons, so ionization energies are low. (d) ionization energy of hydride, $\text{H}^-(g) \longrightarrow \text{H}(g) + 1e^-$ (e) electron affinity of hydrogen, $\text{H}(g) + 1e^- \longrightarrow \text{H}^-(g)$. The value for the ionization energy of hydride is equal in magnitude but opposite in sign to the electron affinity of hydrogen. **7.103** Electron configuration, $[\text{Rn}]7s^25f^46d^{10}7p^5$; first

ionization energy, 805 kJ/mol ; electron affinity, -235 kJ/mol ; atomic size, 1.65 \AA ; common oxidation state, -1 **7.106** (a) Li, $[\text{He}]2s^1$; $Z_{\text{eff}} \approx 1+$ (b) $I_1 \approx 5.45 \times 10^{-19} \text{ J/mol} \approx 328 \text{ kJ/mol}$ (c) The estimated value of 328 kJ/mol is less than the Table 7.4 value of 520 kJ/mol . Our estimate for Z_{eff} was a lower limit; the $[\text{He}]$ core electrons do not perfectly shield the $2s$ electron from the nuclear charge. (d) Based on the experimental ionization energy, $Z_{\text{eff}} = 1.26$. This value is greater than the estimate from part (a) but agrees well with the “Slater” value of 1.3 and is consistent with the explanation in part (c). **7.108** (a) 9.8902 \AA . (b) For Hg, the first ionization energy is 1007 kJ/mol , while the XPS energy of the $4f$ electron is $10,100 \text{ kJ/mol}$. The energy required to remove a $4f$ core electron is 10 times the energy required to remove a $6s$ valence electron. For O, the first ionization energy is 1314 kJ/mol , while the XPS energy of a $1s$ electron is $51,200 \text{ kJ/mol}$. The energy required to remove a $1s$ core electron is 40 times that required to remove a $2p$ valence electron. (c) Hg^{2+} , $[\text{Xe}]4f^{14}5d^{10}$; valence electrons are $5d$. O^{2-} , $[\text{He}]2s^22p^6$ or $[\text{Ne}]$; valence electrons are $2p$ (d) $\text{Hg}^{2+}5d$, $Z_{\text{eff}} = 18.85$; $\text{Hg}^{2+}4f$, $Z_{\text{eff}} = 43.85$; $\text{O}^{2-}4f$, $Z_{\text{eff}} = 3.85$. **7.110** (a) Mg_3N_2 (b) $\text{Mg}_3\text{N}_2(s) + 3\text{H}_2\text{O}(l) \longrightarrow 3\text{MgO}(s) + 2\text{NH}_3(g)$; the driving force is the production of $\text{NH}_3(g)$. (c) $17\% \text{ Mg}_3\text{N}_2$ (d) $3\text{Mg}(s) + 2\text{NH}_3(g) \longrightarrow \text{Mg}_3\text{N}_2(s) + 3\text{H}_2(g)$. NH_3 is the limiting reactant and 0.46 g H_2 is formed. (e) $\Delta H_{\text{rxn}}^\circ = -368.70 \text{ kJ}$

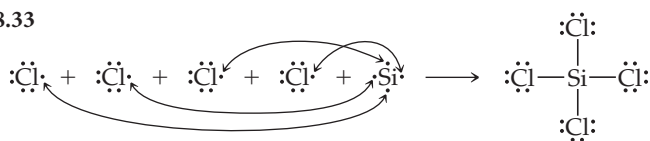
CHAPTER 8

8.1 (a) Group 4A or 14 (b) Group 2A or 2 (c) Group 5A or 15 **8.4** (a) Ru (b) $[\text{Kr}]5s^24d^6$. **8.7** (a) Moving from left to right along the molecule, the first C needs 2 H atoms, the second needs 1, the third needs none, and the fourth needs 1. (b) In order of increasing bond length: $3 < 1 < 2$ (c) In order of increasing bond enthalpy: $2 < 1 < 3$ **8.9** (a) Valence electrons are those that take part in chemical bonding. This usually means the electrons beyond the core noble-gas configuration of the atom, although it is sometimes only the outer-shell electrons. (b) A nitrogen atom has 5 valence electrons. (c) The atom (Si) has 4 valence electrons. **8.11** Si, $1s^22s^22p^63s^23p^2$. The $n = 3$ electrons are valence electrons; the others are nonvalence electrons. Valence electrons participate in chemical bonding; the others do not.

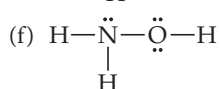
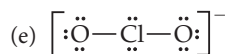
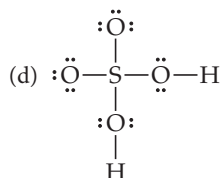
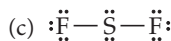
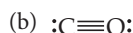
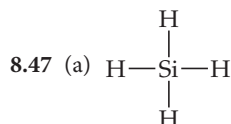


8.17 (a) AlF_3 (b) K_2S (c) Y_2O_3 (d) Mg_3N_2 **8.19** (a) Sr^{2+} , $[\text{Ar}]4s^23d^{10}4p^6 = [\text{Kr}]$, noble-gas configuration (b) Ti^{2+} , $[\text{Ar}]3d^2$ (c) Se^{2-} , $[\text{Ar}]4s^23d^{10}4p^6 = [\text{Kr}]$, noble-gas configuration (d) Ni^{2+} , $[\text{Ar}]3d^8$ (e) Br^- , $[\text{Ar}]4s^23d^{10}4p^6 = [\text{Kr}]$, noble-gas configuration (f) Mn^{3+} , $[\text{Ar}]3d^4$ **8.21** (a) *Lattice energy* is the energy required to totally separate one mole of solid ionic compound into its gaseous ions. (b) The magnitude of the lattice energy depends on the magnitudes of the charges of the two ions, their radii, and the arrangement of ions in the lattice. **8.23** KF, 808 kJ/mol ; CaO, 3414 kJ/mol ; ScN, 7547 kJ/mol . The interionic distances in the three compounds are similar. For compounds with similar ionic separations, the lattice energies should be related as the product of the charges of the ions. The lattice energies above are approximately related as $1 : 4 : 9$. Slight variations are due to the small differences in ionic separations. **8.25** Since the ionic charges are the same in the two compounds, the K—Br and Cs—Cl separations must be approximately equal. **8.27** The large attractive energy between oppositely charged Ca^{2+} and O^{2-} more than compensates for the energy required to form Ca^{2+} and O^{2-} from the neutral atoms. **8.29** The lattice energy of $\text{RbCl}(s)$ is $+692 \text{ kJ/mol}$. This value is smaller than the lattice energy for NaCl because Rb^+ has a larger ionic radius than Na^+ and therefore cannot approach Cl^- as closely as Na^+ can. **8.31** (a) A *covalent bond* is the bond formed when two atoms share one or more pairs of electrons. (b) Any simple compound whose component atoms are nonmetals, such as H_2 , SO_2 , and CCl_4 , are molecular and have covalent bonds between atoms. (c) Covalent, because it is a gas at room temperature and below.

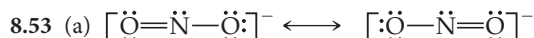
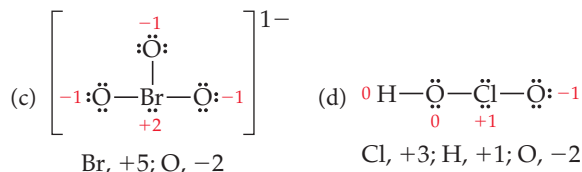
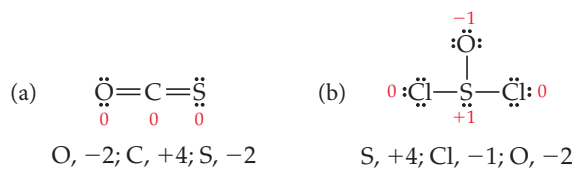
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8.35 (a) $\ddot{\text{O}}=\ddot{\text{O}}$ (b) A double bond is required because there are not enough electrons to satisfy the octet rule with single bonds and unshared pairs. (c) The greater the number of shared electron pairs between two atoms, the shorter the distance between the atoms. An $\text{O}=\text{O}$ double bond is shorter than an $\text{O}-\text{O}$ single bond. 8.37 (a) *Electronegativity* is the ability of an atom in a molecule to attract electrons to itself. (b) The range of electronegativities on the Pauling scale is 0.7–4.0. (c) Fluorine is the most electronegative element. (d) Cesium is the least electronegative element that is not radioactive. 8.39 (a) Mg (b) S (c) C (d) As 8.41 The bonds in (a), (c), and (d) are polar. The more electronegative element in each polar bond is (a) F (c) O (d) I. 8.43 (a) The calculated charge on H and Br is $0.12e$. (b) From Sample Exercise 8.5, the calculated charge on H and Cl in HCl is $0.178e$. HBr has a smaller dipole moment and longer bond length than HCl; these properties both contribute to the smaller charge separation in HBr. 8.45 (a) SiCl_4 , molecular, silicon tetrachloride; LaF_3 , ionic, lanthanum(III) fluoride (b) FeCl_2 , ionic, iron(II) chloride; ReCl_6 , molecular (metal in high oxidation state), rhenium hexachloride. (c) PbCl_4 , molecular (by contrast to the distinctly ionic RbCl), lead tetrachloride; RbCl , ionic, rubidium chloride

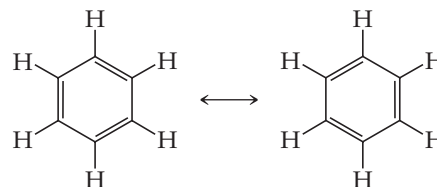


8.49 (a) *Formal charge* is the charge on each atom in a molecule, assuming all atoms have the same electronegativity. (b) Formal charges are not actual charges. They are a bookkeeping system that assumes perfect covalency, one extreme for the possible electron distribution in a molecule. (c) Oxidation numbers are a bookkeeping system that assumes the more electronegative element holds all electrons in a bond. The true electron distribution is some composite of the two extremes. 8.51 Formal charges are shown on the Lewis structures; oxidation numbers are listed below each structure.

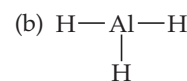
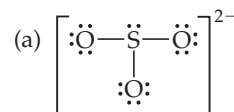


(b) O_3 is isoelectronic with NO_2^- ; both have 18 valence electrons. (c) Since each $\text{N}-\text{O}$ bond has partial double-bond character, the $\text{N}-\text{O}$ bond length in NO_2^- should be shorter than an $\text{N}-\text{O}$ single bond. 8.55 The more electron pairs shared by two atoms, the shorter

the bond. Thus, the $\text{C}-\text{O}$ bond lengths vary in the order $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$. 8.57 (a) Two equally valid Lewis structures can be drawn for benzene.

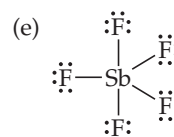
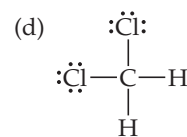
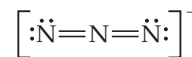
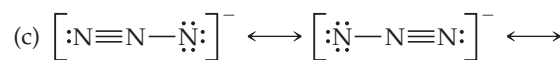


The concept of resonance dictates that the true description of bonding is some hybrid or blend of these two Lewis structures. The most obvious blend of these two resonance structures is a molecule with six equivalent $\text{C}-\text{C}$ bonds with equal lengths. (b) This model predicts a uniform $\text{C}-\text{C}$ bond length that is shorter than a single bond but longer than a double bond. 8.59 (a) The octet rule states that atoms will gain, lose, or share electrons until they are surrounded by eight valence electrons. (b) The octet rule applies to atoms in a covalent compound and the individual ions in an ionic compound. In the covalent compound CCl_4 , the atoms share electrons in order to surround themselves with an octet. In the ionic compound MgCl_2 , Mg loses $2 e^-$ to become Mg^{2+} with the electron configuration of Ne. Each Cl atom gains one electron to form Cl^- with the electron configuration of Ar. 8.61 No chlorine oxide will obey the octet rule. Chlorine has seven valence electrons, and oxygen has six. For neutral chlorine oxides, regardless of the number of oxygen atoms in the molecule, the total number of valence electrons will be an (odd + even) sum, which is always an odd number. 8.63

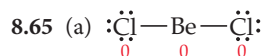


Other resonance structures that minimize formal charges but violate the octet rule can be drawn. The octet rule versus formal charge debate is ongoing.

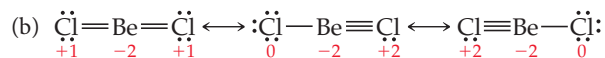
6 electrons around Al



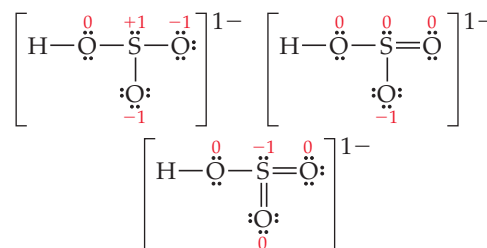
10 electrons around Sb



This structure violates the octet rule.

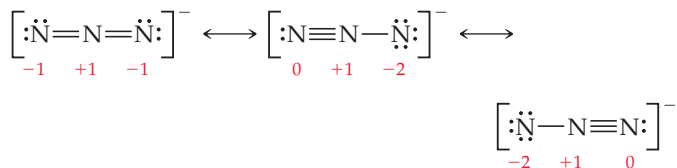


(c) Formal charges are minimized on the structure that violates the octet rule; this form is probably dominant. 8.67 Three resonance structures for HSO_3^- are shown here. Because the ion has a $1-$ charge, the sum of the formal charges of the atoms is -1 .



The structure with no double bonds obeys the octet rule for all atoms, but does not lead to minimized formal charges. The structures with one and two double bonds both minimize formal charge but do not obey the octet rule. Of these two, the structure with one double bond is preferred because the formal charge is localized on the more electronegative oxygen atom.

8.69 (a) $\Delta H = -304$ kJ (b) $\Delta H = -82$ kJ (c) $\Delta H = -467$ kJ
8.71 (a) $\Delta H = -321$ kJ (b) $\Delta H = -103$ kJ (c) $\Delta H = -203$ kJ
8.73 (a) -97 kJ; exothermic (b) The ΔH calculated from bond enthalpies (-97 kJ) is slightly more exothermic (more negative) than that obtained using ΔH_f° values (-92.38 kJ). **8.75** The average Ti—Cl bond enthalpy is 430 kJ/mol. **8.77** (a) Six (nonradioactive) elements. Yes, they are in the same family, assuming H is placed with the alkali metals. The Lewis symbol represents the number of valence electrons of an element, and all elements in the same family have the same number of valence electrons. By definition of a family, all elements with the same Lewis symbol must be in the same family. **8.81** The charge on M is likely to be $3+$. The range of lattice energies for ionic compounds with the general formula MX and a charge of $2+$ on the metal is $3\text{--}4 \times 10^3$ kJ/mol. The lattice energy of 6×10^3 kJ/mol indicates that the charge on M must be greater than $2+$. **8.85** (a) B—O. The most polar bond will be formed by the two elements with the greatest difference in electronegativity. (b) Te—I. These elements have the two largest covalent radii among this group. (c) TeI₂. The octet rule is satisfied for all three atoms. (d) P₂O₃. Each P atom needs to share $3e^-$ and each O atom $2e^-$ to achieve an octet. And B₂O₃. Although this is not a purely ionic compound, it can be understood in terms of gaining and losing electrons to achieve a noble-gas configuration. If each B atom were to lose $3e^-$ and each O atom were to gain $2e^-$, charge balance and the octet rule would be satisfied. **8.90** (a) $+1$ (b) -1 (c) $+1$ (assuming the odd electron is on N) (d) 0 (e) $+3$ **8.95** An experimentally determined molecular structure will reveal bond lengths and angles of the B—A=B molecule. If resonance structures are important, the two B—A bond lengths will be identical. If the molecule features one single and one double bond, the lengths will be significantly different. **8.98** (a) $\Delta H = 7.85$ kJ/g nitroglycerine (b) $4C_7H_5N_3O_6(s) \rightarrow 6N_2(g) + 7CO_2(g) + 10H_2O(g) + 21C(s)$
8.101 (a) Ti²⁺, [Ar]3d²; Ca, [Ar]4s². Yes. The 2 valence electrons in Ti²⁺ and Ca are in different principal quantum levels and different subshells. (b) In Ca the 4s is lower in energy than the 3d, while in Ti²⁺ the 3d is lower in energy than the 4s. (c) No. There is only one 4s orbital, so the 2 valence electrons in Ca are paired; there are 5 degenerate 3d orbitals, so the 2 valence electrons in Ti²⁺ are unpaired. **8.107** (a) Azide ion is N₃⁻. (b) Resonance structures with formal charges are shown.



(c) The structure with two double bonds minimizes formal charges and is probably the main contributor. (d) The N—N distances will be equal and have the approximate length of a N—N double bond, 1.24 Å. **8.112** (a) D(Br—Br)(l) = 223.6 kJ; D(Br—Br)(g) = 193 kJ (b) D(C—Cl)(l) = 336.1 kJ; D(C—Cl)(g) = 328 kJ (c) D(O—O)(l) = 192.7 kJ; D(O—O)(g) = 146 kJ (d) Breaking bonds in the liquid requires more energy than breaking bonds in the gas phase. Bond dissociation in the liquid phase can be thought of in two steps, vaporization of the liquid followed by bond dissociation in the gas phase. The greater bond dissociation enthalpy in the liquid phase is due to the contribution from the enthalpy of vaporization.

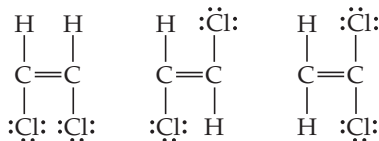
CHAPTER 9

9.1 Removing an atom from the equatorial plane of the trigonal bipyramid in Figure 9.3 creates a seesaw shape. **9.3** (a) 2 electron-domain geometries, linear and trigonal bipyramidal (b) 1 electron-domain

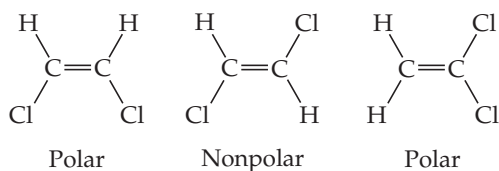
geometry, trigonal bipyramidal (c) 1 electron-domain geometry, octahedral (c) 1 electron-domain geometry, octahedral (d) 1 electron domain geometry, octahedral (e) 1 electron domain geometry, octahedral (f) 1 electron-domain geometry, trigonal bipyramidal (This triangular pyramid is an unusual molecular geometry not listed in Table 9.3. It could occur if the equatorial substituents on the trigonal bipyramid were extremely bulky, causing the nonbonding electron pair to occupy an axial position.) **9.5** (a) Zero energy corresponds to two separate, noninteracting Cl atoms. This infinite Cl—Cl distance is beyond the right extreme of the horizontal axis on the diagram. (b) According to the valence bond model, valence orbitals on the approaching atoms overlap, allowing two electrons to mutually occupy space between the two nuclei and be stabilized by two nuclei rather than one. (c) The Cl—Cl distance at the energy minimum on the plot is the Cl—Cl bond length. (d) At interatomic separations shorter than the bond distance, the two nuclei begin to repel each other, increasing the overall energy of the system. (e) The y -coordinate of the minimum point on the plot is a good estimate of the Cl—Cl bond energy or bond strength. **9.6** SiCl₄, 109° ; PF₃, 107° ; SF₂, 105° . Each molecule has tetrahedral electron domain geometry, but the number of nonbonding electron pairs increases from 0 to 2, respectively. Because nonbonding electron pairs occupy more space than bonding pairs, we expect the bond angles to decrease in the series. **9.9** (a) i, Two s atomic orbitals; ii, two p atomic orbitals overlapping end to end; iii, two p atomic orbitals overlapping side to side (b) i, σ -type MO; ii, σ -type MO; iii, π -type MO (c) i, antibonding; ii, bonding; iii, antibonding (d) i, the nodal plane is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. ii, there are two nodal planes; both are perpendicular to the interatomic axis. One is left of the left atom and the second is right of the right atom. iii, there are two nodal planes; one is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. The second contains the interatomic axis and is perpendicular to the first. **9.11** (a) Yes. The stated shape defines the bond angle and the bond length tells the size. (b) No. Atom A could have 2, 3, or 4 nonbonding electron pairs. **9.13** A molecule with tetrahedral molecular geometry has an atom at each vertex of the tetrahedron. A trigonal-pyramidal molecule has one vertex of the tetrahedron occupied by a nonbonding electron pair rather than an atom. **9.15** (a) An *electron domain* is a region in a molecule where electrons are most likely to be found. (b) Like the balloons in Figure 9.5, each electron domain occupies a finite volume of space, so they also adopt an arrangement where repulsions are minimized. **9.17** (a) The number of electron domains in a molecule or ion is the number of bonds (double and triple bonds count as one domain) plus the number of nonbonding electron pairs. (b) A *bonding electron domain* is a region between two bonded atoms that contains one or more pairs of bonding electrons. A *nonbonding electron domain* is localized on a single atom and contains one pair of nonbonding electrons. **9.19** (a) No effect on molecular shape (b) 1 nonbonding pair on P influences molecular shape (c) no effect (d) no effect (e) 1 nonbonding pair on S influences molecular shape **9.21** (a) 2 (b) 1 (c) none (d) 3 **9.23** The electron-domain geometry indicated by VSEPR describes the arrangement of all bonding and nonbonding electron domains. The molecular geometry describes just the atomic positions. In H₂O there are 4 electron domains around oxygen, so the electron-domain geometry is tetrahedral. Because there are 2 bonding and 2 nonbonding domains, the molecular geometry is bent. We make this distinction because all electron domains must be considered when describing the atomic arrangement and bond angles in a molecule but the molecular geometry or shape is a description of just the atom positions. **9.25** (a) Tetrahedral, tetrahedral (b) trigonal bipyramidal, T-shaped (c) octahedral, square pyramidal (d) octahedral, square planar **9.27** (a) Linear, linear (b) tetrahedral, trigonal pyramidal (c) trigonal bipyramidal, seesaw (d) octahedral, octahedral (e) tetrahedral, tetrahedral (f) linear, linear **9.29** (a) i, trigonal planar; ii, tetrahedral; iii, trigonal bipyramidal (b) i, 0; ii, 1; iii, 2 (c) N and P (d) Cl (or Br or I). This T-shaped molecular geometry arises from a trigonal-bipyramidal electron-domain geometry with 2 nonbonding domains. Assuming each F atom has 3 nonbonding domains and forms only single bonds with A, A must have 7 valence electrons and be in or below the third row of the periodic table

to produce these electron-domain and molecular geometries. **9.31** (a) 1–109°, 2–109° (b) 3–109°, 4–109° (c) 5–180° (d) 6–120°, 7–109°, 8–109° **9.33** The two molecules with trigonal-bipyramidal electron-domain geometry, PF₅ and SF₆, have more than one F—A—F bond angle. **9.35** (a) Although both ions have 4 bonding electron domains, the 6 total domains around Br require octahedral domain geometry and square-planar molecular geometry, while the 4 total domains about B lead to tetrahedral domain and molecular geometry. (b) The less electronegative the central atom, the larger the non-bonding electron domain, and the greater the effect of repulsive forces on adjacent bonding domains. The less electronegative the central atom, the greater the deviation from ideal tetrahedral angles. The angles will vary as H₂O > H₂S > H₂Se. **9.37** A bond dipole is the asymmetric charge distribution between two bonded atoms with unequal electronegativities. A molecular dipole moment is the three-dimensional sum of all the bond dipoles in a molecule. **9.39** (a) Yes. The net dipole moment vector points along the Cl—S—Cl angle bisector. (b) No, BeCl₂ does not have a dipole moment. **9.41** (a) In Exercise 9.29, molecules (ii) and (iii) will have nonzero dipole moments. Molecule (i) has no nonbonding electron pairs on A, and the 3 A—F bond dipoles are oriented so that they cancel. Molecules (ii) and (iii) have nonbonding electron pairs on A and their bond dipoles do not cancel. (b) In Exercise 9.30, molecules (i) and (ii) have a zero dipole moment. **9.43** (a) IF (d) PCl₃ and (f) IF₅ are polar.

9.45 (a) Lewis structures



Molecular geometries



(b) The middle isomer has a zero net dipole moment. (c) C₂H₃Cl has only one isomer, and it has a dipole moment. **9.47** (a) *Orbital overlap* occurs when valence atomic orbitals on two adjacent atoms share the same region of space. (b) A chemical bond is a concentration of electron density between the nuclei of two atoms. This concentration can take place because orbitals on the two atoms overlap. **9.49** (a) H—Mg—H, linear electron domain and molecular geometry (b) The linear electron-domain geometry in MgH₂ requires *sp* hybridization.

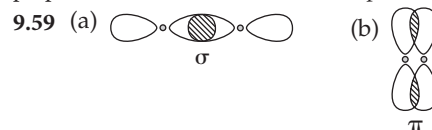


9.51

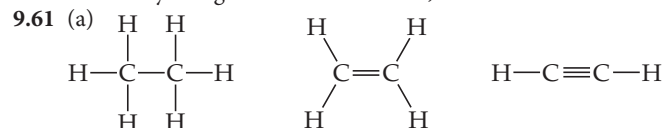
Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO ₂	Linear	<i>sp</i>	No
NH ₃	Tetrahedral	<i>sp</i> ³	Yes
CH ₄	Tetrahedral	<i>sp</i> ³	No
BH ₃	Trigonal planar	<i>sp</i> ²	No
SF ₄	Trigonal bipyramidal	Not applicable	Yes
SF ₆	Octahedral	Not applicable	No
H ₂ CO	Trigonal planar	<i>sp</i> ²	Yes
PF ₅	Trigonal bipyramidal	Not applicable	No
XeF ₂	Trigonal bipyramidal	Not applicable	No

9.53 (a) B, [He]2s²2p¹. One 2s electron is “promoted” to an empty 2p orbital. The 2s and two 2p orbitals that each contain one electron are

hybridized to form three equivalent hybrid orbitals in a trigonal-planar arrangement. (b) *sp*² (d) A single 2p orbital is unhybridized. It lies perpendicular to the trigonal plane of the *sp*² hybrid orbitals. **9.55** (a) *sp*² (b) *sp*³ (c) *sp* (d) *sp*³ **9.57** No hybrid orbitals discussed in this chapter form angles of 90° with each other; *p* atomic orbitals are perpendicular to each other. 109.5°, *sp*³; 120°, *sp*²

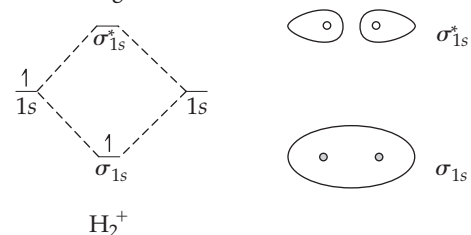


(c) A σ bond is generally stronger than a π bond because there is more extensive orbital overlap. (d) No. Overlap of two *s* orbitals results in electron density along the internuclear axis, while a π bond has none.



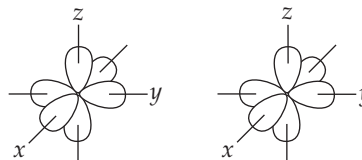
(b) *sp*³, *sp*², *sp* (c) nonplanar, planar, planar (d) 7 σ , 0 π ; 5 σ , 1 π ; 3 σ , 2 π (e) The Si analogs would have the same hybridization as the C compounds given in part (b). That Si is in the row below C means it has a larger bonding atomic radius and atomic orbitals than C. The close approach of Si atoms required to form strong, stable π bonds in Si₂H₄ and Si₂H₂ is not possible and these Si analogs do not readily form. **9.63** (a) 18 valence electrons (b) 16 valence electrons form σ bonds. (c) 2 valence electrons form π bonds. (d) No valence electrons are nonbonding. (e) The left and central C atoms are *sp*² hybridized; the right C atom is *sp*³ hybridized. **9.65** (a) ~109° about the leftmost C, *sp*³; ~120° about the right-hand C, *sp*² (b) The doubly bonded O can be viewed as *sp*², and the other as *sp*³; the nitrogen is *sp*³ with approximately 109° bond angles. (c) nine σ bonds, one π bond **9.67** (a) In a localized π bond, the electron density is concentrated between the two atoms forming the bond. In a delocalized π bond, the electron density is spread over all the atoms that contribute *p* orbitals to the network.

(b) The existence of more than one resonance form is a good indication that a molecule will have delocalized π bonding. (c) delocalized **9.69** (a) Linear (b) The two central C atoms each have trigonal planar geometry with ~120° bond angles about them. The C and O atoms lie in a plane with the H atoms free to rotate in and out of this plane. (c) The molecule is planar with ~120° bond angles about the two N atoms. **9.71** (a) Hybrid orbitals are mixtures of atomic orbitals from a single atom and remain localized on that atom. Molecular orbitals are combinations of atomic orbitals from two or more atoms and are delocalized over at least two atoms. (b) Each MO can hold a maximum of two electrons. (c) Antibonding molecular orbitals can have electrons in them. **9.73** (a)



(b) There is one electron in H₂⁺. (c) σ_{1s}^1 (d) BO = $\frac{1}{2}$ (e) Fall apart. If the single electron in H₂⁺ is excited to the σ_{1s}^* orbital, its energy is higher than the energy of an H 1s atomic orbital and H₂⁺ will decompose into a hydrogen atom and a hydrogen ion.

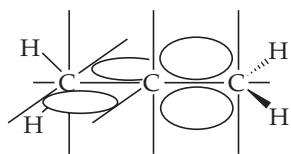
9.75



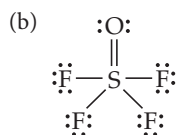
(a) 1 σ bond (b) 2 π bonds (c) 1 σ^* and 2 π^* **9.77** (a) When comparing the same two bonded atoms, bond order and bond energy are

directly related, while bond order and bond length are inversely related. When comparing different bonded nuclei, there are no simple relationships. (b) Be_2 is not expected to exist; it has a bond order of zero and is not energetically favored over isolated Be atoms. Be_2^+ has a bond order of 0.5 and is slightly lower in energy than isolated Be atoms. It will probably exist under special experimental conditions.

9.79 (a, b) Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called *diamagnetism*. (c) O_2^{2-} , Be_2^{2+} **9.81** (a) B_2^+ , $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^1$, increase (b) Li_2^+ , $\sigma_{1s}^2\sigma_{1s}^*\sigma_{2s}^1$, increase (c) N_2^+ , $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^4\sigma_{2p}^1$, increase (d) Ne_2^{2+} , $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^4\pi_{2p}^4$, decrease **9.83** CN, $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^2\pi_{2p}^3$, bond order = 2.5; CN^+ , $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^2\pi_{2p}^2$, bond order = 2.0; CN^- , $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^2\pi_{2p}^4$, bond order = 3.0. (a) CN^- (b) CN, CN^+ **9.85** (a) $3s, 3p_x, 3p_y, 3p_z$ (b) π_{3p} (c) 2 (d) If the MO diagram for P_2 is similar to that of N_2 , P_2 will have no unpaired electrons and be diamagnetic. **9.89** SiF_4 is tetrahedral, SF_4 is seesaw, XeF_4 is square planar. The shapes are different because the number of nonbonding electron domains is different in each molecule, even though all have four bonding electron domains. Bond angles and thus molecular shape are determined by the total number of electron domains. **9.92** (a) 2 σ bonds, 2 π bonds (b) 3 σ bonds, 4 π bonds (c) 3 σ bonds, 1 π bond (d) 4 σ bonds, 1 π bond **9.94** BF_3 is trigonal planar, the B—F bond dipoles cancel and the molecule is nonpolar. PF_3 has a tetrahedral electron-domain geometry with one position occupied by a nonbonding electron pair. The nonbonding electron pair ensures an asymmetrical electron distribution and the molecule is polar. **9.99**



(a) The molecule is nonplanar. (b) Allene has no dipole moment. (c) The bonding in allene would not be described as delocalized. The π electron clouds of the two adjacent $\text{C}=\text{C}$ are mutually perpendicular, so there is no overlap and no delocalization of π electrons. **9.101** (a) All O atoms have sp^2 hybridization. (b) The two σ bonds are formed by overlap of sp^2 hybrid orbitals, the π bond is formed by overlap of atomic p orbitals, one nonbonded pair is in a p atomic orbital and the other five nonbonded pairs are in sp^2 hybrid orbitals. (c) unhybridized p atomic orbitals (d) four, two from the π bond and two from the nonbonded pair in the p atomic orbital **9.104** $\sigma_{2s}^2\sigma_{2s}^*\sigma_{2p}^4\sigma_{2p}^1\pi_{2p}^*1$ (a) Paramagnetic (b) The bond order of N_2 in the ground state is 3; in the first excited state it has a bond order of 2. Owing to the reduction in bond order, N_2 in the first excited state has a weaker N—N bond. **9.110** (a) $2\text{SF}_4(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{OSF}_4(\text{g})$



(c) $\Delta H = -551 \text{ kJ}$, exothermic (d) The electron-domain geometry is trigonal bipyramidal. The O atom can be either equatorial or axial. (e) Since F is more electronegative than O, the structure that minimizes 90°F—S—F angles, the one with O axial, is preferred.

CHAPTER 10

10.1 It would be much easier to drink from a straw on Mars. When a straw is placed in a glass of liquid, the atmosphere exerts equal pressure inside and outside the straw. When we drink through a straw, we withdraw air, thereby reducing the pressure on the liquid inside. If only 0.007 atm is exerted on the liquid in the glass, a very small reduction in pressure inside the straw will cause the liquid to rise. **10.4** (a) As the reaction proceeds at constant temperature and pressure, the number of particles decreases and the container volume decreases. (b) As the reaction proceeds at constant volume and temperature, the number of particles decreases and pressure decreases. **10.7** (a) $P_{\text{red}} < P_{\text{yellow}} < P_{\text{blue}}$

(b) $P_{\text{red}} = 0.28 \text{ atm}$; $P_{\text{yellow}} = 0.42 \text{ atm}$; $P_{\text{blue}} = 0.70 \text{ atm}$ **10.10** (a) $P(\text{ii}) < P(\text{i}) = P(\text{iii})$ (b) $P_{\text{He}}(\text{iii}) < P_{\text{He}}(\text{ii}) < P_{\text{He}}(\text{i})$ (c) $d(\text{ii}) < d(\text{i}) < d(\text{iii})$ (d) The average kinetic energies of the particles in the three containers are equal. **10.13** (a) A gas is much less dense than a liquid. (b) A gas is much more compressible than a liquid. (c) All mixtures of gases are homogenous. Similar liquid molecules form homogeneous mixtures, while very dissimilar molecules form heterogeneous mixtures. (d) Both gases and liquids conform to the shape of their container. A gas also adopts the volume of its container, while a liquid maintains its own volume. **10.15** (a) $1.8 \times 10^3 \text{ kPa}$ (b) 18 atm (c) $2.6 \times 10^2 \text{ lb/in.}^2$ **10.17** (a) 10.3 m (b) 2.1 atm **10.19** (a) The tube can have any cross-sectional area. (b) At equilibrium the force of gravity per unit area acting on the mercury column is not equal to the force of gravity per unit area acting on the atmosphere. (c) The column of mercury is held up by the pressure of the atmosphere applied to the exterior pool of mercury. (d) If you took the mercury barometer with you on a trip from the beach to high mountains, the height of the mercury column would decrease with elevation. **10.21** (a) 0.349 atm (b) 265 mm Hg (c) $3.53 \times 10^4 \text{ Pa}$ (d) 0.353 bar (e) 5.13 psi **10.23** (a) $P = 773.4 \text{ torr}$ (b) $P = 1.018 \text{ atm}$ (c) The pressure in Chicago is greater than standard atmospheric pressure, and so it makes sense to classify this weather system as a “high-pressure system.” **10.25** (i) 0.31 atm (ii) 1.88 atm (iii) 0.136 atm **10.27** (a) If V decreases by a factor of 4, P increases by a factor of 4. (b) If T decreases by a factor of 2, P decreases by a factor of 2. (c) If n decreases by a factor of 4, P decreases by a factor of 4. **10.29** (a) If equal volumes of gases at the same temperature and pressure contain equal numbers of molecules and molecules react in the ratios of small whole numbers, it follows that the volumes of reacting gases are in the ratios of small whole numbers. (b) Since the two gases are at the same temperature and pressure, the ratio of the numbers of atoms is the same as the ratio of volumes. There are 1.5 times as many Xe atoms as Ne atoms. (c) Yes. By definition, one mole of an ideal gas contains Avogadro’s number of particles. At a given temperature and pressure, equal numbers of particles occupy the same volume, so one mole of an ideal gas will always occupy the same volume at the given temperature and pressure. **10.31** (a) An ideal gas exhibits pressure, volume, and temperature relationships described by the equation $PV = nRT$. (b) Boyle’s law, $V = \text{constant}/P$; Charles’s law, $V = \text{constant} \times T$; Avogadro’s law, $V = \text{constant} \times n$. Collect all the equalities: $V = (\text{constant} \times T \times n)/P$. Call the constant R and multiply both sides of the equation by P , $PV = nRT$. (c) $PV = nRT$; P in atmospheres, V in liters, n in moles, T in kelvins. (d) $R = 0.08315 \text{ L}\cdot\text{bar}/\text{mol}\cdot\text{K}$. **10.33** Flask A contains the gas with $\mathcal{M} = 30 \text{ g/mol}$, and flask B contains the gas with $\mathcal{M} = 60 \text{ g/mol}$.

10.35

P	V	n	T
2.00 atm	1.00 L	0.500 mol	48.7 K
0.300 atm	0.250 L	$3.05 \times 10^{-3} \text{ mol}$	27 °C
650 torr	11.2 L	0.333 mol	350 K
10.3 atm	585 mL	0.250 mol	295 K

10.37 $8.2 \times 10^2 \text{ kg He}$ **10.39** (a) 5.15×10^{22} molecules (b) 6.5 kg air **10.41** (a) 91 atm (b) $2.3 \times 10^2 \text{ L}$ **10.43** (a) 29.8 g Cl_2 (b) 9.42 L (c) 501 K (d) 2.28 atm **10.45** (a) $n = 2 \times 10^{-4} \text{ mol O}_2$ (b) The roach needs $8 \times 10^{-3} \text{ mol O}_2$ in 48 h, approximately 100% of the O_2 in the jar. **10.47** (a) $1.32 \times 10^7 \text{ L}$ (b) $5.1 \times 10^8 \text{ mol Hg}$ **10.49** For gas samples at the same conditions, molar mass determines density. Of the three gases listed, (c) Cl_2 has the largest molar mass. **10.51** (c) Because the helium atoms are of lower mass than the average air molecule, the helium gas is less dense than air. The balloon thus weighs less than the air displaced by its volume. **10.53** (a) $d = 1.77 \text{ g/L}$ (b) $\mathcal{M} = 80.1 \text{ g/mol}$ **10.55** $\mathcal{M} = 89.4 \text{ g/mol}$ **10.57** $4.1 \times 10^{-9} \text{ g Mg}$ **10.59** (a) 21.4 L CO_2 (b) 40.7 L O_2 **10.61** 0.402 g Zn **10.63** (a) When the stopcock is opened, the volume occupied by $\text{N}_2(\text{g})$ increases from 2.0 L to 5.0 L. $P_{\text{N}_2} = 0.40 \text{ atm}$ (b) When the gases mix, the volume of $\text{O}_2(\text{g})$ increases from 3.0 L to 5.0 L. $P_{\text{O}_2} = 1.2 \text{ atm}$ (c) $P_t = 1.6 \text{ atm}$

10.65 (a) $P_{\text{He}} = 1.87 \text{ atm}$, $P_{\text{Ne}} = 0.807 \text{ atm}$, $P_{\text{Ar}} = 0.269 \text{ atm}$, (b) $P_t = 2.95 \text{ atm}$ **10.67** $\chi_{\text{CO}_2} = 0.00039$ **10.69** $P_{\text{CO}_2} = 0.305 \text{ atm}$, $P_t = 1.232 \text{ atm}$ **10.71** $P_{\text{N}_2} = 1.3 \text{ atm}$, $P_{\text{O}_2} = 0.54 \text{ atm}$, $P_{\text{CO}_2} = 0.27 \text{ atm}$ **10.73** 2.5 mole % O_2 **10.75** $P_t = 2.47 \text{ atm}$ **10.77** (a) Increase in temperature at constant volume or decrease in volume or increase in pressure (b) decrease in temperature (c) increase in volume, decrease in pressure (d) increase in temperature **10.79** The fact that gases are readily compressible supports the assumption that most of the volume of a gas sample is empty space. **10.81** Average speed is the sum of the speeds of all particles divided by the total number of particles. The root mean square speed is the speed of a molecule with the same kinetic energy as the average kinetic energy of the sample. The root mean square speed is larger for a given gas sample at a fixed temperature, but the difference between the two is small. **10.83** (a) Average kinetic energy of the molecules increases. (b) Root mean square speed of the molecules increases. (c) Strength of an average impact with the container walls increases. (d) Total collisions of molecules with walls per second increases. **10.85** (a) In order of increasing speed and decreasing molar mass: $\text{HBr} < \text{NF}_3 < \text{SO}_2 < \text{CO} < \text{Ne}$ (b) $u_{\text{NF}_3} = 324 \text{ m/s}$ (c) The most probable speed of an ozone molecule in the stratosphere is 306 m/s. **10.87** Effusion is the escape of gas molecules through a tiny hole. Diffusion is the distribution of a gas throughout space or throughout another substance. **10.89** The order of increasing rate of effusion is ${}^2\text{H}^{37}\text{Cl} < {}^1\text{H}^{37}\text{Cl} < {}^2\text{H}^{35}\text{Cl} < {}^1\text{H}^{35}\text{Cl}$. **10.91** As_4S_6 **10.93** (a) Non-ideal-gas behavior is observed at very high pressures and low temperatures. (b) The real volumes of gas molecules and attractive intermolecular forces between molecules cause gases to behave nonideally. (c) According to the ideal-gas law, the ratio PV/RT should be constant for a given gas sample at all combinations of pressure, volume, and temperature. If this ratio changes with increasing pressure, the gas sample is not behaving ideally. **10.95** Ar ($a = 1.34$, $b = 0.0322$) will behave more like an ideal gas than CO_2 ($a = 3.59$, $b = 0.427$) at high pressures. **10.97** (a) $P = 4.89 \text{ atm}$ (b) $P = 4.69 \text{ atm}$ (c) Qualitatively, molecular attractions are more important as the amount of free space decreases and the number of molecular collisions increases. Molecular volume is a larger part of the total volume as the container volume decreases. **10.99** From the value of b for Xe, the nonbonding radius is 2.72 Å. From Figure 7.6, the bonding atomic radius of Xe is 1.30 Å. We expect the bonding radius of an atom to be smaller than its nonbonding radius, but this difference is quite large. **10.101** $V = 3.1 \text{ mm}^3$ **10.105** (a) 13.4 mol $\text{C}_3\text{H}_8(\text{g})$ (b) $1.47 \times 10^3 \text{ mol C}_3\text{H}_8(\text{l})$ (c) The ratio of moles liquid to moles gas is 110. Many more molecules and moles of liquid fit in a container of fixed volume because there is much less space between molecules in the liquid phase. **10.108** $P_t = 5.3 \times 10^2 \text{ torr}$ **10.111** 42.2 g O_2 **10.115** $T_2 = 687^\circ\text{C}$ **10.120** (a) $P(\text{ideal}) = 177 \text{ atm}$ (b) $P(\text{van der Waals}) = 187.4 \text{ atm}$ (c) Under the conditions of this problem (large number of moles of gas), the correction for the real volume of molecules dominates. **10.123** (a) 44.58% C, 6.596% H, 16.44% Cl, 32.38% N (b) $\text{C}_8\text{H}_{14}\text{N}_5\text{Cl}$ (c) Molar mass of the compound is required in order to determine molecular formula when the empirical formula is known. **10.128** (a) $5.02 \times 10^8 \text{ L CH}_3\text{OH}(\text{l})$ (b) $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$, $\Delta H^\circ = -890.4 \text{ kJ}$; ΔH for combustion of the methane is $-1.10 \times 10^{13} \text{ kJ}$. $\text{CH}_3\text{OH}(\text{l}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$, $\Delta H^\circ = -726.6 \text{ kJ}$; ΔH for combustion of the methanol is $-9.00 \times 10^{12} \text{ kJ}$. (c) The enthalpy change upon combustion of 1.00 L of $\text{CH}_4(\text{l})$ is $-2.59 \times 10^4 \text{ kJ}$ and for 1.00 L of $\text{CH}_3\text{OH}(\text{l})$, $-1.79 \times 10^4 \text{ kJ}$. Clearly $\text{CH}_4(\text{l})$ has the higher enthalpy of combustion per unit volume.

CHAPTER 11

11.1 The diagram best describes a liquid. The particles are close together, mostly touching, but there is no regular arrangement or order. This rules out a gaseous sample, where the particles are far apart, and a crystalline solid, which has a regular repeating structure in all three directions. **11.4** (a) In its final state, methane is a gas at 185°C . **11.5** (a) 385 mm Hg (b) 22°C (c) 47°C **11.6** The stronger the inter-

molecular forces, the higher the boiling point of a liquid. Propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, has hydrogen bonding and the higher boiling point. **11.7** (a) Normal boiling point, 360 K; normal freezing point, 260 K (b) (i) gas (ii) solid (iii) liquid (c) The triple point is approximately 185 K at 0.45 atm. **11.9** (a) Solid < liquid < gas (b) gas < liquid < solid (c) Matter in the gaseous state is most easily compressed because particles are far apart and there is much empty space. **11.11** $\text{Ar} < \text{CCl}_4 < \text{Si}$ **11.13** (a) The molar volumes of Cl_2 and NH_3 are nearly the same because they are both gases. (b) On cooling to 160 K, both compounds condense from the gas phase to the solid-state, so we expect a significant decrease in the molar volume. (c) The molar volumes are 0.0351 L/mol Cl_2 and 0.0203 L/mol NH_3 (d) Solid-state molar volumes are not as similar as those in the gaseous state, because most of the empty space is gone and molecular characteristics determine properties. $\text{Cl}_2(\text{s})$ is heavier, has a longer bond distance and weaker intermolecular forces, so it has a significantly larger molar volume than $\text{NH}_3(\text{s})$. (e) There is little empty space between molecules in the liquid state, so we expect their molar volumes to be closer to those in the solid state than those in the gaseous state. **11.15** (a) London dispersion forces (b) dipole-dipole and London dispersion forces (c) dipole-dipole forces and in certain cases hydrogen bonding **11.17** (a) SO_2 , dipole-dipole and London dispersion forces (b) CH_3COOH , London dispersion, dipole-dipole, and hydrogen bonding (c) H_2Se , dipole-dipole and London dispersion forces (but not hydrogen bonding) **11.19** (a) *Polarizability* is the ease with which the charge distribution in a molecule can be distorted to produce a transient dipole. (b) Sb is most polarizable because its valence electrons are farthest from the nucleus and least tightly held. (c) in order of increasing polarizability: $\text{CH}_4 < \text{SiH}_4 < \text{SiCl}_4 < \text{GeCl}_4 < \text{GeBr}_4$ (d) The magnitudes of London dispersion forces and thus the boiling points of molecules increase as polarizability increases. The order of increasing boiling points is the order of increasing polarizability given in (c). **11.21** (a) H_2S (b) CO_2 (c) GeH_4 **11.23** Both rodlike butane molecules and spherical 2-methylpropane molecules experience dispersion forces. The larger contact surface between butane molecules facilitates stronger forces and produces a higher boiling point. **11.25** (a) A molecule must contain H atoms, bound to either N, O, or F atoms, in order to participate in hydrogen bonding with like molecules. (b) CH_3NH_2 and CH_3OH **11.27** (a) Replacing a hydroxyl hydrogen with a CH_3 group eliminates hydrogen bonding in that part of the molecule. This reduces the strength of intermolecular forces and leads to a lower boiling point. (b) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ is a larger, more polarizable molecule with stronger London dispersion forces and thus a higher boiling point.

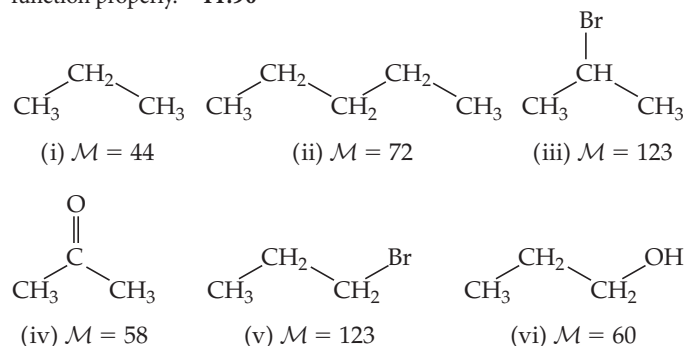
11.29

Physical Property	H_2O	H_2S
Normal boiling point, $^\circ\text{C}$	100.00	-60.7
Normal melting point, $^\circ\text{C}$	0.00	-85.5

(a) Based on its much higher normal melting point and boiling point, H_2O has much stronger intermolecular forces. H_2O has hydrogen bonding, while H_2S has dipole-dipole forces. (b) H_2S is probably a typical compound with less empty space in the ordered solid than the liquid, so that the solid is denser than the liquid. For H_2O , maximizing the number of hydrogen bonds to each molecule in the solid requires more empty space than in the liquid, and the solid is less dense. (c) Specific heat is the energy required to raise the temperature of one gram of the substance one degree Celsius. Hydrogen bonding in water is such a strong attractive interaction that the energy required to disrupt it and increase molecular motion is large. **11.31** SO_4^{2-} has a greater negative charge than BF_4^- , so ion-ion electrostatic attractions are greater in sulfate salts and they are less likely to form liquids. **11.33** (a) As temperature increases, the number of molecules with sufficient kinetic energy to overcome intermolecular attractive forces increases, and viscosity and surface tension decrease. (b) The same attractive forces that cause surface molecules to be difficult to separate

(high surface tension) cause molecules elsewhere in the sample to resist movement relative to each other (high viscosity). **11.35** (a) CHBr_3 has a higher molar mass, is more polarizable, and has stronger dispersion forces, so the surface tension is greater. (b) As temperature increases, the viscosity of the oil decreases because the average kinetic energy of the molecules increases. (c) Adhesive forces between polar water and nonpolar car wax are weak, so the large surface tension of water draws the liquid into the shape with the smallest surface area, a sphere. (d) Adhesive forces between nonpolar oil and nonpolar car wax are similar to cohesive forces in oil, so the oil drops spread out on the waxed car hood. **11.37** (a) The three molecules have similar structures and experience the same types of intermolecular forces. As molar mass increases, the strength of dispersion forces increases and the boiling points, surface tension, and viscosities all increase. (b) Ethylene glycol has an $-\text{OH}$ group at both ends of the molecule. This greatly increases the possibilities for hydrogen bonding; the overall intermolecular attractive forces are greater and the viscosity of ethylene glycol is much greater. (c) Water has the highest surface tension but lowest viscosity because it is the smallest molecule in the series. There is no hydrocarbon chain to inhibit their strong attraction to molecules in the interior of the drop, resulting in high surface tension. The absence of an alkyl chain also means the molecules can move around each other easily, resulting in the low viscosity. **11.39** (a) Melting, endothermic (b) evaporation, endothermic (c) deposition, exothermic (d) condensation, exothermic **11.41** Melting does not require separation of molecules, so the energy requirement is smaller than for vaporization, where molecules must be separated. **11.43** $2.3 \times 10^3 \text{ g H}_2\text{O}$ **11.45** (a) 39.3 kJ (b) 60 kJ **11.47** (a) The critical pressure is the pressure required to cause liquefaction at the critical temperature. (b) As the force of attraction between molecules increases, the critical temperature of the compound increases. (c) All the gases in Table 11.5 can be liquefied at the temperature of liquid nitrogen, given sufficient pressure. **11.49** (a) No effect (b) no effect (c) Vapor pressure decreases with increasing intermolecular attractive forces because fewer molecules have sufficient kinetic energy to overcome attractive forces and escape to the vapor phase. (d) Vapor pressure increases with increasing temperature because average kinetic energies of molecules increase. (e) Vapor pressure decreases with increasing density because attractive intermolecular forces increase. **11.51** (a) $\text{CBr}_4 < \text{CHBr}_3 < \text{CH}_2\text{Br}_2 < \text{CH}_2\text{Cl}_2 < \text{CH}_3\text{Cl} < \text{CH}_4$. The trend is dominated by dispersion forces even though four of the molecules are polar. The order of increasing volatility is the order of increasing vapor pressure, decreasing molar mass, and decreasing strength of dispersion forces. (b) Boiling point increases as the strength of intermolecular forces increases; this is the order of decreasing volatility and the reverse of the order in part (a). $\text{CH}_4 < \text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CH}_2\text{Br}_2 < \text{CHBr}_3 < \text{CBr}_4$ **11.53** (a) The temperature of the water in the two pans is the same. (b) Vapor pressure does not depend on either volume or surface area of the liquid. At the same temperature, the vapor pressures of water in the two containers are the same. **11.55** (a) Approximately 48°C (b) approximately 340 torr (c) approximately 17°C (d) approximately 1000 torr **11.57** (a) The critical point is the temperature and pressure beyond which the gas and liquid phases are indistinguishable. (b) The line that separates the gas and liquid phases ends at the critical point because at conditions beyond the critical temperature and pressure, there is no distinction between gas and liquid. In experimental terms a gas cannot be liquefied at temperatures higher than the critical temperature, regardless of pressure. **11.59** (a) $\text{H}_2\text{O}(\text{g})$ will condense to $\text{H}_2\text{O}(\text{l})$ at approximately 4 torr; at a higher pressure, perhaps 5 atm or so, $\text{H}_2\text{O}(\text{s})$ will melt to form $\text{H}_2\text{O}(\text{l})$. (b) At 100°C and 0.50 atm, water is in the vapor phase. As it cools, water vapor condenses to the liquid at approximately 82°C , the temperature where the vapor pressure of liquid water is 0.50 atm. Further cooling results in freezing at approximately 0°C . The freezing point of water increases with decreasing pressure, so at 0.50 atm the freezing temperature is very slightly above 0°C . **11.61** (a) 24 K (b) Neon sublimates at pressures less than the triple point pressure, 0.43 atm. (c) No **11.63** (a) Methane on the surface of Titan is likely to exist in both solid and liquid forms. (b) As

pressure decreases upon moving away from the surface of Titan, $\text{CH}_4(\text{l})$ (at -178°C) will vaporize to $\text{CH}_4(\text{g})$, and $\text{CH}_4(\text{s})$ (at temperatures below -180°C) will sublime to $\text{CH}_4(\text{g})$. **11.65** In a nematic liquid crystalline phase, molecules are aligned along their long axes, but the molecular ends are not aligned. Molecules are free to translate in all dimensions, but they cannot tumble or rotate out of the molecular plane, or the order of the nematic phase is lost and the sample becomes an ordinary liquid. In an ordinary liquid, molecules are randomly oriented and free to move in any direction. **11.67** The presence of polar groups or nonbonded electron pairs leads to relatively strong dipole-dipole interactions between molecules. These are a significant part of the orienting forces necessary for liquid crystal formation. **11.69** Because order is maintained in at least one dimension, the molecules in a liquid-crystalline phase are not totally free to change orientation. This makes the liquid-crystalline phase more resistant to flow, more viscous, than the isotropic liquid. **11.71** Melting provides kinetic energy sufficient to disrupt molecular alignment in one dimension in the solid, producing a smectic phase with ordering in two dimensions. Additional heating of the smectic phase provides kinetic energy sufficient to disrupt alignment in another dimension, producing a nematic phase with one-dimensional order. **11.73** (a) Decrease (b) increase (c) increase (d) increase (e) increase (f) increase (g) increase **11.77** When a halogen is substituted for H in benzene, molar mass, polarizability and strength of dispersion forces increase; the order of increasing molar mass is the order of increasing boiling points for the first three compounds. $\text{C}_6\text{H}_5\text{OH}$ experiences hydrogen bonding, the strongest force between neutral molecules, so it has the highest boiling point. **11.82** (a) Evaporation is an endothermic process. The heat required to vaporize sweat is absorbed from your body, helping to keep it cool. (b) The vacuum pump reduces the pressure of the atmosphere above the water until atmospheric pressure equals the vapor pressure of water and the water boils. Boiling is an endothermic process, and the temperature drops if the system is not able to absorb heat from the surroundings fast enough. As the temperature of the water decreases, the water freezes. **11.86** At low Antarctic temperatures, molecules in the liquid crystalline phase have less kinetic energy due to temperature, and the applied voltage may not be sufficient to overcome orienting forces among the ends of molecules. If some or all of the molecules do not rotate when the voltage is applied, the display will not function properly. **11.90**



(a) Molar mass: Compounds (i) and (ii) have similar rodlike structures. The longer chain in (ii) leads to greater molar mass, stronger London dispersion forces, and higher heat of vaporization. (b) Molecular shape: Compounds (iii) and (v) have the same chemical formula and molar mass but different molecular shapes. The more rodlike shape of (v) leads to more contact between molecules, stronger dispersion forces, and higher heat of vaporization. (c) Molecular polarity: Compound (iv) has a smaller molar mass than (ii) but a larger heat of vaporization, which must be due to the presence of dipole-dipole forces. (d) Hydrogen bonding interactions: Molecules (v) and (vi) have similar structures. Even though (v) has larger molar mass and dispersion forces, hydrogen bonding causes (vi) to have the higher heat of vaporization. **11.93** $P(\text{benzene vapor}) = 98.7 \text{ torr}$

CHAPTER 12

12.1

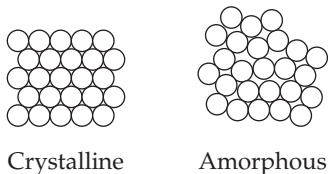
Two-dimensional structure

	(i)	(ii)
(a) unit cell		
(b) lattice	square	square
(c) cell contents	one black, one white	one black

12.3 (a) 1 Re and 3 O atoms per unit cell (b) 3.92 \AA (c) 6.46 g/cm^3

12.5 We expect linear polymer (a), with ordered regions, to be denser and have a higher melting point than branched polymer (b). 12.7 In molecular solids, relatively weak intermolecular forces bind the molecules in the lattice, so relatively little energy is required to disrupt these forces. In covalent-network solids, covalent bonds join atoms into an extended network. Melting or deforming a covalent-network solid means breaking covalent bonds, which requires a large amount of energy. 12.9 (a) Hydrogen bonding, dipole-dipole forces, London dispersion forces (b) covalent chemical bonds (c) ionic bonds (d) metallic bonds 12.11 (a) Ionic (b) metallic (c) covalent-network (It could also be characterized as ionic with some covalent character to the bonds.) (d) molecular (e) molecular (f) molecular 12.13 Because of its relatively high melting point and properties as a conducting solution, the solid must be ionic.

12.15



12.17

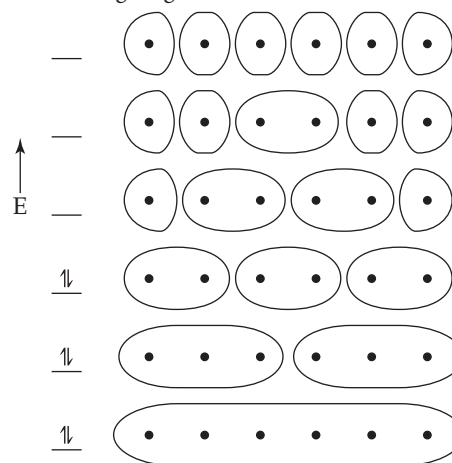
Two-dimensional structure

	(i)	(ii)
(a) unit cell		
(b) γ, a, b	$\lambda = 90^\circ, a = b$	$\lambda = 120^\circ, a = b$
(c) lattice type	square	hexagonal

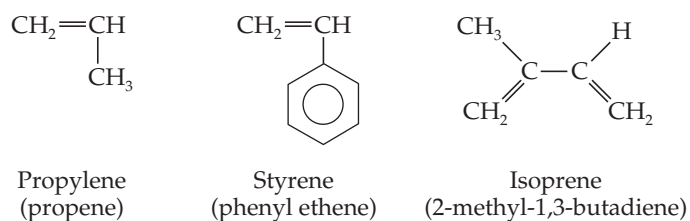
12.19 (a) Orthorhombic (d) tetragonal 12.21 Triclinic, rhombohedral 12.23 There is a minimum of two (metal) atoms in a body-centered cubic unit cell. 12.25 (a) Primitive hexagonal unit cell (b) NiAs 12.27 Moving left to right in the period, atomic mass and Z_{eff} increase. The increase in Z_{eff} leads to smaller bonding atomic radii and atomic volume. Mass increases, volume decreases, and density increases in the series. The variation in densities reflects shorter metal-metal bond distances and an increase in the extent of metal-metal bonding. The strength of metal-metal bonds in the series

is probably the most important factor influencing the increase in density. 12.29 (a) Structure types A and C have equally dense packing and are more densely packed than structure type B. (b) Structure type B is least densely packed. 12.31 (a) The radius of an Ir atom is 1.355 \AA . (b) The density of Ir is 22.67 g/cm^3 12.33 (a) 4 Al atoms per unit cell (b) coordination number = 12 (c) $a = 4.04 \text{ \AA}$ or $4.04 \times 10^{-8} \text{ cm}$ (d) density = 2.71 g/cm^3 12.35 An alloy contains atoms of more than one element and has the properties of a metal. In a solution alloy the components are randomly dispersed. In a heterogeneous alloy the components are not evenly dispersed and can be distinguished at a macroscopic level. In an intermetallic compound the components have interacted to form a compound substance, as in Cu_3As . 12.37 (a) Interstitial alloy (b) substitutional alloy (c) intermetallic compound 12.39 (a) True (b) false (c) false 12.41 (a) Nickel or palladium, substitutional alloy (b) copper, substitutional alloy (c) indium, intermetallic compound (d) silver, substitutional alloy 12.43 In the electron-sea model, valence electrons move about the metallic lattice, while metal atoms remain more or less fixed in position. Under the influence of an applied potential, the electrons are free to move throughout the structure, giving rise to thermal and electrical conductivity.

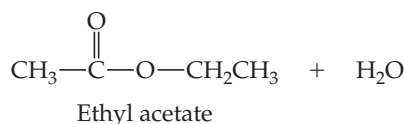
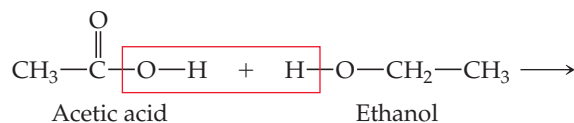
12.45



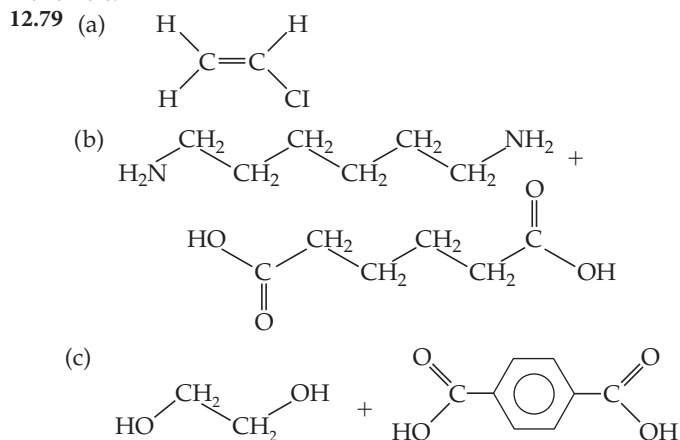
(a) Six AOs require six MOs (b) zero nodes in the lowest energy orbital (c) five nodes in highest energy orbital (d) two nodes in the HOMO (e) three nodes in the LUMO. 12.47 (a) Ag (b) Zn. Ductility decreases as the strength of metal-metal bonding increases, producing a stiffer lattice, less susceptible to distortion. 12.49 Moving from Y to Mo, the number of valence electrons, occupancy of the bonding band, and strength of metallic bonding increase. Stronger metallic bonding requires more energy to break bonds and mobilize atoms, resulting in higher melting points. 12.51 (a) SrTiO_3 (b) Each Sr atom is coordinated to twelve O atoms in eight unit cells that contain the Sr atom. 12.53 (a) $a = 4.70 \text{ \AA}$ (b) 2.69 g/cm^3 12.55 (a) 7.711 g/cm^3 (b) We expect Se^{2-} to have a larger ionic radius than S^{2-} , so HgSe will occupy a larger volume and the unit cell edge will be longer. (c) The density of HgSe is 8.241 g/cm^3 . The greater mass of Se accounts for the greater density of HgSe. 12.57 (a) Cs^+ and I^- have the most similar radii and will adopt the CsCl-type structure. The radii of Na^+ and I^- are somewhat different; NaI will adopt the NaCl-type structure. The radii of Cu^+ and I^- are very different; CuI has the ZnS-type structure. (b) CsI, 8; NaI, 6; CuI, 4 12.59 (a) 6 (b) 3 (c) 6 12.61 (a) False (b) true 12.63 (a) Ionic solids are much more likely to dissolve in water. (b) Covalent-network solids can become electrical conductors via chemical substitution. 12.65 (a) CdS (b) GaN (c) GaAs 12.67 Ge or Si (Ge is closer to Ga in bonding atomic radius.) 12.69 (a) A 1.1 eV photon corresponds to a wavelength of $1.1 \times 10^{-6} \text{ m}$. (b) According to the figure, Si can absorb a portion of the visible light that comes from the sun. 12.71 $\lambda = 560 \text{ nm}$ 12.73 The band gap is approximately 1.85 eV , which corresponds to a wavelength of 672 nm . 12.75 Monomers are small molecules with low molecular mass that are joined together to form polymers. Three monomers mentioned in this chapter are



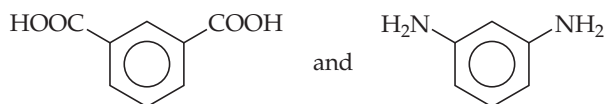
12.77



If a dicarboxylic acid and a dialcohol are combined, there is the potential for propagation of the polymer chain at both ends of both monomers.



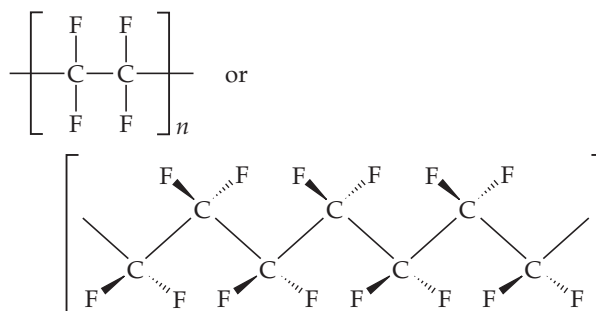
12.81



12.83 Flexibility of molecular chains causes flexibility of the bulk polymer. Flexibility is enhanced by molecular features that inhibit order, such as branching, and diminished by features that encourage order, such as cross-linking or delocalized π electron density. Cross-linking, the formation of chemical bonds between polymer chains, reduces flexibility of the molecular chains, increases the hardness of the material, and decreases the chemical reactivity of the polymer. 12.85 No. The function of the polymer determines whether high molecular mass and high degree of crystallinity are desirable properties. If the polymer will be used as a flexible wrapping or fiber, rigidity that is due to high molecular mass is an undesirable property. 12.87 If a solid has nanoscale dimensions of 1–10 nm, there may not be enough atoms contributing atomic orbitals to produce continuous energy bands of molecular orbitals. 12.89 (a) False. As particle size decreases, the band gap increases. (b) False. As particle size decreases, wavelength decreases. 12.91 2.47×10^5 Au atoms 12.94 The face-centered structure will have the greater density. 12.98 (a) CsCl, primitive cubic lattice (b) Au, face-centered cubic lattice (c) NaCl, face-centered cubic lattice (d) Po, primitive cubic lattice, rare for metals (e) ZnS, face-centered cubic lattice 12.99 White tin has a structure characteristic of a metal, while gray tin has the diamond structure characteristic of group 4A semiconductors. Metallic white tin has the

longer bond distance because the valence electrons are shared with twelve nearest neighbors rather than being localized in four bonds as in gray tin.

12.103



Teflon™ is formed by addition polymerization. 12.105 Diffraction, the phenomenon that enables us to measure interatomic distances in crystals, is most efficient when the wavelength of light is similar to or smaller than the size of the object doing the diffracting. Atom sizes are on the order of 1–10 Å, and the wavelengths of X-rays are also in this range. Visible light, 400–700 nm or 4000–7000 Å, is too long to be diffracted effectively by atoms (electrons) in crystals. 12.107 In a diffraction experiment, we expect a Ge crystal to diffract X-rays at a smaller θ angle than a Si crystal, assuming the X-rays have the same wavelength. 12.109 (a) The bonds in a semiconductor will be weakened by *n*-type doping. (b) The bonds in a semiconductor will also be weakened by *p*-type doping. 12.112 (a) 109° (b) 120° 12.113 (a) $\Delta H = -82$ kJ/mol (b) $\Delta H = -14$ kJ/mol (of either reactant) (c) $\Delta H = 0$ kJ

CHAPTER 13

13.1 (a) < (b) < (c) 13.3 The greater the lattice energy of an ionic solid, the more endothermic the dissolving process and the less soluble the salt in water. 13.7 Vitamin B₆ is largely water soluble because of its small size and capacity for extensive hydrogen-bonding interactions. Vitamin E is largely fat soluble. The long, rodlike hydrocarbon chain will lead to strong dispersion forces among vitamin E and mostly nonpolar fats. 13.9 (a) Yes, the molarity changes with a change in temperature. Molarity is defined as moles solute per unit volume of solution. A change of temperature changes solution volume and molarity. (b) No, molarity does not change with change in temperature. Molarity is defined as moles solute per kilogram of solvent. Temperature affects neither mass nor moles. 13.13 If the magnitude of ΔH_{mix} is small relative to the magnitude of ΔH_{solute} , ΔH_{soln} will be large and endothermic (energetically unfavorable) and not much solute will dissolve. 13.15 (a) Dispersion (b) hydrogen bonding (c) ion-dipole (d) dipole-dipole 13.17 Very soluble. In order for ΔH_{soln} to be negative, ΔH_{mix} must have a greater magnitude than $(\Delta H_{\text{solute}} + \Delta H_{\text{solvent}})$. The entropy of mixing always encourages solubility. In this case, the enthalpy of the system decreases and the entropy increases, so the ionic compound dissolves. 13.19 (a) ΔH_{solute} (b) ΔH_{mix} 13.21 (a) Since the solute and solvent experience very similar London dispersion forces, the energy required to separate them individually and the energy released when they are mixed are approximately equal. $\Delta H_{\text{solute}} + \Delta H_{\text{solvent}} \approx -\Delta H_{\text{mix}}$. Thus, ΔH_{soln} is nearly zero. (b) Since no strong intermolecular forces prevent the molecules from mixing, they do so spontaneously because of the increase in randomness. 13.23 (a) Supersaturated (b) Add a seed crystal. A seed crystal provides a nucleus of prealigned molecules, so that ordering of the dissolved particles (crystallization) is more facile. 13.25 (a) Unsaturated (b) saturated (c) saturated (d) unsaturated 13.27 The liquids water and glycerol form homogenous mixtures (solutions) regardless of the relative amounts of the two components. The —OH groups of glycerol facilitate strong hydrogen bonding similar to that in water; like dissolves like. 13.29 Toluene, C₆H₅CH₃, is the best solvent for nonpolar solutes. Without polar groups or nonbonding electron pairs, it forms only dispersion interactions with itself and other molecules. 13.31 (a) Dispersion interactions among nonpolar CH₃(CH₂)₁₆— chains dominate the properties of stearic acid, causing