# Answers to Selected Exercises

The answers listed here are from the *Complete Solutions Guide*, in which rounding is carried out at each intermediate step in a calculation in order to show the correct number of significant figures for that step. Therefore, an answer given here may differ in the last digit from the result obtained by carrying extra digits throughout the entire calculation and rounding at the end (the procedure you should follow).

## Chapter 2

**19.** $ClF_3$ **21.** All the masses of hydrogen in these three compounds can be expressed as simple whole-number ratios. The g H/g N in hydrazine, ammonia, and hydrogen azide are in the ratios 6:9:1. **23.** O, 7.94; Na, 22.8; Mg, 11.9; O and Mg are incorrect by a factor of ≈2; correct formulas are $H_2O$, $Na_2O$, and MgO. **25.** d(nucleus) = $3 \times 10^{15}$ g/cm$^3$; d(atom) = 0.4 g/cm$^3$ **27.** Since all charges are whole-number multiples of $6.40 \times 10^{-13}$ zirkombs, then the charge on one electron could be $6.40 \times 10^{-13}$ zirkombs. However, $6.40 \times 10^{-13}$ zirkombs could be the charge of two electrons (or three electrons, etc.). All one can conclude is that the charge of an electron is $6.40 \times 10^{-13}$ zirkombs or an integer fraction of $6.40 \times 10^{-13}$. **29.** If the plum pudding model were correct (a diffuse positive charge with electrons scattered throughout), then $\alpha$ particles should have traveled through the thin foil with very minor deflections in their path. This was not the case because a few of the $\alpha$ particles were deflected at very large angles. Rutherford reasoned that the large deflections of these $\alpha$ particles could be caused only by a center of concentrated positive charge that contains most of the atom's mass (the nuclear model of the atom). **31.** The atomic number of an element is equal to the number of protons in the nucleus of an atom of that element. The mass number is the sum of the number of protons plus neutrons in the nucleus. The atomic mass is the actual mass of a particular isotope (including electrons). As we will see in Chapter 3, the average mass of an atom is taken from a measurement made on a large number of atoms. The average atomic mass value is listed in the periodic table. **33.** a. The noble gases are He, Ne, Ar, Kr, Xe, and Rn (helium, neon, argon, krypton, xenon, and radon). Radon has only radioactive isotopes. In the periodic table, the whole number enclosed in parentheses is the mass number of the longest-lived isotope of the element. b. promethium (Pm) and technetium (Tc) **35.** a. Five; F, Cl, Br, I, and At; b. Six; Li, Na, K, Rb, Cs, Fr (H is not considered an alkali metal.) c. 14; Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu; d. 40; all elements in the block defined by Sc, Zn, Uub, and Ac are transition metals. **37.** a. 12 p, 12 n, 12 e; b. 12 p, 12 n, 10 e; c. 27 p, 32 n, 25 e; d. 27 p, 32 n, 24 e; e. 27 p, 32 n, 27 e; f. 34 p, 45 n, 34 e; g. 34 p, 45 n, 36 e; h. 28 p, 35 n, 28 e; i. 28 p, 31 n, 26 e **39.** $^{151}_{63}Eu^{3+}$; $^{118}_{50}Sn^{2+}$ **41.** a. Lose 2 $e^-$ to form $Ra^{2+}$; b. Lose 3 $e^-$ to form $In^{3+}$; c. Gain 3 $e^-$ to form $P^{3-}$; d. Gain 2 $e^-$ to form $Te^{2-}$; e. Gain 1 $e^-$ to form $Br^-$; f. Lose 1 $e^-$ to form $Rb^+$ **43.** $AlCl_3$, aluminum chloride; $CrCl_3$, chromium(III) chloride; $ICl_3$, iodine trichloride; $AlCl_3$ and $CrCl_3$ are ionic compounds following the rules for naming ionic compounds. The major difference is that $CrCl_3$ contains a transition metal (Cr) that generally exhibits two or more stable charges when in ionic compounds. We need to indicate which charged ion we have in the compound. This is generally true whenever the metal in the ionic compound is a transition metal. $ICl_3$ is made from only nonmetals and is a covalent compound. Predicting formulas for covalent compounds is extremely difficult. Because of this, we need to indicate the number of each nonmetal in the binary covalent compound. The exception is when there is only one of the first species present in the formula; when this is the case, *mono-* is not used (it is assumed). **45.** a. sulfur difluoride; b. dinitrogen tetroxide; c. iodine trichloride; d. tetraphosphorus hexoxide **47.** a. copper(I) iodide; b. copper(II) iodide; c. cobalt(II) iodide; d. sodium carbonate; e. sodium hydrogen carbonate or sodium bicarbonate; f. tetrasulfur tetranitride; g. sulfur hexafluoride; h. sodium hypochlorite; i. barium chromate; j. ammonium nitrate **49.** a. $SO_2$; b. $SO_3$; c. $Na_2SO_3$; d. $KHSO_3$; e. $Li_3N$; f. $Cr_2(CO_3)_3$; g. $Cr(C_2H_3O_2)_2$; h. $SnF_4$; i. $NH_4HSO_4$ (composed of $NH_4^+$ and $HSO_4^-$ ions); j. $(NH_4)_2HPO_4$; k. $KClO_4$; l. NaH; m. HBrO; n. HBr **51.** a. lead(II) acetate; b. copper(II) sulfate; c. calcium oxide; d. magnesium sulfate; e. magnesium hydroxide; f. calcium sulfate; g. dinitrogen monoxide or nitrous oxide (common) **53.** a. nitric acid, $HNO_3$; b. perchloric acid, $HClO_4$; c. acetic acid, $HC_2H_3O_2$; d. sulfuric acid, $H_2SO_4$; e. phosphoric acid, $H_3PO_4$ **55.** 116 g S; 230. g O **57.** a. True; b. False. The isotope has 34 protons; c. False. The isotope has 45 neutrons; d. False. The identity is selenium, Se. **59.** Ra; 142 n **61.** $SeO_4^{2-}$: selenate; $SeO_3^{2-}$: selenite; $TeO_4^{2-}$: tellurate; $TeO_3^{2-}$: tellurite **63.** InO, atomic mass of In = 76.54; $In_2O_3$, atomic mass of In = 114.8 **65.** $SbCl_3$; antimony(III) chloride **67.** chlorine; 18 electrons **69.** a. The compounds have the same number and types of atoms (same formula), but the atoms in the molecules are bonded together differently. Therefore, the two compounds are different compounds with different properties. The compounds are called isomers of each other. b. When wood burns, most of the solid material in wood is converted to gases, which escape. The gases produced are most likely $CO_2$ and $H_2O$. c. The atom is not an indivisible particle, but is instead composed of other smaller particles—electrons, neutrons, and protons. d. The two hydride samples contain different isotopes of either hydrogen or lithium. Although the compounds are composed of different isotopes, their properties are similar because different isotopes of the same element have similar properties (except, of course, their mass). **71.** The ratio of the masses of R that combine with 1.00 g Q is 3:1, as expected by the law of multiple proportions. $R_3Q$ **73.** C:H ratio = 8:18 or 4:9

## Chapter 3

**23.** 47.88 amu; Ti **25.** 185 amu **27.** There are three peaks in the mass spectrum, each two mass units apart. This is consistent with two isotopes, differing in mass by two mass units. The peak at 157.84 corresponds to a $Br_2$ molecule composed of two atoms of the lighter isotope. This isotope has mass equal to 157.84/2 or 78.92, which corresponds to $^{79}Br$. The second isotope is $^{81}Br$ with mass equal to 161.84/2 = 80.92. The peaks in the mass spectrum correspond to $^{79}Br_2$, $^{79}Br^{81}Br$, and $^{81}Br_2$, in order of increasing mass. The intensities of the highest and lowest masses tell us the two isotopes are present at about equal abundance. The actual abundance is 50.68% $^{79}Br$ and 49.32% $^{81}Br$. **29.** GaAs can be either $^{69}GaAs$ or $^{71}GaAs$. The mass spectrum for GaAs will have 2 peaks at 144 (69 + 75) and 146 (71 + 75) with intensities in the ratio of 60:40 or 3:2. $Ga_2As_2$ can be $^{69}Ga_2As_2$, $^{69}Ga^{71}GaAs_2$, or $^{71}Ga_2As_2$. The mass spectrum will have 3 peaks at 288, 290, and 292 with intensities in the ratio of 36:48:16 or 9:12:4. **31.** a. $1.03 \times 10^{-4}$ mol; b. $4.52 \times 10^{-3}$ mol; c. $3.41 \times 10^{-2}$ mol **33.** 4.0 g He $<$ 1.0 mol $F_2$ $<$ 44.0 g $CO_2$ $<$ 4.0 g $H_2$ $<$ 146 g $SF_6$ **35.** a. 165.39 g/mol; b. 3.023 mol; c. 3.3 g; d. $5.5 \times 10^{22}$ atoms; e. 1.6 g; f. $1.373 \times 10^{-19}$ g **37.** 71.40% C; 8.689% H; 5.648% F; 14.26% O **39.** a. 46.681%; b. 30.447%; c. 30.447%; d. 63.649% **41.** $6.54 \times 10^{4}$ g/mol **43.** a. 40.002% C, 6.7135% H, 53.285% O; b. 40.002% C, 6.7136% H, 53.284% O; c. 40.002% C, 6.7135% H, 53.285% O; All three compounds have the same empirical formula, $CH_2O$, but different molecular formulas. The composition of all three in mass percent is also the same (within rounding differences). Therefore, elemental analysis will give us only the empirical formula. **45.** HgO and $Hg_2O$ **47.** $C_7H_5N_3O_6$ **49.** $C_3H_5O_2$; $C_6H_{10}O_4$ **51.** $C_3H_4O_3$; $C_6H_8O_6$ **53.** a. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$; b. $Fe_2S_3(s) + 6HCl(g) \rightarrow 2FeCl_3(s) + 3H_2S(g)$; c. $CS_2(l) + 2NH_3(g) \rightarrow H_2S(g) + NH_4SCN(s)$ **55.** a. $16Cr(s) + 3S_8(s) \rightarrow 8Cr_2S_3(s)$; b. $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$; c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$; d. $2Eu(s) + 6HF(g) \rightarrow 2EuF_3(s) + 3H_2(g)$; e. $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$ **57.** 4355 g **59.** 21.5 g $Fe_2O_3$; 7.26 g Al; 13.7 g $Al_2O_3$ **61.** 2.8 days **63.** 150 g **65.** $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; NO is limiting. **67.** 0.301 g $H_2O_2$; $3.6 \times 10^{-2}$ g HCl **69.** 1.20 metric tons **71.** $2.81 \times 10^{6}$ g HCN; $5.63 \times 10^{6}$ g $H_2O$ **73.** 99.8 g $F_2$ **75.** $4.30 \times 10^{-2}$ mol; 2.50 g **77.** M is yttrium, and X is chlorine. Yttrium(III) chloride; 1.84 g **79.** 5 **81.** $Al_2Se_3$ **83.** 42.8% **85.** 86.2% **87.** 86.92 amu **89.** I. $NH_3$; II. $N_2H_4$; III. $HN_3$; If we set the atomic mass of H equal to 1.008, then the atomic mass of N is 14.01. **91.** 87.8 amu **93.** $C_{20}H_{30}O$ **95.** The gas mixture consists of $^{16}O^{16}O$, $^{16}O^{18}O$, and $^{40}Ar$. The isotope composition is 42.82% $^{16}O$, $8.6 \times 10^{-2}$% $^{18}O$, and 57.094% $^{40}Ar$. **97.** 207 amu; Pb **99.** Ge **101.** 184 amu **103.** 1.05 mol **105.** 10.% $La^{2+}$, 90.% $La^{3+}$ **107.** 32.9% **109.** 0.48 mol

## Chapter 4

**11.** a. *Polarity* is a term applied to covalent compounds. Polar covalent compounds have an unequal sharing of electrons in bonds that results in unequal charge distribution in the overall molecule. Polar molecules have a partial negative end and a partial positive end. These are not full charges as in ionic compounds but are charges much smaller in magnitude. Water is a polar molecule and dissolves other polar solutes readily. The oxygen end of water (the partial negative end of the polar water molecule) aligns with the partial positive end of the polar solute, whereas the hydrogens of water (the partial positive end of the polar water molecule) align with the partial negative end of the solute. These opposite-charge attractions stabilize polar solutes in water. This process is called *hydration*. Nonpolar solutes do not have permanent partial negative and partial positive ends; nonpolar solutes are not stabilized in water and do not dissolve. b. KF is a soluble ionic compound, so it is a strong electrolyte. KF(*aq*) actually exists as separate hydrated $K^+$ ions and hydrated $F^-$ ions in solution: $C_6H_{12}O_6$ is a polar covalent molecule that is a nonelectrolyte. $C_6H_{12}O_6$ is hydrated as described in part a. c. RbCl is a soluble ionic compound, so it exists as separate hydrated $Rb^+$ ions and hydrated $Cl^-$ ions in solution. AgCl is an insoluble ionic compound, so the ions stay together in solution and fall to the bottom of the container as a precipitate. d. $HNO_3$ is a strong acid and exists as separate hydrated $H^+$ ions and hydrated $NO_3^-$ ions in solution. CO is a polar covalent molecule and is hydrated as explained in part a. **13.** a. picture iv; b. picture ii; c. picture iii; d. picture i; **15.** a. Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH, and fill to the mark with water, mixing several times along the way. b. Add 500. mL of 1.00 *M* NaOH stock solution to a 2-L volumetric flask; fill to the mark with water, mixing several times along the way. c. Similar to the solution made in part a, instead using 38.8 g $K_2CrO_4$. d. Similar to the solution made in part b, instead using 114 mL of the 1.75 *M* $K_2CrO_4$ stock solution. **17.** 4.5 *M* **19.** $5.95 \times 10^{-8}$ *M* **21.** a. $2.5 \times 10^{-8}$ *M*; b. $8.4 \times 10^{-9}$ *M*; c. $1.33 \times 10^{-4}$ *M*; d. $2.8 \times 10^{-7}$ *M* **23.** Bromides: NaBr, KBr, and $NH_4Br$ (and others) would be soluble, and AgBr, $PbBr_2$, and $Hg_2Br_2$ would be insoluble. Sulfates: $Na_2SO_4$, $K_2SO_4$, and $(NH_4)_2SO_4$ (and others) would be soluble, and $BaSO_4$, $CaSO_4$, and $PbSO_4$ (or $Hg_2SO_4$) would be insoluble. Hydroxides: NaOH, KOH, $Ca(OH)_2$ (and others) would be soluble, and $Al(OH)_3$, $Fe(OH)_3$, and $Cu(OH)_2$ (and others) would be insoluble. Phosphates: $Na_3PO_4$, $K_3PO_4$, $(NH_4)_3PO_4$ (and others) would be soluble, and $Ag_3PO_4$, $Ca_3(PO_4)_2$, and $FePO_4$ (and others) would be insoluble. Lead: $PbCl_2$, $PbBr_2$, $PbI_2$, $Pb(OH)_2$, $PbSO_4$, and PbS (and others) would be insoluble. $Pb(NO_3)_2$ would be a soluble $Pb^{2+}$ salt. **25.** a. $(NH_4)_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow 2NH_4NO_3(aq) + BaSO_4(s)$; $2NH_4^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow 2NH_4^+(aq) + 2NO_3^-(aq) + BaSO_4(s)$; $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$; b. $Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$; $Pb^{2+}(aq) + 2NO_3^-(aq) + 2Na^+(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s) + 2Na^+(aq) + 2NO_3^-(aq)$; $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$; c. No reaction occurs since all possible products are soluble. d. No reaction occurs since all possible products are soluble. e. $CuCl_2(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + 2NaCl(aq)$; $Cu^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s) + 2Na^+(aq) + 2Cl^-(aq)$; $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$ **27.** a. When $CuSO_4(aq)$ is added to $Na_2S(aq)$, the precipitate that forms is CuS(*s*). Therefore, $Na^+$ (the gray spheres) and $SO_4^{2-}$ (the bluish green spheres) are the spectator ions. $CuSO_4(aq) + Na_2S(aq) \rightarrow CuS(s) + Na_2SO_4(aq)$; $Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)$ b. When $CoCl_2(aq)$ is added to NaOH(*aq*), the precipitate that forms is $Co(OH)_2(s)$. Therefore, $Na^+$ (the gray spheres) and $Cl^-$ (the green spheres) are the spectator ions. $CoCl_2(aq) + 2NaOH(aq) \rightarrow Co(OH)_2(s) + 2NaCl(aq)$; $Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$ c. When $AgNO_3(aq)$ is added to KI(*aq*), the precipitate that forms is AgI(*s*). Therefore, $K^+$ (the red spheres) and $NO_3^-$ (the blue spheres) are the spectator ions. $AgNO_3(aq) + KI(aq) \rightarrow AgI(s) + KNO_3(aq)$; $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ **29.** From the solubility rules in Table 4.1, the possible cations could be $Ba^{2+}$ and $Ca^{2+}$. **31.** 2.9 g AgCl; 0.050 *M* $Cl^-$; 0.10 *M* $NO_3^-$; 0.075 *M* $Ca^{2+}$ **33.** 0.607 g **35.** 16.2% **37.** 39.49 mg/tablet; 67.00% **39.** 23 amu; Na **41.** a. Perchloric acid reacted with potassium hydroxide is a possibility. $HClO_4(aq) + KOH(aq) \rightarrow H_2O(l) + KClO_4(aq)$; b. Nitric acid reacted with cesium hydroxide is a possibility. $HNO_3(aq) + CsOH(aq) \rightarrow H_2O(l) + CsNO_3(aq)$; c. Hydroiodic acid reacted with calcium hydroxide is a possibility. $2HI(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + CaI_2(aq)$ **43.** a. 50.0 mL; b. 25.0 mL; c. 8.33 mL; d. 33.3 mL; e. 25.0 mL; f. 8.33 mL **45.** The acid is a diprotic acid ($H_2A$), meaning that it has two $H^+$ ions in the formula to donate to a base. The reaction is $H_2A(aq) + 2NaOH(aq) \rightarrow 2H_2O(l) + Na_2A(aq)$, where $A^{2-}$ is what is left over from the acid formula when the two protons ($H^+$ ions) are reacted. For the HCl reaction, the base has the ability to accept two protons. The most common examples are $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. A possible reaction would be $2HCl(aq) + Ca(OH)_2(aq) \rightarrow 2H_2O(l) + CaCl_2(aq)$. **47.** $4.7 \times 10^{-2}$ *M* **49.** a. 0.8393 *M*; b. 5.010% **51.** The resulting solution is not neutral. $5.9 \times 10^{-3}$ *M* $OH^-$ **53.** $2.0 \times 10^{-2}$ *M* $OH^-$ **55.** a. K, +1; O, −2; Mn, +7; b. Ni, +4; O, −2; c. Fe, +2; d. H, +1; O, −2; N, −3; P, +5; e. P, +3; O, −2; f. O, −2; Fe, $+\frac{8}{3}$; g. O, −2; F, −1; Xe, +6; h. S, +4; F, −1; i. C, +2; O, −2; j. C, 0; H, +1; O, −2 **57.** a. Sr, +2; O, −2; Cr, +6; b. Cu, +2; Cl, −1; c. O, 0; d. H, +1; O, −1; e. Mg, +2; O, −2; C, +4; f. Ag, 0; g. Pb, +2; O, −2; S, +4; h. O, −2; Pb, +4; i. Na, +1; O, −2; C, +3; j. O, −2; C, +4; k. H, +1; N, −3; O, −2; S, +6; Ce, +4; l. O, −2; Cr, +3 **59.** a. $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$; H is reduced, and Al is oxidized. b. $CH_4(g) + 4S(s) \rightarrow CS_2(l) + 2H_2S(g)$; S is reduced, and C is oxidized. c. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$; O is reduced, and C is oxidized. d. $Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$; Ag is reduced, and Cu is oxidized. **61.** a. $3Cu(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$; b. $14H^+(aq) + Cr_2O_7^{2-}(aq) + 6Cl^-(aq) \rightarrow 3Cl_2(g) + 2Cr^{3+}(aq) + 7H_2O(l)$; c. $Pb(s) + 2H_2SO_4(aq) + PbO_2(s) \rightarrow 2PbSO_4(s) + 2H_2O(l)$; d. $14H^+(aq) + 2Mn^{2+}(aq) + 5NaBiO_3(s) \rightarrow 2MnO_4^-(aq) + 5Bi^{3+}(aq) + 5Na^+(aq) + 7H_2O(l)$; e. $8H^+(aq) + H_3AsO_4(aq) + 4Zn(s) \rightarrow 4Zn^{2+}(aq) + AsH_3(g) + 4H_2O(l)$; f. $7H_2O(l) + 4H^+(aq) + 3As_2O_3(s) + 4NO_3^-(aq) \rightarrow 4NO(g) + 6H_3AsO_4(aq)$; g. $16H^+(aq) + 2MnO_4^-(aq) + 10Br^-(aq) \rightarrow 5Br_2(l) + 2Mn^{2+}(aq) + 8H_2O(l)$; h. $8H^+(aq) + 3CH_3OH(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 3CH_2O(aq) + 7H_2O(l)$ **63.** a. $8HCl(aq) + 2Fe(s) \rightarrow 2HFeCl_4(aq) + 3H_2(g)$; b. $6H^+(aq) + 8I^-(aq) + IO_3^-(aq) \rightarrow 3I_3^-(aq) + 3H_2O(l)$; c. $97Ce^{4+}(aq) + 54H_2O(l) + Cr(NCS)_6^{4-}(aq) \rightarrow 97Ce^{3+}(aq) + Cr^{3+}(aq) + 6NO_3^-(aq) + 6CO_2(g) + 6SO_4^{2-}(aq) + 108H^+(aq)$; d. $64OH^-(aq) + 2CrI_3(s) + 27Cl_2(g) \rightarrow 54Cl^-(aq) + 2CrO_4^{2-}(aq) + 6IO_4^-(aq) + 32H_2O(l)$; e. $258OH^-(aq) + Fe(CN)_6^{4-}(aq) + 61Ce^{4+}(aq) \rightarrow Fe(OH)_3(s) + 61Ce(OH)_3(s) + 6CO_3^{2-}(aq) + 6NO_3^-(aq) + 36H_2O(l)$ **65.** $1.622 \times 10^{-2}$ *M* **67.** 34.6% **69.** 49.4 mL **71.** 173 mL **73.** a. 14.2%; b. 8.95 mL **75.** a. 24.8% Co, 29.7% Cl, 5.09% H, 40.4% O; b. $CoCl_2 \cdot 6H_2O$; c. $CoCl_2 \cdot 6H_2O(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Co(NO_3)_2(aq) + 6H_2O(l)$, $CoCl_2 \cdot 6H_2O(aq) + 2NaOH(aq) \rightarrow Co(OH)_2(s) + 2NaCl(aq) + 6H_2O(l)$, $4Co(OH)_2(s) + O_2(g) \rightarrow 2Co_2O_3(s) + 4H_2O(l)$ **77.** 72.4% KCl; 27.6% NaCl **79.** 2.00 *M* **81.** 0.0785 ± 0.0002 *M* **83.** three acidic hydrogens **85.** a. 31.3%; b. 6.00 *M* **87.** 14.6 g Zn, 14.4 g Ag **89.** 77.1% KCl; 22.9% KBr **91.** a. $\dfrac{\text{mass of AgCl}}{\text{mass of PCB}} = \dfrac{143.4\,n}{154.20 + 34.44\,n}$ or $\text{mass}_{\text{AgCl}}\,(154.20 + 34.44\,n) = \text{mass}_{\text{PCB}}\,(143.4\,n)$; b. 7.097 **93.** a. $5.35 \times 10^4$ L/s; b. 4.25 ppm; c. $1.69 \times 10^6$ g; d. 10.3 ppm **95.** a. $YBa_2Cu_3O_{6.5}$: +2; only $Cu^{2+}$ present; $YBa_2Cu_3O_7$: +2.33; two $Cu^{2+}$ and one $Cu^{3+}$ present; $YBa_2Cu_3O_8$: +3; only $Cu^{3+}$ present; b. $2Cu^{2+}(aq) + 5I^-(aq) \rightarrow 2CuI(s) + I_3^-(aq)$; $Cu^{3+}(aq) + 4I^-(aq) \rightarrow CuI(s) + I_3^-(aq)$; $2S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow 3I^-(aq) + S_4O_6^{2-}(aq)$; c. $YBa_2Cu_3O_{7.25}$; +2.50 **97.** 24.99% $AgNO_3$; 40.07% $CuCl_2$; 34.94% $FeCl_3$

## Chapter 5

**21.** 47.5 torr; $6.33 \times 10^3$ Pa; $6.25 \times 10^{-2}$ atm **23.** $1.01 \times 10^5$ Pa; 10.3 m **25.** a. $3.6 \times 10^3$ mm Hg; b. $3.6 \times 10^3$ torr; c. $4.9 \times 10^5$ Pa; d. 71 psi **27.** $P_{H_2} = 317$ torr; $P_{N_2} = 50.7$ torr; $P_{\text{Total}} = 368$ torr **29.** 309 g **31.** 3.08 atm; $P_{CO_2} = 3.08$ atm, $P_{\text{Total}} = 4.05$ atm **33.** $4.44 \times 10^3$ g He; $2.24 \times 10^3$ g $H_2$ **35.** $7.0 \times 10^{2}$°C **37.** 12.5 mL **39.** $n_2/n_1 = 0.921$ **41.** $BrF_3$ **43.** 3.69 L **45.** a. $\chi_{CH_4} = 0.412$, $\chi_{O_2} = 0.588$; b. 0.161 mol; c. 1.06 g $CH_4$, 3.03 g $O_2$ **47.** $P_{\text{methane}} = 1.32$ atm; $P_{\text{ethane}} = 0.12$ atm; 33.7 g **49.** $N_2H_4$ **51.** The calculated molar masses are 209 g/mol from data set I and 202 g/mol from data set II. These values are close to the expected molar mass (207 g/mol) for the divalent metal compound, $Be(C_5H_7O_2)_2$. **53.** 1.16% **55.** $1.5 \times 10^7$ g Fe; $2.6 \times 10^7$ g 98% $H_2SO_4$ **57.** 46.5% **59.** $P_{N_2} = 0.74$ atm; $P_{\text{Total}} = 2.2$ atm **61.** 18.0% **63.** 13.3% **65.** 0.333 atm **67.** Rigid container (constant volume): As reactants are converted to products, the moles of gas particles present decrease by one-half. As *n* decreases, the pressure will decrease (by one-half). Density is the mass per unit volume. Mass is conserved in a chemical reaction, so the density of the gas will not change since mass and volume do not change. Flexible container (constant pressure): Pressure is constant since the container changes volume to keep a constant pressure. As the moles of gas particles decrease by a factor of 2, the volume of the container will decrease (by one-half). We have the same mass of gas in a smaller volume, so the gas density will increase (doubles). **69.** $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$: As reactants are converted into products, we go from 2 mol of gaseous reactants to 4 mol of gaseous products (1 mol $N_2$ + 3 mol $H_2$). Because the moles of gas double as reactants are converted into products, the volume of the gases will double (at constant *P* and *T*). Pressure is directly related to *n* at constant *T* and *V*. As the reaction occurs, the moles of gas will double, so the pressure will double. Because 1 mol of $N_2$ is produced for every 2 mol of $NH_3$ reacted, $P_{N_2} = \frac{1}{2}P^{\circ}_{NH_3}$. Due to the 3:2 mole ratio in the balanced equation, $P_{H_2} = \frac{3}{2}P^{\circ}_{NH_3}$. Note: $P_{\text{Total}} = P_{H_2} + P_{N_2} = \frac{3}{2}P^{\circ}_{NH_3} + \frac{1}{2}P^{\circ}_{NH_3} = 2P^{\circ}_{NH_3}$. As said earlier, the total pressure will double from the initial pressure of $NH_3$ as the reactants are completely converted into products. **71.** a. Both gas samples have the same number of molecules present (*n* is constant); b. Since *T* is constant, $(\text{KE})_{\text{avg}}$ must be the same for both gases $[(\text{KE})_{\text{avg}} = \frac{3}{2}RT]$; c. The lighter gas A molecules will have the faster average velocity; d. The heavier gas B molecules do collide more forcefully, but gas A molecules, with the faster average velocity, collide more frequently. The end result is that *P* is constant between the two containers. **73.** $3.40 \times 10^3$ J/mol $= 5.65 \times 10^{-21}$ J/molecule (for each gas at 273 K); $6.81 \times 10^3$ J/mol $= 1.13 \times 10^{-20}$ J/molecule (for each gas at 546 K) **75.** No; there is a distribution of energies with only the average kinetic energy equal to $\frac{3}{2}RT$. Similarly, there is always a distribution of velocities for a gas sample at some temperature. **77.** a. All the same; b. Flask C; c. Flask A **79.** $CF_2Cl_2$ **81.** 63.7 g/mol **83.** a. 12.24 atm; b. 12.13 atm; c. The ideal gas law is high by 0.91%. **85.** The kinetic molecular theory assumes that gas particles do not exert forces on each other and that gas particles are volumeless. Real gas particles do exert attractive forces on each other, and real gas particles do have volumes. A gas behaves most ideally at low pressures and high temperatures. The effect of attractive forces is minimized at high temperatures since the gas particles are moving very rapidly. At low pressure, the container volume is relatively large (*P* and *V* are inversely related), so the volume of the container taken up by the gas particles is negligible. **87.** The pressure measured for real gases is too low compared to ideal gases. This is due to the attractions gas particles do have for each other; these attractions "hold" them back from hitting the container walls as forcefully. To make up for this slight decrease in pressure for real gases, a factor is added to the measured pressure. The measured volume is too large. A fraction of the space of the container volume is taken up by the volume of gas of the molecules themselves. Therefore, the actual volume available to real gas molecules is slightly less than the container volume. A term is subtracted from the container volume to correct for the volume taken up by real gas molecules. **89.** $CO_2$ since it has the largest $a$ value. **91.** $u_{\text{rms}} = 667$ m/s; $u_{\text{mp}} = 545$ m/s; $u_{\text{avg}} = 615$ m/s **93.** Impact force ($H_2$)/impact force (He) = 0.7097 **95.** The change in momentum per impact is 2.827 times larger for $O_2$ molecules than for He atoms. There are 2.827 times as many impacts per second for He as compared with those for $O_2$. **97.** $1.0 \times 10^9$ collisions/s; $1.3 \times 10^{-6}$ m **99.** a. 0.19 torr; b. $6.6 \times 10^{21}$ molecules/m$^3$; c. $6.6 \times 10^{15}$ molecules/cm$^3$ **101.** Benzene: $9.47 \times 10^{-3}$ ppmv; $2.31 \times 10^{11}$ molecules/cm$^3$; toluene: $1.37 \times 10^{-2}$ ppmv; $3.33 \times 10^{11}$ molecules/cm$^3$ **103.** 46 mL **105.** $MnCl_4$ **107.** $1.61 \times 10^3$ g **109.** 0.990 atm; 0.625 g Zn **111.** $P_{\text{He}} = 50.0$ torr; $P_{\text{Ne}} = 76.0$ torr; $P_{\text{Ar}} = 90.0$ torr; $P_{\text{Total}} = 216.0$ torr **113.** a. 78.0%; b. 0.907 L **115.** 1490 **117.** 60.6 kJ **119.** 7.00 mL **121.** a. $2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(g) + 6H_2O(g)$ b. 15.6 g/s **123.** 30.% **125.** 29.0% **127.** $dT = \dfrac{P(\text{molar mass})}{R} = \text{constant so } d = \text{constant}\left(\dfrac{1}{T}\right)$; $-272.6°\text{C}$ **129.** 16.03 g/mol **131.** From Figure 5.16 of the text, as temperature increases, the probability that a gas particle has the most probable velocity decreases. Since the probability of the gas particle with the most probable velocity decreased by one-half, the temperature must be higher than 300. K. The temperature is $1.20 \times 10^3$ K. **133.** 1.3 L **135.** $\chi_{CO} = 0.291$; $\chi_{CO_2} = 0.564$; $\chi_{O_2} = 0.145$ **137.** a. $8.7 \times 10^3$ L air/min; b. $\chi_{CO} = 0.0017$, $\chi_{CO_2} = 0.032$, $\chi_{O_2} = 0.13$, $\chi_{N_2} = 0.77$, $\chi_{H_2O} = 0.067$; c. $P_{CO} = 0.0017$ atm, $P_{CO_2} = 0.032$ atm, $P_{O_2} = 0.13$ atm, $P_{N_2} = 0.77$ atm, $P_{H_2O} = 0.067$ atm **139.** $2.1 \times 10^2$ stages **141.** a. A given volume of air at a given set of conditions has a larger density than helium at those conditions. We need to heat the air to greater than 25°C to lower the air density (by driving air out of the hot-air balloon) until the density is the same as that for helium (at 25°C and 1.00 atm). b. 2150 K **143.** $C_3H_8$ is possible.

## Chapter 6

**11.** $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$; $K = 1.6 \times 10^{-5}$ mol/L
The expression for $K$ is the product concentrations divided by the reactant concentrations. When $K$ has a value much less than 1, the product concentrations are relatively small and the reactant concentrations are relatively large.

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g);\ K = 1 \times 10^{31}$$

When $K$ has a value much greater than 1, the product concentrations are relatively large and the reactant concentrations are relatively small. In both cases, however, the rate of the forward reaction equals the rate of the reverse reaction at equilibrium (this is a definition of equilibrium). **13.** No, it doesn't matter in which direction the equilibrium position is reached. Both experiments will give the same equilibrium position since both experiments started with stoichiometric amounts of reactants or products. **15.** When equilibrium is reached, there is no net change in the amount of reactants and products present since the rates of the forward and reverse reactions are equal. The first diagram has 4 $A_2B$ molecules, 2 $A_2$ molecules, and 1 $B_2$ molecule present. The second diagram has 2 $A_2B$ molecules, 4 $A_2$ molecules, and 2 $B_2$ molecules. The first diagram cannot represent equilibrium because there was a net change in reactants and products. Is the second diagram the equilibrium mixture? That depends on whether there is a net change between reactants and products when going from the second diagram to the third diagram. The third diagram contains the same number and type of molecules as the second diagram, so the second diagram is the first illustration that represents equilibrium. The reaction container initially contained only $A_2B$. From the first diagram, 2 $A_2$ molecules and 1 $B_2$ molecule are present (along with 4 $A_2B$ molecules). From the balanced reaction, these 2 $A_2$ molecules and 1 $B_2$ molecule were formed when 2 $A_2B$ molecules decomposed. Therefore, the initial number of $A_2B$ molecules present equals 4 + 2 = 6 $A_2B$ molecules. **17.** $K$ and $K_p$ are equilibrium constants as determined by the law of mass action. For $K$, concentration units of mol/L are used, and for $K_p$, partial pressures in units of atm are used (generally). $Q$ is called the reaction quotient. $Q$ has the exact same form as $K$ or $K_p$, but instead of equilibrium concentrations, initial concentrations are used to calculate the $Q$ value. The use of $Q$ is when it is compared to the $K$ value. When $Q = K$ (or when $Q_p = K_p$), the reaction is at equilibrium. When $Q \neq K$, the reaction is not at equilibrium, and one can deduce the net change that must occur for the system to get to equilibrium.

**19.** a. $K = \dfrac{[H_2O]}{[NH_3]^2[CO_2]}$; $K_p = \dfrac{P_{H_2O}}{{P_{NH_3}}^2 \times P_{CO_2}}$; b. $K = [N_2][Br_2]^3$; $K_p = P_{N_2} \times {P_{Br_2}}^3$; c. $K = [O_2]^3$; $K_p = {P_{O_2}}^3$; d. $K = \dfrac{[H_2O]}{[H_2]}$; $K_p = \dfrac{P_{H_2O}}{P_{H_2}}$ **21.** $4.6 \times 10^3$ atm$^3$ **23.** $4.08 \times 10^8$ L/mol; yes, this set of concentrations represents a system at equilibrium because the calculated value of $K$ using these concentrations gives $4.08 \times 10^8$. **25.** 4.07 **27.** 0.72 atm; 0.017 mol/L **29.** 0.056 mol/L **31.** a. decrease; b. will not change; c. will not change; d. increase **33.** a. $[HOCl] = 9.2 \times 10^{-3}$ $M$, $[Cl_2O] = 1.8 \times 10^{-2}$ $M$, $[H_2O] = 5.1 \times 10^{-2}$ $M$; b. $[HOCl] = 0.07$ $M$, $[Cl_2O] = [H_2O] = 0.22$ $M$ **35.** $P_{SO_2} = 0.38$ atm, $P_{O_2} = 0.44$ atm, $P_{SO_3} = 0.12$ atm **37.** The assumption comes from the value of $K$ being much less than 1. For these reactions, the equilibrium mixture will not have a lot of products present; mostly reactants are present at equilibrium. If we define the change that must occur in terms of $x$ as the amount (molarity or partial pressure) of a reactant that must react to reach equilibrium, then $x$ must be a small number because $K$ is a very small number. We want to know the value of $x$ in order to solve the problem, so we don't assume $x = 0$. Instead, we concentrate on the equilibrium row in the ICE table. Those reactants (or products) that have equilibrium concentrations in the form of $0.10 - x$ or $0.25 + x$ or $3.5 - 3x$, etc., is where an important assumption can be made. The assumption is that because $K << 1$, $x$ will be small ($x << 1$) and when we add $x$ or subtract $x$ from some initial concentration, it will make little or no difference. That is, we assume that $0.10 - x \approx 0.10$ or $0.25 + x \approx 0.25$ or $3.5 - 3x \approx 3.5$; we assume that the initial concentration of a substance is equal to the equilibrium concentration. This assumption makes the math much easier and usually gives a value of $x$ that is well within 5% of the true value of $x$ (we get about the same answer with a lot less work). When the 5% rule fails, the equation must be solved exactly or by using the method of successive approximations (see Appendix A1.4). **39.** $[CO_2] = 0.39$ $M$; $[CO] = 8.6 \times 10^{-3}$ $M$; $[O_2] = 4.3 \times 10^{-3}$ $M$ **41.** 66.0% **43.** a. $1.5 \times 10^8$ atm$^{-1}$; b. $P_{CO} = P_{Cl_2} = 1.8 \times 10^{-4}$ atm; $P_{COCl_2} = 5.0$ atm **45.** Only statement d is correct. Addition of a catalyst has no effect on the equilibrium position; the reaction just reaches equilibrium more quickly. Statement a is false for reactants that are either solids or liquids (adding more of these has no effect on the equilibrium). Statement b is false always. If temperature remains constant, then the value of $K$ is constant. Statement c is false for exothermic reactions where an increase in temperature decreases the value of $K$. **47.** a. no effect; b. shifts left; c. shifts right **49.** $H^+ + OH^- \rightarrow H_2O$; sodium hydroxide (NaOH) will react with the $H^+$ on the product side of the reaction. This effectively removes $H^+$ from the equilibrium, which will shift the reaction to the right to produce more $H^+$ and $CrO_4^{2-}$. Since more $CrO_4^{2-}$ is produced, the solution turns yellow. **51.** a. right; b. right; c. no effect; d. left; e. no effect **53.** a. left; b. right; c. left; d. no effect; e. no effect; f. right **55.** An endothermic reaction, where heat is a reactant, will shift right to products with an increase in temperature. The amount of $NH_3(g)$ will increase as the reaction shifts right, so the smell of ammonia will increase. **57.** a. $2 \times 10^3$ molecules/cm$^3$ b. There is more NO in the atmosphere than expected from the value of $K$. The reason is the slow rate (kinetics) of the reaction at low temperatures. Nitric oxide is produced in high-energy or high-temperature environments. In nature some NO is produced by lightning, and the primary man-made source is automobiles. The production of NO is endothermic. At high temperatures $K$ will increase and the rates of the reaction will also increase, resulting in a higher production of NO. Once the NO gets into a more normal temperature environment, it doesn't go back to $N_2$ and $O_2$ because of the slow rate of the reaction. **59.** $2.6 \times 10^{81}$ L/mol **61.** $[H_2]_0 = 11.0\ M$, $[N_2]_0 = 10.0\ M$ **63.** a. $P_{PCl_3} = P_{Cl_2} = 0.2230$ atm; $P_{PCl_5} = 0.0259$ atm; $K_p = 1.92$ atm; b. $P_{PCl_3} = 0.0650$ atm; $P_{Cl_2} = 5.44$ atm; $P_{PCl_5} = 0.1839$ atm **65.** $P_{NO_2} = 0.704$ atm; $P_{N_2O_4} = 0.12$ atm **67.** a. $P_{CO_2} = P_{H_2O} = 0.50$ atm; b. 7.5 g $NaHCO_3$, 1.6 g $Na_2CO_3$; c. 3.9 L **69.** 192 g $NH_4HS$; 1.3 atm **71.** $6.74 \times 10^{-6}$ mol$^3$/L$^3$ **73.** a. 134 atm$^{-1}$; b. $P_{NO} = 0.052$ atm; $P_{Br_2} = 0.18$ atm; $P_{NOBr} = 0.25$ atm **75.** $P_{P_4} = 0.73$ atm, $P_{P_2} = 0.270$ atm; 0.16 dissociated **77.** 1.5 atm$^{-1}$ **79.** 0.23 mol$^2$/L$^2$ **81.** a. $P_{PCl_5} = 0.137$ atm; $P_{PCl_3} = P_{Cl_2} = 0.191$ atm; b. 39.4 g **83.** 71 atm **85.** 0.63 atm$^{1/2}$ **87.** See the *Solutions Guide* for the plot. The data for the plot follow. At $P_{Total} = 1.0$ atm, $P_{NH_3} = 0.024$ atm; at $P_{Total} = 10.0$ atm, $P_{NH_3} = 1.4$ atm; at $P_{Total} = 100.$ atm, $P_{NH_3} = 32$ atm; at $P_{Total} = 1000.$ atm, $P_{NH_3} = 440$ atm; notice that as $P_{Total}$ increases larger fractions of both $N_2$ and $H_2$ are converted to $NH_3$, i.e., as $P_{Total}$ increases ($V$ decreases), the reaction shifts further to the right, as predicted by Le Châtelier's principle. **89.** 4.81 g/L; $5.5 \times 10^{-3}$ mol/L

### Chapter 7

| **17.** | Acid | Base | Conjugate Base of Acid | Conjugate Acid of Base |
|---|---|---|---|---|
| a. | $H_2CO_3$ | $H_2O$ | $HCO_3^-$ | $H_3O^+$ |
| b. | $C_5H_5NH^+$ | $H_2O$ | $C_5H_5N$ | $H_3O^+$ |
| c. | $C_5H_5NH^+$ | $HCO_3^-$ | $C_5H_5N$ | $H_2CO_3$ |

**19.** a. $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$; $K_a = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$; b. $Co(H_2O)_6^{3+}(aq) \rightleftharpoons H^+(aq) + Co(H_2O)_5(OH)^{2+}(aq)$; $K_a = \dfrac{[H^+][Co(H_2O)_5(OH)^{2+}]}{[Co(H_2O)_6^{3+}]}$; c. $CH_3NH_3^+(aq) \rightleftharpoons H^+(aq) + CH_3NH_2(aq)$; $K_a = \dfrac{[H^+][CH_3NH_2]}{[CH_3NH_3^+]}$

**21.** The beaker on the left represents a strong acid in solution; the acid HA is 100% dissociated into the $H^+$ and $A^-$ ions. The beaker on the right represents a weak acid in solution; only a little bit of the acid HB dissociates into ions, so the acid exists mostly as undissociated HB molecules in water.
a. $HNO_2$: weak acid beaker; b. $HNO_3$: strong acid beaker; c. HCl: strong acid beaker; d. HF: weak acid beaker; e. $HC_2H_3O_2$: weak acid beaker **23.** $HClO_4 > HClO_2 > NH_4^+ > H_2O$ **25.** a. $H_2SO_4$; b. HOCl; c. $HC_2H_2ClO_2$ **27.** a. $H_2O$ and $CH_3CO_2^-$; b. An acid–base reaction can be thought of as a competition between two opposing bases. Since this equilibrium lies far to the left ($K_a < 1$), then $CH_3CO_2^-$ is a stronger base than $H_2O$. c. The acetate ion is a better base than water and produces basic solutions in water. When we put acetate ion into solution as the only major basic species, the reaction is

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$

Now the competition is between $CH_3CO_2^-$ and $OH^-$ for the proton. Hydroxide ion is the strongest base possible in water. The above equilibrium lies far to the left, resulting in a $K_b$ value less than 1. Those species we specifically call weak bases ($10^{-14} < K_b < 1$) lie between $H_2O$ and $OH^-$ in base strength. Weak bases are stronger than water but are weaker bases than $OH^-$.
**29.** a. weak acid; b. strong acid; c. weak base; d. strong base; e. weak base; f. weak acid; g. weak acid; h. strong base; i. strong acid **31.** a. $[H^+] = [OH^-] = 1.71 \times 10^{-7}\ M$; b. 6.767; c. 12.54 **33.** a. $[H^+] = 4.0 \times 10^{-8}\ M$; $[OH^-] = 2.5 \times 10^{-7}\ M$; basic; b. $[H^+] = 5 \times 10^{-16}\ M$; $[OH^-] = 20\ M$; basic; c. $[H^+] = 10\ M$; $[OH^-] = 1 \times 10^{-15}\ M$; acidic; d. $[H^+] = 6.3 \times 10^{-4}\ M$; $[OH^-] = 1.6 \times 10^{-11}\ M$; acidic; e. $[H^+] = 1 \times 10^{-9}\ M$; $[OH^-] = 1 \times 10^{-5}\ M$; basic; f. $[H^+] = 4.0 \times 10^{-5}\ M$; $[OH^-] = 2.5 \times 10^{-10}\ M$; acidic **35.** a. 1.00; b. −0.70; c. 7.00 **37.** Use 4.2 mL of 12 $M$ HCl with enough water added to make 1600 mL of solution. **39.** a. $H^+$, $Br^-$, $H_2O$; 0.602; b. $H^+$, $ClO_4^-$, $H_2O$; 0.602; c. $H^+$, $NO_3^-$, $H_2O$; 0.602; d. $HNO_2$, $H_2O$; 2.00; e. $CH_3CO_2H$, $H_2O$; 2.68; f. HCN, $H_2O$; 4.92 **41.** a. $[H^+] = [OCl^-] = 8.4 \times 10^{-5}\ M$; $[OH^-] = 1.2 \times 10^{-10}\ M$; $[HOCl] = 0.20\ M$; 4.08; b. $[H^+] = [OC_6H_5^-] = 1.5 \times 10^{-5}\ M$; $[OH^-] = 6.7 \times 10^{-10}\ M$; $[HOC_6H_5] = 1.5\ M$; 4.82; c. $[H^+] = [F^-] = 3.5 \times 10^{-3}\ M$; $[OH^-] = 2.9 \times 10^{-12}\ M$; $[HF] = 0.017\ M$; 2.46 **43.** 2.02 **45.** $[C_6H_5CO_2H] = 4.1 \times 10^{-3}\ M$; $[C_6H_5CO_2^-] = [H^+] = 5.1 \times 10^{-4}\ M$; $[OH^-] = 1.9 \times 10^{-11}\ M$; 3.29 **47.** 2.68 **49.** a. 1.00; b. 1.30 **51.** 0.033 **53.** $3.5 \times 10^{-4}$ **55.** 0.024 $M$ **57.** $NH_3 > C_5H_5N > H_2O > NO_3^-$ **59.** a. $C_6H_5NH_2$; b. $C_6H_5NH_2$; c. $OH^-$; d. $CH_3NH_2$ **61.** a. 13.00; b. 7.00; c. 14.30 **63.** $1.6 \times 10^{-4}\ M$ **65.** Neutrally charged organic compounds containing at least one nitrogen atom generally behave as weak bases. The nitrogen atom has an unshared pair of electrons around it. This lone pair of electrons is used to form a bond to $H^+$. **67.** 12.00 **69.** 9.59 **71.** a. 1.3%; b. 4.2%; c. 6.4% **73.** $1.0 \times 10^{-9}$
**75.** $H_3C_6H_5O_7(aq) \rightleftharpoons H_2C_6H_5O_7^-(aq) + H^+(aq)$; $K_{a_1} = \dfrac{[H_2C_6H_5O_7^-][H^+]}{[H_3C_6H_5O_7]}$; $H_2C_6H_5O_7^-(aq) \rightleftharpoons HC_6H_5O_7^{2-}(aq) + H^+(aq)$; $K_{a_2} = \dfrac{[HC_6H_5O_7^{2-}][H^+]}{[H_2C_6H_5O_7^-]}$;

$HC_6H_5O_7^{2-}(aq) \rightleftharpoons C_6H_5O_7^{3-}(aq) + H^+(aq)$; $K_{a_3} = \dfrac{[C_6H_5O_7^{3-}][H^+]}{[HC_6H_5O_7^{2-}]}$ **77.** $[H^+] = 3 \times 10^{-2}\ M$, $[OH^-] = 3 \times 10^{-13}\ M$, $[H_3AsO_4] = 0.17\ M$, $[H_2AsO_4^-] = 3 \times 10^{-2}\ M$; $[HAsO_4^{2-}] = 8 \times 10^{-8}\ M$, $[AsO_4^{3-}] = 2 \times 10^{-15}\ M$ **79.** 3.00 **81.** −0.30 **83.** a. These are strong acids such as HCl, HBr, HI, $HNO_3$, $H_2SO_4$, and $HClO_4$. b. These are salts of the conjugate acids of the bases in Table 7.3. These conjugate acids are all weak acids. $NH_4Cl$, $CH_3NH_3NO_3$, and $C_2H_5NH_3Br$ are three examples. Note that the anions used to form these salts ($Cl^-$, $NO_3^-$, and $Br^-$) are conjugate bases of strong acids; this is so because they have no acidic or basic properties in water (with the exception of $HSO_4^-$, which has weak acid properties). c. These are strong bases such as LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$. d. These are salts of the conjugate bases of the neutrally charged weak acids in Table 7.2. The conjugate bases of weak acids are weak bases themselves. Three examples are $NaClO_2$, $KC_2H_3O_2$, and $CaF_2$. The cations used to form these salts are $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ since these cations have no acidic or basic properties in water. Notice that these are the cations of the strong bases you should memorize. e. There are two ways to make a neutral salt. The easiest way is to combine a conjugate base of a strong acid (except for $HSO_4^-$) with one of the cations from a strong base. These ions have no acidic/basic properties in water so salts of these ions are neutral. Three examples are NaCl, $KNO_3$, and $SrI_2$. Another type of strong electrolyte that can produce neutral solutions are salts that contain an ion with weak acid properties combined with an ion of opposite charge having weak base properties. If the $K_a$ for the weak acid ion is equal to the $K_b$ for the weak base ion, then the salt will produce a neutral solution. The most common example of this type of salt is ammonium acetate ($NH_4C_2H_3O_2$). For this salt, $K_a$ for $NH_4^+ = K_b$ for $C_2H_3O_2^- = 5.6 \times 10^{-10}$. This salt at any concentration produces a neutral solution. **85.** a. HI < HF < NaI < NaF; b. HBr < $NH_4Br$ < KBr < $NH_3$; c. $HNO_3 < C_6H_5NH_3NO_3 < HOC_6H_5 < NaNO_3 < C_6H_5NH_2 < KOC_6H_5 < NaOH$ **87.** a. Neutral; $K^+$ and $Cl^-$ have no acidic or basic properties; b. Basic; $K_b$ for $CN^- > K_a$ for $C_2H_5NH_3^+$ ($CN^-$ is a better base than $C_2H_5NH_3^+$ is as an acid); c. Acidic; $K_a$ for $C_5H_5NH^+ > K_b$ for $F^-$; d. Neutral; $K_a$ for $NH_4^+ = K_b$ for $C_2H_3O_2^-$; e. Acidic; $HSO_3^-$ is a stronger acid than a base because $K_a$ for $HSO_3^- > K_b$ for $HSO_3^-$; f. Basic; $HCO_3^-$ is a stronger base than an acid because $K_b$ for $HCO_3^- > K_a$ for $HCO_3^-$. **89.** a. 8.23; b. 10.56; c. 4.82 **91.** $[HN_3] = [OH^-] = 2.3 \times 10^{-6}$ *M*; $[N_3^-] = 0.010$ *M*; $[Na^+] = 0.010$ *M*; $[H^+] = 4.3 \times 10^{-9}$ *M* **93.** NaF; this was determined by calculating $K_b$ for $F^-$. **95.** 3.00 **97.** 8.37 **99.** 7.4; when an acid is added to water, the pH cannot be basic. Must account for the autoionization of water. **101.** 6.24 **103.** 6.15 **105.** a. $1.8 \times 10^9$; b. $2.5 \times 10^3$; c. $3.1 \times 10^{-5}$; d. $1.0 \times 10^{14}$; e. $5.6 \times 10^4$; f. $4.0 \times 10^{10}$ **107.** $NH_4Cl$ **109.** 11.77 **111.** 3.36 **113.** a. 1.66; b. −0.78; c. Because of the lower charge, $Fe^{2+}(aq)$ will not be as strong an acid as $Fe^{3+}(aq)$. A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate. **115.** 0.022 *M* **117.** 0.022 *M* **119.** a. 2.80; b. $1.1 \times 10^{-3}$ *M* **121.** 1.96 **123.** a. $1.1 \times 10^{-4}$; b. $[H_2CO_3] = [CO_3^{2-}]$;

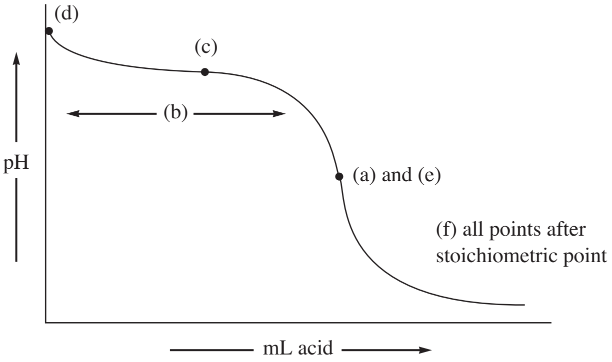
c. $\text{pH} = \dfrac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$ (see *Solutions Guide* for derivation);

d. 8.35 **125.** 20.0 g **127.** $K_a$ for HX = $1.0 \times 10^{-5}$ **129.** 2.492 **131.** 6.18 L **133.** 10.00 **135.** 7.20 **137.** 6.72

## Chapter 8

**15.** A buffer solution is one that resists a change in its pH when either hydroxide ions or protons ($H^+$) are added. Any solution that contains a weak acid and its conjugate base or a weak base and its conjugate acid is classified as a buffer. The pH of a buffer depends on the [base]/[acid] ratio. When $H^+$ is added to a buffer, the weak base component of the buffer reacts with the $H^+$ and forms the acid component of the buffer. Even though the concentrations of the acid and base components of the buffer change some, the ratio of [base]/[acid] does not change that much. This translates into a pH that doesn't change much. When $OH^-$ is added to a buffer, the weak acid component is converted into the base component of the buffer. Again, the ratio of [base]/[acid] does not change a lot (unless a large quantity of $OH^-$ is added), so the pH does not change much. $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$; $OH^-(aq) + HCO_3^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$ **17.** When [weak acid] > [conjugate base], pH < p$K_a$. When [conjugate base] > [weak acid], pH > p$K_a$. **19.** a. 2.96; b. 8.94; c. 7.00; d. 4.89 **21.** a. 4.29; b. 12.30; c. 12.30; d. 5.07 **23.** 3.37 **25.** 3.48; 3.14 **27.** 4.37 **29.** a. 0.19; b. 0.59; c. 1.0; d. 1.9 **31.** a. 0.50 mol; b. 0.78 mol; c. 0.36 mol **33.** 15 g **35.** a. 1.2 *M*; b. 4.32 **37.** a. 0.091; b. 1.1 ≈ 1; c. A best buffer has approximately equal concentrations of weak acid and conjugate base so that pH ≈ p$K_a$ for a best buffer. The p$K_a$ value for a $H_3PO_4/H_2PO_4^-$ buffer is $-\log(7.5 \times 10^{-3}) = 2.12$. A pH of 7.1 is too high for a $H_3PO_4/H_2PO_4^-$ buffer to be effective. At this high pH, there would be so little $H_3PO_4$ present that we could hardly consider it a buffer; this solution would not be effective in resisting pH changes, especially when a strong base is added. **39.** Only mixture c results in a buffered solution. **41.** HOCl; there are many possibilities. One possibility is a solution with [HOCl] = 1.0 *M* and [NaOCl] = 0.35 *M*. **43.** $7.0 \times 10^{-7}$ *M* **45.** 6.89

**47.**



$B + H^+ \rightarrow BH^+$; added $H^+$ from the strong acid converts the weak base, B, into its conjugate acid, $BH^+$. Initially, before any $H^+$ is added (point d), B is the dominant species present. After $H^+$ is added, both B and $BH^+$ are present and a buffered solution results (region b). At the equivalence point (points a and e), exactly enough $H^+$ has been added to convert all of the weak base present initially into its conjugate acid, $BH^+$. Past the equivalence point (region f), excess $H^+$ is present. For the answer to part b, we included almost the entire buffer region. The maximum buffer region is around the halfway point to equivalence (point c) where [B] = $[BH^+]$. Here, pH = p$K_a$, which is a characteristic of a best buffer. **49.** a. all the same; b. i < iv < iii < ii; c. i < iv < iii < ii; d. iii < ii = i < iv; the only different answer would be part c. The ordering would be i < iii < iv < ii. **51.** a. f; b. a; the best point to look at to differentiate a strong acid from a weak acid titration (if initial concentrations are not known) is the equivalence point pH. If the pH = 7.00, the acid titrated is a strong acid; if the pH is greater than 7.00, the acid titrated is a weak acid. c. d **53.** a. 0.699; b. 0.854; c. 1.301; d. 7.00; e. 12.15 **55.** a. 2.72; b. 4.26; c. 4.74; d. 5.22; e. 8.79; f. 12.15

**57.**

| Volume (mL) | pH |
|---|---|
| 0.0 | 2.43 |
| 4.0 | 3.14 |
| 8.0 | 3.53 |
| 12.5 | 3.86 |
| 20.0 | 4.46 |
| 24.0 | 5.24 |
| 24.5 | 5.6 |
| 24.9 | 6.3 |
| 25.0 | 8.28 |
| 25.1 | 10.3 |
| 26.0 | 11.29 |
| 28.0 | 11.75 |
| 30.0 | 11.96 |

See *Solutions Guide* for pH plot.

**59.**

| Volume (mL) | pH |
|---|---|
| 0.0 | 11.11 |
| 4.0 | 9.97 |
| 8.0 | 9.58 |
| 12.5 | 9.25 |
| 20.0 | 8.65 |
| 24.0 | 7.87 |
| 24.5 | 7.6 |
| 24.9 | 6.9 |
| 25.0 | 5.28 |
| 25.1 | 3.7 |
| 26.0 | 2.71 |
| 28.0 | 2.24 |
| 30.0 | 2.04 |

See *Solutions Guide* for pH plot.

**61.** a. 4.19, 8.45; b. 10.74, 5.96; c. 0.89, 7.00 **63.** a. 100. g/mol; b. 3.02 **65.** a. yellow; b. 8.0; c. blue **67.** The pH is between 5 and 8. **69.** Bromthymol blue or phenol red are possible indicators for Exercise 53, and *o*-cresolphthalein or phenolphthalein are possible indicators for Exercise 55. **71.** Phenolphthalein is a possible indicator for Exercise 57, and bromcresol green is a possible indicator for Exercise 59. **73.** Methyl red changes color in a pH range of about pH = p$K_a$ ± 1 = 5.3 ± 1. Therefore, methyl red is a useful indicator at pH values approximately between 4.3 and 6.3. In titrating a weak acid with a base, we start off with an acidic solution with pH < 4.3 so the color would change from red to reddish-orange at pH ~ 4.3. In titrating a weak base with an acid, the color change would be from yellow to yellowish-orange at pH ~ 6.3. Only a weak base–strong acid titration would have an acidic pH at the equivalence point, so only in this type of titration would the color change of methyl red indicate the approximate endpoint. **75.** a. 2.18; b. 2.55; c. 3.00; d. 5.00; e. 6.40; f. 7.00; g. 9.50; h. 11.63; i. 12.00; j. 12.34 **77.** a. $K_{a_1} = 1.5 \times 10^{-4}$; $K_{a_2} = 2.8 \times 10^{-7}$; $K_{a_3} = 3.6 \times 10^{-10}$; b. The pH at the third halfway point to equivalence (60.5 mL of NaOH added) will be equal to p$K_{a_3}$ = 9.44. The pH at 59.0 mL NaOH added should be slightly less than 9.44. c. 9.34 **79.** a. $Na^+$ is present in all solutions. A. $CO_3^{2-}$, $H_2O$; B. $CO_3^{2-}$, $HCO_3^-$, $H_2O$, $Cl^-$; C. $HCO_3^-$, $H_2O$, $Cl^-$; D. $HCO_3^-$, $CO_2(H_2CO_3)$, $H_2O$, $Cl^-$; E. $CO_2(H_2CO_3)$, $H_2O$, $Cl^-$; F. $H^+$ (excess), $CO_2(H_2CO_3)$, $H_2O$, $Cl^-$; b. A, 11.66; B, 10.32; C, 8.35; D, 6.37; E, 3.92 **81.** a. $1.6 \times 10^{-5}$ mol/L; $6.7 \times 10^{-3}$ g/L; b. $9.3 \times 10^{-5}$ mol/L; $9.3 \times 10^{-3}$ g/L; c. $6.5 \times 10^{-7}$ mol/L; $3.1 \times 10^{-4}$ g/L **83.** a. $2.3 \times 10^{-9}$; b. $8.20 \times 10^{-19}$ **85.** $5.3 \times 10^{-12}$ **87.** a. $CaF_2$ has the smallest molar solubility since it has the smaller $K_{sp}$ value. b. $FePO_4$ has the smallest molar solubility (must be calculated). **89.** a. $4 \times 10^{-17}$ mol/L; b. $4 \times 10^{-11}$ mol/L; c. $4 \times 10^{-29}$ mol/L **91.** $1.5 \times 10^{-19}$ g **93.** If the anion in the salt can act as a base in water, then the solubility of the salt will increase as the solution becomes more acidic. Added $H^+$ will react with the base, forming the conjugate acid. As the basic anion is removed, more of the salt will dissolve to replenish the basic anion. The salts with basic anions are $Ag_3PO_4$, $CaCO_3$, $CdCO_3$, and $Sr_3(PO_4)_2$. $Hg_2Cl_2$ and $PbI_2$ do not have any pH dependence since $Cl^-$ and $I^-$ are terrible bases (the conjugate bases of strong acids). $Ag_3PO_4(s) + H^+(aq) \rightarrow 3Ag^+(aq) + HPO_4^{2-}(aq) \xrightarrow{\text{Excess } H^+} 3Ag^+(aq) + H_3PO_4(aq)$; $CaCO_3(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) \xrightarrow{\text{Excess } H^+} Ca^{2+}(aq) + H_2CO_3(aq)\ [H_2O(l) + CO_2(g)]$; $CdCO_3(s) + H^+(aq) \rightarrow Cd^{2+}(aq) + HCO_3^-(aq) \rightarrow Cd^{2+}(aq) + H_2CO_3(aq)\ [H_2O(l) + CO_2(g)]$; $Sr_3(PO_4)_2(s) + 2H^+(aq) \rightarrow 3Sr^{2+}(aq) + 2HPO_4^{2-} \xrightarrow{\text{Excess } H^+} 3Sr^{2+}(aq) + 2H_3PO_4(aq)$ **95.** a. AgF; b. $Pb(OH)_2$; c. $Sr(NO_2)_2$; d. $Ni(CN)_2$ **97.** $[Ba^{2+}] = 6.0 \times 10^{-5}$ *M*; $[Br^-] = 1.2 \times 10^{-4}$ *M*; $[K^+] = 4.8 \times 10^{-4}$ *M*; $[C_2O_4^{2-}] = 2.4 \times 10^{-4}$ *M* **99.** When $[AgNO_3]_0$ is greater than $5.6 \times 10^{-5}$ *M*, then $Ag_3PO_4(s)$ will precipitate. **101.** See the *Solutions Guide* for the flowchart for each separation. A possible order of chemicals necessary to separate the ions follows. a. NaCl(*aq*) followed by $NH_3(aq)$ followed by $H_2S(aq)$; b. NaCl(*aq*) followed by $Na_2SO_4(aq)$ followed by the basic addition of $H_2S(aq)$; c. $AgNO_3(aq)$ followed by $NH_3(aq)$ followed by $Na_2S_2O_3(aq)$; d. $Na_2SO_4$ followed by the basic addition of $H_2S(aq)$ **103.** $Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$, orange ppt.; $HgI_2(s) + 2I^-(aq) \rightarrow HgI_4^{2-}(aq)$, soluble complex ion **105.** $3.3 \times 10^{-32}$ *M* **107.** $[Ag^+] = 4.6 \times 10^{-9}$ *M*; $[NH_3] = 1.6$ *M*; $[Ag(NH_3)_2^+] = 0.20$ *M*; $[AgNH_3^+] = 1.5 \times 10^{-5}$ *M* **109.** a. $1.6 \times 10^{-6}$; b. 0.056 mol/L **111.** 42 g **113.** Test tube 1: added $Cl^-$ reacts with $Ag^+$ to form a silver chloride precipitate. The net ionic equation is $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Test tube 2: added $NH_3$ reacts with $Ag^+$ ions to form a soluble complex ion, $Ag(NH_3)_2^+$. As this complex ion forms, $Ag^+$ is removed from the solution, which causes the AgCl(*s*) to dissolve. When enough $NH_3$ is added, all of the silver chloride precipitate will dissolve. The equation is $AgCl(s) + 2NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)$. Test tube 3: added $H^+$ reacts with the weak base, $NH_3$, to form $NH_4^+$. As $NH_3$ is removed from the $Ag(NH_3)_2^+$ complex ion, $Ag^+$ ions are released to solution and can then react with $Cl^-$ to re-form AgCl(*s*). The equations are $Ag(NH_3)_2^+(aq) + 2H^+(aq) \rightarrow Ag^+(aq) + 2NH_4^+(aq)$ and $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. **115.** a. 8.1; b. pH = 7.00: 0.083; pH = 9.00: 8.3; c. 8.08; 7.95 **117.** a. potassium fluoride + HCl; b. benzoic acid + NaOH; c. sodium acetate + acetic acid; d. HOCl + NaOH or ammonium chloride + sodium acetate; e. ammonium chloride + NaOH **119.** 99.5%; for a strong base–strong acid titration, the equivalence point occurs at pH = 7.0. Bromthymol blue is a good indicator choice since it changes color at pH ~ 7 (from base color to acid color). **121.** Since the equivalence point occurs at pH = 8.9, phenolphthalein would be a good indicator choice because it changes color at pH ~ 9 (from acid color to base color). **123.** a. $6.7 \times 10^{-6}$ *M*; b. $1.2 \times 10^{-13}$ *M*; c. $2.3 \times 10^{-19}$ *M*; no, since *Q* (= $2.3 \times 10^{-21}$) is less than the $K_{sp}$ value. **125.** 65 mL **127.** 4.92 **129.** 180. g/mol; $3.3 \times 10^{-4}$ **131.** $K_{a_3}$ is so small ($4.8 \times 10^{-13}$) that a break is not seen at the third stoichiometric point. **133.** 49 mL **135.** a. See the *Solutions Guide* for the derivation. b. ammonium formate, 6.50; ammonium acetate, 7.00; ammonium bicarbonate, 7.81; c. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$, $C_2H_3O_2^-(aq) + H^+(aq) \rightarrow HC_2H_3O_2(aq)$ **137.** a. 0.33 mol/L; b. 0.33 *M*; c. $4.8 \times 10^{-3}$ *M* **139.** a. $5.8 \times 10^{-4}$ mol/L; b. Greater; since $F^-$ is a weak base, the $F^-$ concentration is lowered by reaction with water, which causes more $SrF_2(s)$ to dissolve. c. $3.5 \times 10^{-3}$ mol/L **141.** a. See the *Solutions Guide* for derivation of the equation; b. The data for the plot follow. See the *Solutions Guide* for the plot. As can be seen from the data, the solubility of $Al(OH)_3(s)$ is increased by very acidic conditions or by very basic conditions.

| pH | Solubility (*S*, mol/L) | log *S* |
|---|---|---|
| 4.0 | $2 \times 10^{-2}$ | −1.7 |
| 5.0 | $2 \times 10^{-5}$ | −4.7 |
| 6.0 | $4.2 \times 10^{-7}$ | −6.38 |
| 7.0 | $4.0 \times 10^{-6}$ | −5.40 |
| 8.0 | $4.0 \times 10^{-5}$ | −4.40 |
| 9.0 | $4.0 \times 10^{-4}$ | −3.40 |
| 10.0 | $4.0 \times 10^{-3}$ | −2.40 |
| 11.0 | $4.0 \times 10^{-2}$ | −1.40 |
| 12.0 | $4.0 \times 10^{-1}$ | −0.40 |

**143.** 3.9 L **145.** a. 2.21; b. $2.30 \times 10^{-2}$ *M* **147.** 12.34

**149.** pH = 9.50: 10.0 mL; pH = 4.00: 4.55 mL **151.** a. Since there are two sources of $HCO_3^-$, $V_2 > V_1$. b. Since $OH^-$ will be titrated first, $V_1 > V_2$. c. 57.1% $Na_2CO_3$; 42.9% $NaHCO_3$

## Chapter 9

**15.** KE = 78 J; PE = 118 J **17.** Path-dependent functions for a trip from Chicago to Denver are those quantities that depend on the route taken. One can fly directly from Chicago to Denver or one could fly from Chicago to Atlanta to Los Angeles and then to Denver. Some path-dependent quantities are miles traveled, fuel consumption of the airplane, time traveling, airplane snacks eaten, etc. State functions are path-independent; they depend only on the initial and final states. Some state functions for an airplane trip from Chicago to Denver would be longitude change, latitude change, elevation change, and overall time zone change. **19.** 70. J **21.** $q = 30.9$ kJ; $w = -12.4$ kJ; $\Delta E = 18.5$ kJ **23.** −37.56 kJ **25.** $\Delta H = \Delta E + P\Delta V$ at constant $P$; from the strict definition of enthalpy, the difference between $\Delta H$ and $\Delta E$ is the quantity $P\Delta V$. Thus, when a system at constant $P$ can do pressure-volume work, then $\Delta H \neq \Delta E$. When the system cannot do $PV$ work, then $\Delta H = \Delta E$ at constant pressure. An important way to differentiate $\Delta H$ from $\Delta E$ is to concentrate on $q$, the heat flow; the heat flow by a system at constant pressure equals $\Delta H$, and the heat flow by a system at constant volume equals $\Delta E$. **27.** Since the reaction is exothermic (heat is a product), one should provide cooling for the reaction mixture to prevent $H_2SO_4(aq)$ from boiling. **29.** a. 1650 kJ of heat released; b. 826 kJ of heat released; c. 7.39 kJ of heat released; d. 34.4 kJ of heat released **31.** When a liquid is converted into gas, there is an increase in volume. The 2.5 kJ/mol quantity is the work done by the vaporization process in pushing back the atmosphere. **33.** Constant $V$: $\Delta E = q = 74.3$ kJ, $w = 0$, $\Delta H = 88.1$ kJ; constant $P$: $\Delta H = q = 88.1$ kJ, $w = -13.8$ kJ, $\Delta E = 74.3$ kJ **35.** Pathway one: step 1: $q = 30.4$ kJ, $w = -12.2$ kJ, $\Delta E = 18.2$ kJ, $\Delta H = 30.4$ kJ; step 2: $q = -28.1$ kJ, $w = 21.3$ kJ, $\Delta E = -6.8$ kJ, $\Delta H = -11$ kJ; total: $q = 2.3$ kJ, $w = 9.1$ kJ, $\Delta E = 11.4$ kJ, $\Delta H = 19$ kJ; pathway two: step 3: $q = 6.84$ kJ, $w = 0$, $\Delta E = 6.84$ kJ, $\Delta H = 11.40$ kJ; step 4: $q = 7.6$ kJ, $w = -3.0$ kJ, $\Delta E = 4.6$ kJ, $\Delta H = 7.6$ kJ; total: $q = 14.4$ kJ, $w = -3.0$ kJ, $\Delta E = 11.4$ kJ, $\Delta H = 19.0$ kJ; state functions are independent of the particular pathway taken between two states; path functions are dependent on the particular pathway. In this problem, the overall values of $\Delta H$ and $\Delta E$ for the two pathways are the same; hence, $\Delta H$ and $\Delta E$ are state functions. The overall values of $q$ and $w$ for the two pathways are different; hence, $q$ and $w$ are path functions. **37.** In calorimetry, heat flow is determined into or out of the surroundings. Because $\Delta E_{\text{univ}} = 0$ by the first law of thermodynamics, $\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$; what happens to the surroundings is the exact opposite of what happens to the system. To determine heat flow, we need to know the heat capacity of the surroundings, the mass of the surroundings that accepts/donates the heat, and the change in temperature. If we know these quantities, $q_{\text{surr}}$ can be calculated and then equated to $q_{\text{sys}}$ ($-q_{\text{surr}} = q_{\text{sys}}$). For an endothermic reaction, the surroundings (the calorimeter contents) donate heat to the system. This is accompanied by a decrease in temperature of the surroundings. For an exothermic reaction, the system donates heat to the surroundings (the calorimeter) so temperature increases. $q_{\text{p}} = \Delta H$; $q_{\text{v}} = \Delta E$; a coffee cup calorimeter is at constant (atmospheric) pressure. The heat released or gained at constant pressure is $\Delta H$. A bomb calorimeter is at constant volume. The heat released or gained at constant volume is $\Delta E$. **39.** $H_2O(l)$, $2.30 \times 10^3$ J; $Hg(l)$, 140°C **41.** 75.0 g **43.** −66 kJ/mol **45.** 39.2°C **47.** −25 kJ/g; −2700 kJ/mol **49.** a. $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$; b. −5630 kJ/mol; c. −5630 kJ/mol **51.** 226 kJ **53.** −713 kJ **55.** −158 kJ **57.** −202.6 kJ **59.** 1268 kJ; since the reaction is very endothermic (requires a lot of heat), high energy costs would make it an impractical way of making ammonia. **61.** a. −940. kJ; b. −265 kJ; c. −176 kJ; d. −1235 kJ; e. −320. kJ; f. −37 kJ **63.** −832 kJ; −368 kJ; −133 kJ; in both cases sodium metal reacts with the "extinguishing agent." Both reactions are exothermic and each reaction produces a flammable gas—$H_2$ and CO, respectively. **65.** −4594 kJ **67.** a. 632 kJ; b. Since $3C_2H_2(g)$ is higher in energy than $C_6H_6(l)$, acetylene will release more energy per gram when burned in air. **69.** −169 kJ/mol **71.** 3.97 g **73.** −22.7 kJ/g versus −29.67 kJ/g for ethanol. Ethanol has a higher fuel value than methanol. **75.** 25 J **77.** 282.1 kJ **79.** $C_{H_2O} = 4.18$ kJ/°C; $C_{\text{cal}} = 6.66$ kJ/°C **81.** −306 kJ/mol **83.** 4.2 kJ of heat released **85.** When $\Delta V > 0$ ($\Delta n > 0$), then $w < 0$ and the system does work on the surroundings (c and e). When $\Delta V < 0$ ($\Delta n < 0$), then $w > 0$ and the surroundings do work on the system (a and d). When $\Delta V = 0$ ($\Delta n = 0$), then $w = 0$ (b). **87.** a. $2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s)$; b. $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$; c. $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow 2H_2O(l) + BaCl_2(aq)$ d. $2C(\text{graphite}) + \frac{3}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow C_2H_3Cl(g)$; e. $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$ (Note: $\Delta H_{\text{comb}}$ values generally assume 1 mol of compound combusted); f. $NH_4Br(s) \rightarrow NH_4^+(aq) + Br^-(aq)$ **89.** 6.02 kJ/mol **91.** 43.58 kJ/mol; from Appendix 4 data, $\Delta H° = 44$ kJ/mol. The $\Delta H$ values agree to two significant figures (as they should). **93.** 37 $m^2$ **95.** For an isothermal expansion of an ideal gas, $\Delta T = 0$, so $\Delta E = 0$ (and $\Delta H = 0$); therefore, $q = -w = P\Delta V$. As long as the gas expands against a nonzero external pressure, $q \neq 0$ because $w \neq 0$.

## Chapter 10

| | | | | | | |
|---|---|---|---|---|---|---|
| **13.** 2 kJ | | | x | | x | xx |
| 1 kJ | | x | | xx | x | |
| 0 kJ | xx | x | x | | | |
| Total $E$ = | 0 kJ | 1 kJ | 2 kJ | 2 kJ | 3 kJ | 4 kJ |

The most likely total energy is 2 kJ.

**15.** c, e, f **17.** a. Positional probability increases; there is a greater volume accessible to the randomly moving gas molecules, which increases positional probability. b. The positional probability does not change. There is no change in volume and thus no change in the numbers of positions of the molecules. c. Positional probability decreases; volume decreases. **19.** There are six ways to get a seven, more than any other number. The seven is not favored by energy; rather it is favored by probability. To change the probability we would have to expend energy (do work). **21.** $q_{\text{v}} = \Delta E = 71.9$ kJ; $q_{\text{p}} = \Delta H = 85.3$ kJ; $\Delta E = 71.9$ kJ for both constant-volume and constant-pressure processes. **23.** 77.0°C **25.** $w = q = 0$; $q_{\text{rev}} = 350$ J **27.** a. constant $V$, 1.51 kJ; constant $P$, 1.94 kJ; b. 219.63 J $K^{-1}$ $mol^{-1}$; c. 218.30 J $K^{-1}$ $mol^{-1}$ **29.** $2.50 \times 10^4$ J **31.** 2.9 J/K **33.** Living organisms need an external source of energy to carry out these processes. Green plants use the energy from sunlight to produce glucose from carbon dioxide and water by photosynthesis. In the human body, the energy released from the metabolism of glucose helps drive the synthesis of proteins. For all processes combined, $\Delta S_{\text{univ}}$ must be greater than zero (second law). **35.** $\Delta S_{\text{surr}}$ is primarily determined by heat flow. This heat flow into or out of the surroundings comes from the heat flow out of or into the system. In an exothermic process ($\Delta H < 0$), heat flows into the surroundings from the system. The heat flow into the surroundings increases the random motions in the surroundings and increases the entropy of the surroundings ($\Delta S_{\text{surr}} > 0$). This is a favorable driving force for

spontaneity. In an endothermic reaction ($\Delta H > 0$), heat is transferred from the surroundings into the system. This heat flow out of the surroundings decreases the random motions in the surroundings and decreases the entropy of the surroundings ($\Delta S_{\text{surr}} < 0$). This is unfavorable. The magnitude of $\Delta S_{\text{surr}}$ also depends on the temperature. The relationship is inverse; at low temperatures, a specific amount of heat exchange makes a larger percent change in the surroundings than the same amount of heat flow at a higher temperature. The negative sign in the $\Delta S_{\text{surr}} = -\Delta H/T$ equation is necessary to get the signs correct. For an exothermic reaction where $\Delta H$ is negative, this increases $\Delta S_{\text{surr}}$, so the negative sign converts the negative $\Delta H$ value into a positive quantity. For an endothermic process where $\Delta H$ is positive, the sign of $\Delta S_{\text{surr}}$ is negative and the negative sign converts the positive $\Delta H$ value into a negative quantity.
**37.** a. $7.45 \times 10^3$ J/K; b. $-376$ J/K **39.** a. negative; b. positive; c. negative; d. negative; e. negative; f. positive **41.** 262 J $\text{K}^{-1}$ $\text{mol}^{-1}$ **43.** 184 J $\text{K}^{-1}$ $\text{mol}^{-1}$ **45.** 629.7 K **47.** a. Yes, $NH_3$ will melt since $\Delta G < 0$. b. 196 K **49.** 43.7 K **51.** $-16$ kJ/mol **53.** $-5.40$ kJ; 328.6 K; $\Delta G°$ is negative below 328.6 K where the favorable $\Delta H°$ term dominates. **55.** a. 464 kJ; b. Since $\Delta G°$ is positive, this reaction is not spontaneous at standard conditions at 298 K. c. This reaction will be spontaneous at standard conditions ($\Delta G° < 0$) at $T > 2890$ K where the favorable entropy term will dominate. **57.** $CH_4(g) + CO_2(g) \rightarrow CH_3CO_2H(l)$, $\Delta H° = -16$ kJ, $\Delta S° = -240.$ J/K, $\Delta G° = 56$ kJ; $CH_3OH(g) + CO(g) \rightarrow CH_3CO_2H(l)$, $\Delta H° = -173$ kJ, $\Delta S° = -278$ J/K, $\Delta G° = -90.$ kJ; the second reaction is preferred at standard conditions since it will be spontaneous at high enough temperatures so that the rate of the reaction should be reasonable. It should be run at temperatures below 622 K. **59.** Enthalpy is not favorable, so $\Delta S$ must provide the driving force for the change. Thus $\Delta S$ is positive. There is an increase in positional probability, so the original enzyme has the more ordered structure. **61.** Since there are more product gas molecules than reactant gas molecules ($\Delta n > 0$), $\Delta S$ will be positive. From the signs of $\Delta H$ and $\Delta S$, this reaction is spontaneous at all temperatures. It will cost money to heat the reaction mixture. Since there is no thermodynamic reason to do this, the purpose of the elevated temperature must be to increase the rate of the reaction, i.e., kinetic reasons. **63.** The sign of $\Delta G$ (positive or negative) tells us which reaction is spontaneous (the forward or reverse reaction). If $\Delta G < 0$, then the forward reaction is spontaneous and if $\Delta G > 0$, then the reverse reaction is spontaneous. If $\Delta G = 0$, then the reaction is at equilibrium (neither the forward reaction nor the reverse reaction is spontaneous). $\Delta G°$ gives the equilibrium position by determining $K$ for a reaction utilizing the equation $\Delta G° = -RT \ln K$. $\Delta G°$ can be used to predict spontaneity only when all reactants and products are present at standard pressures of 1 atm and/or standard concentrations of 1 $M$. **65.** a. shifts right; b. no shift (at equilibrium); c. shifts left **67.** $\Delta H° = -92$ kJ, $\Delta S° = -199$ J/K, $\Delta G° = -34$ kJ, $K = 9.1 \times 10^5$; a. $\Delta G = -67$ kJ; b. $\Delta G = -68$ kJ; c. $\Delta G = -85$ kJ; d. $\Delta G = -41$ kJ **69.** To determine $K$ at a temperature other than 25°C, one needs to know $\Delta G°$ at that temperature. We assume $\Delta H°$ and $\Delta S°$ are temperature-independent and use the equation $\Delta G° = \Delta H° - T\Delta S°$ to estimate $\Delta G°$ at the different temperature. For $K = 1$, we want $\Delta G° = 0$, which occurs when $\Delta H° = T\Delta S°$. Again, assume $\Delta H°$ and $\Delta S°$ are temperature-independent, and then solve for $T$ ($= \Delta H°/\Delta S°$). At this temperature, $K = 1$ because $\Delta G° = 0$. This works only for reactions where the signs of $\Delta H°$ and $\Delta S°$ are the same (either both positive or both negative). When the signs are opposite, $K$ will always be greater than one (when $\Delta H°$ is negative and $\Delta S°$ is positive) or $K$ will always be less than one (when $\Delta H°$ is positive and $\Delta S°$ is negative). When the signs of $\Delta H°$ and $\Delta S°$ are opposite, $K$ can never equal one.
**71.** $-71$ kJ/mol **73.** $-4.1$ kJ/mol **75.** 60 **77.** At 25.0°C, $K = 8.72$; at 100.0°C, $K = 0.0789$ **79.** a. $\Delta H° = 57.5$ kJ, $\Delta S° = -75.6$ J/K; b. 106.4 kJ **81.** 310 K; $-310$ J $\text{K}^{-1}$ $\text{mol}^{-1}$ **83.** 12.8 L; $3.84 \times 10^3$ J **85.** a. $q = 4.01 \times 10^3$ J; $w = -4.01 \times 10^3$ J; $\Delta E = 0$; b. $q = 1.99 \times 10^3$ J; $w = -1.99 \times 10^3$ J; $\Delta E = 0$; c. $q = 0$; $w = \Delta E = -2.76 \times 10^3$ J **87.** All are positive. **89.** $w_{\text{max}} = \Delta G$; when $\Delta G$ is negative, the magnitude of $\Delta G$ is equal to the maximum possible useful work obtainable from the process (at constant $T$ and $P$). When $\Delta G$ is positive, the magnitude of $\Delta G$ is equal to the minimum amount of work that must be expended to make the process spontaneous. Due to waste energy (heat) in any real process, the amount of useful work obtainable from a spontaneous process is always less than $w_{\text{max}}$, and for a nonspontaneous reaction, an amount of work greater than $w_{\text{max}}$ must be applied to make the process spontaneous. **91.** a. $\Delta G = \Delta G° = 1.8 \times 10^4$ J/mol, shifts left; b. $\Delta G = 0$, at equilibrium; c. $\Delta G = -1.1 \times 10^4$ J/mol, shifts right; d. $\Delta G = 0$, at equilibrium; e. $\Delta G = 2 \times 10^3$ J/mol, shifts left **93.** $\Delta S°$ will be negative because 2 mol of gaseous reactants forms 1 mol of gaseous product. For $\Delta G°$ to be negative, $\Delta H°$ must be negative (exothermic). For this sign combination, $K$ decreases as $T$ increases. Therefore, the ratio of the partial pressure of $PCl_5$ to the partial pressure of $PCl_3$ will decrease when $T$ is raised. **95.** Using Le Châtelier's principle: A decrease in pressure (volume increases) will favor the side with the greater number of particles. Thus 2I($g$) will be favored at low pressure. Looking at $\Delta G$: $\Delta G = \Delta G° + RT \ln(P_{\text{I}}^2/P_{\text{I}_2})$; $\ln(P_{\text{I}}^2/P_{\text{I}_2}) > 0$ for $P_{\text{I}} = P_{\text{I}_2} = 10$ atm and $\Delta G$ is positive (not spontaneous). But at $P_{\text{I}} = P_{\text{I}_2} = 0.10$ atm, the logarithm term is negative. If $|RT \ln(Q)| > \Delta G°$, then $\Delta G$ becomes negative, and the reaction is spontaneous. **97.** 6 $M$
**99.** $\Delta S$ is more favorable for reaction two than for reaction one. In reaction one, seven particles in solution are forming one particle in solution. In reaction two, four particles are forming one particle, which results in a smaller decrease in positional probability than for reaction one and a larger equilibrium constant value for reaction two. **101.** Note that these substances are not in the solid state but are in the aqueous state; water molecules are also present. There is an apparent increase in ordering (decrease in positional probability) when these ions are placed in water as compared to the separated state. The hydrating water molecules must be in a highly ordered arrangement when surrounding these anions.
**103.** $1.6 \times 10^6$ **105.** $\Delta G = 11.5$ kJ; $\Delta H = 0$; $\Delta S = -38.3$ J/K
**107.** a. $\Delta E = 0$, $\Delta H = 0$, $\Delta S = 7.62$ J/K, $\Delta G = -2320$ J, $w = -1500$ J, $q = 1500$ J; b. Since $\Delta S_{\text{univ}}$ (2.7 J/K) is positive, the process is spontaneous. **109.** a. 226 K; b. 239 K
**111.** a. $-2.87$ J/K; b. 2.87 J/K **113.** 88 J/K **115.** greater than 7.5 torr **117.** $\Delta H° = 286$ kJ, $\Delta G° = 326$ kJ, $K = 7.22 \times 10^{-58}$; $P_{O_3} = 3.3 \times 10^{-41}$ atm; this partial pressure represents one molecule of ozone per $9.5 \times 10^{17}$ L of air. Equilibrium is probably not maintained under these conditions since the concentration of ozone is not large enough to maintain equilibrium. **119.** a. 0.333; b. $P_{\text{A}} = 1.50$ atm, $P_{\text{B}} = 0.50$ atm; c. $\Delta G = 2722\text{ J} + (8.3145)(298) \ln(0.50/1.50) = 2722\text{ J} - 2722\text{ J} = 0$ (carrying extra sig. figs.)

**121.**

|  | $q$ | $w$ | $\Delta E$ | $\Delta S$ | $\Delta H$ | $\Delta G$ |
|---|---|---|---|---|---|---|
| Step 1 | 1480 J | $-1480$ J | 0 | 7.56 J/K | 0 | $-2250$ J |
| Step 2 | 1240 J | $-1240$ J | 0 | 5.77 J/K | 0 | $-1720$ J |
| Step 3 | 1250 J | $-1250$ J | 0 | 5.81 J/K | 0 | $-1730$ J |
| Total | 3970 J | $-3970$ J | 0 | 19.14 J/K | 0 | $-5.70 \times 10^3$ J |

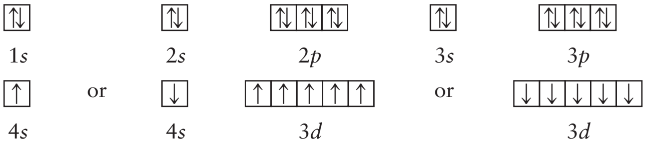
**123.** a. $1.24 \times 10^{90}$; b. $-154$ J/K **125.** $\Delta S = 29 \text{ J K}^{-1} \text{ mol}^{-1}$ **127.** $\Delta S_{\text{sys}} = -34.3$ J/K, $\Delta S_{\text{surr}} = 33.7$ J/K

## Chapter 11

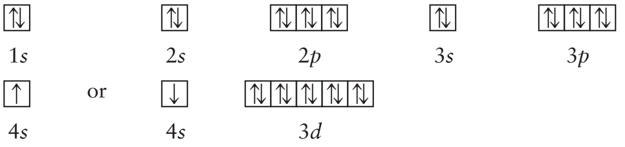
**15.** Electrochemistry is the study of the interchange of chemical and electrical energy. A redox (oxidation–reduction) reaction is a reaction in which one or more electrons are transferred. In a galvanic cell, a spontaneous redox reaction occurs that produces an electric current. In an electrolytic cell, electricity is used to force a nonspontaneous redox reaction to occur. **17.** See Fig. 11.2 for a typical galvanic cell. The anode compartment contains the oxidation half-reaction compounds/ions, and the cathode compartment contains the reduction half-reaction compounds/ions. The electrons flow from the anode to the cathode. In the salt bridge, cations flow to the cathode and anions flow to the anode. For each of the following answers, all solutes are 1.0 *M* and all gases are at 1.0 atm. a. $7H_2O(l) + 2Cr^{3+}(aq) + 3Cl_2(g) \rightarrow Cr_2O_7^{2-}(aq) + 6Cl^-(aq) + 14H^+(aq)$; $\mathscr{E}^\circ_{\text{cell}} = 0.03$ V; cathode: Pt electrode; $Cl_2$ bubbled into solution, $Cl^-$ in solution; anode: Pt electrode; $Cr^{3+}$, $H^+$, and $Cr_2O_7^{2-}$ in solution; b. $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$; $\mathscr{E}^\circ_{\text{cell}} = 2.71$ V; cathode: Cu electrode; $Cu^{2+}$ in solution; anode: Mg electrode; $Mg^{2+}$ in solution; c. $12\ H^+(aq) + 2IO_3^-(aq) + 10Fe^{2+}(aq) \rightarrow 10Fe^{3+}(aq) + I_2(s) + 6H_2O(l)$; $\mathscr{E}^\circ_{\text{cell}} = 0.43$ V; cathode: Pt electrode; $IO_3^-$, $I_2$, and $H_2SO_4$ ($H^+$ source) in solution; anode: Pt electrode; $Fe^{2+}$ and $Fe^{3+}$ in solution; d. $Zn(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Zn^{2+}(aq)$; $\mathscr{E}^\circ = 1.56$ V; cathode: Ag electrode; $Ag^+$ in solution; anode: Zn electrode; $Zn^{2+}$ in solution **19.** See Exercise 17 for a description of a galvanic cell. For each of the following answers, all solutes are 1.0 *M* and all gases are at 1.0 atm. a. $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$; $\mathscr{E}^\circ = 0.27$ V; cathode: Pt electrode; $Cl_2(g)$ bubbled in, $Cl^-$ in solution; anode: Pt electrode; $Br_2$ and $Br^-$ in solution; b. $3H_2O(l) + 5IO_4^-(aq) + 2Mn^{2+}(aq) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$; $\mathscr{E}^\circ = 0.09$ V; cathode: Pt electrode; $IO_4^-$, $IO_3^-$, and $H_2SO_4$ (as a source of $H^+$) in solution; anode: Pt electrode; $Mn^{2+}$, $MnO_4^-$, and $H_2SO_4$ in solution; c. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$; $\mathscr{E}^\circ_{\text{cell}} = 1.10$ V; cathode: Pt electrode; $H_2O_2$ and $H^+$ in solution; anode: Pt electrode; $O_2(g)$ bubbled in, $H_2O_2$ and $H^+$ in solution; d. $2Fe^{3+}(aq) + 3Mn(s) \rightarrow 2Fe(s) + 3Mn^{2+}(aq)$; $\mathscr{E}^\circ_{\text{cell}} = 1.14$ V; cathode: Fe electrode; $Fe^{3+}$ in solution; anode: Mn electrode; $Mn^{2+}$ in solution **21.** a. Pt | $Br^-$ (1.0 *M*), $Br_2$ (1.0 *M*) ‖ $Cl_2$ (1.0 atm) | $Cl^-$ (1.0 *M*) | Pt; b. Pt | $Mn^{2+}$ (1.0 *M*), $MnO_4^-$ (1.0 *M*), $H^+$ (1.0 *M*) ‖ $IO_4^-$ (1.0 *M*), $IO_3^-$ (1.0 *M*), $H^+$ (1.0 *M*) | Pt; c. Pt | $H_2O_2$ (1.0 *M*), $H^+$ (1.0 *M*) | $O_2$ (1.0 atm) ‖ $H_2O_2$ (1.0 *M*), $H^+$ (1.0 *M*) | Pt; d. Mn | $Mn^{2+}$ (1.0 *M*) ‖ $Fe^{3+}$ (1.0 *M*) | Fe **23.** a. no; b. yes; c. yes; d. no **25.** $F^- < H_2O < I_2 < Cu^+ < H^- < K$ **27.** a. $Cr_2O_7^{2-}$, $O_2$, $MnO_2$, $IO_3^-$; b. $PbSO_4$, $Cd^{2+}$, $Fe^{2+}$, $Cr^{3+}$, $Zn^{2+}$, $H_2O$ **29.** Since $\mathscr{E}^\circ_{\text{cell}}$ is positive for this reaction, at standard conditions $ClO^-$ can spontaneously oxidize $NH_3$ to the somewhat toxic $N_2H_4$. **31.** An extensive property is one that depends directly on the amount of substance. The free energy change for a reaction depends on whether 1 mole of product is produced or 2 moles of product are produced or 1 million moles of product are produced. This is not the case for cell potentials, which do not depend on the amount of substance. The equation that relates $\Delta G$ to $\mathscr{E}$ is $\Delta G = -nF\mathscr{E}$. It is the *n* term that converts the intensive property $\mathscr{E}$ into the extensive property $\Delta G$. *n* is the number of moles of electrons transferred in the balanced reaction that $\Delta G$ is associated with. **33.** a. $-388$ kJ; b. $-270.$ kJ **35.** a. $\Delta G^\circ = -52$ kJ, $K = 1.4 \times 10^9$; b. $\Delta G^\circ = -90$ kJ, $K = 2 \times 10^{15}$; c. $\Delta G^\circ = -212$ kJ, $K = 1.68 \times 10^{37}$; d. $\Delta G^\circ = -660.$ kJ, $K = 5.45 \times 10^{115}$ **37.** a. $3Mn(s) + 8H^+(aq) + 2NO_3^-(aq) \rightarrow 2NO(g) + 4H_2O(l) + 3Mn^{2+}(aq)$; $5IO_4^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$; b. reaction one: $\mathscr{E}^\circ_{\text{cell}} = 2.14$ V, $\Delta G^\circ = -1240$ kJ, $K \approx 10^{217}$; reaction two: $\mathscr{E}^\circ_{\text{cell}} = 0.09$ V, $\Delta G^\circ = -90$ kJ, $K = 2 \times 10^{15}$ **39.** $\mathscr{E}^\circ = \dfrac{T\Delta S^\circ}{nF} - \dfrac{\Delta H^\circ}{nF}$; if we graph $\mathscr{E}^\circ$ vs. *T*, we should get a straight line ($y = mx + b$). The slope of the line is equal to $\Delta S^\circ/nF$ and the *y*-intercept is equal to $-\Delta H^\circ/nF$. $\mathscr{E}^\circ$ will have a small temperature dependence when $\Delta S^\circ$ is close to zero. **41.** a. spontaneous; $-35$ kJ; $1.2 \times 10^6$; b. not spontaneous; c. spontaneous; $-85$ kJ; $7.8 \times 10^{14}$ **43.** $6.5 \times 10^{20}$ **45.** $-0.19$ V **47.** a. $Au^{3+}(aq) + 3Tl(s) \rightarrow Au(s) + 3Tl^+(aq)$; $\mathscr{E}^\circ_{\text{cell}} = 1.84$ V; b. $\Delta G^\circ = -533$ kJ; $K = 2.52 \times 10^{93}$; c. 2.04 V **49.** 1.50 V **51.** a. 2.12 V; b. 1.98 V; c. 2.05 V; d. Cell potential decreases with decreasing *T* (also, oil becomes more viscous). **53.** Concentration cell: a galvanic cell in which both compartments contain the same components but at different concentrations. All concentration cells have $\mathscr{E}^\circ_{\text{cell}} = 0$ because both compartments contain the same contents. The driving force for the cell is the different ion concentrations at the anode and cathode. The cell produces a voltage as long as the ion concentrations are different. The lower ion concentration is always at the anode. The magnitude of the cell potential depends on the magnitude of the differences in ion concentrations between the anode and cathode. The larger the difference in ion concentrations, the more negative is the log *Q* term, and the more positive is the cell potential. Thus, as the difference in ion concentrations between the anode and cathode compartments increase, the cell potential increases. This can be accomplished by decreasing the ion concentration at the anode and/or by increasing the ion concentration at the cathode. **55.** Electron flow is always from the anode to the cathode. For the cells with a nonzero cell potential, we will identify the cathode, which means the other compartment is the anode. a. 0.0 V; b. $8.9 \times 10^{-3}$ V; compartment with $[Ni^{2+}] = 2.0\ M$ is the cathode; c. 0.030 V; compartment with $[Ni^{2+}] = 1.0\ M$ is the cathode; d. 0.13 V; compartment with $[Ni^{2+}] = 1.0\ M$ is the cathode; e. 0.0 V **57.** a. 0.23 V; b. 0.16 V (the reverse reaction from part a occurs); c. $1.2 \times 10^{-5}\ M$; d. A graph of $\mathscr{E}$ versus $\log[Cu^{2+}]$ will yield a straight line with slope equal to 0.0296 V or 29.6 mV. **59.** a. $1.4 \times 10^{-14}\ M$; b. $2.9 \times 10^{13}$ **61.** a. 16 g; b. 25 g; c. 71 g; d. 4.9 g **63.** 554 s **65.** a. cathode: $Ni^{2+} + 2e^- \rightarrow Ni$, anode: $2Br^- \rightarrow Br_2 + 2e^-$; b. cathode: $Al^{3+} + 3e^- \rightarrow Al$, anode: $2F^- \rightarrow F_2 + 2e^-$; c. cathode: $Mn^{2+} + 2e^- \rightarrow Mn$, anode: $2I^- \rightarrow I_2 + 2e^-$; d. cathode: $Ni^{2+} + 2e^- \rightarrow Ni$, anode: $2Br^- \rightarrow Br_2 + 2e^-$; e. cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; f. cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, anode: $2I^- \rightarrow I_2 + 2e^-$ **67.** Au(*s*) will plate out first since it has the most positive reduction potential, followed by Ag(*s*), which is followed by Ni(*s*), and finally Cd(*s*) will plate out last since it has the most negative reduction potential of the metals listed. **69.** Yes, since the range of potentials for plating out each metal do not overlap, we should be able to separate the three metals. The order of plating will be Ir(*s*) first, followed by Pt(*s*), and finally Pd(*s*) as the potential is gradually increased. **71.** $MgCl_2$ **73.** 9.12 L $F_2$ at the anode; 29.2 g K at the cathode **75.** 6.00 L **77.** 0.98 V **79.** 1.14 V **81.** $-212$ kJ **83.** a. Paint: covers the metal surface so no contact occurs between the metal and air. This works only as long as the painted surface is not scratched. b. Durable oxide coatings: covers the metal surface so no contact occurs between the metal and air. c. Galvanizing: coating steel with zinc; Zn forms an effective oxide coating over steel; also, zinc is more easily oxidized than the iron in the steel. d. Sacrificial metal: a more easily oxidized metal attached to an iron surface; the more active metal is preferentially oxidized instead of iron. e. Alloying: adding chromium and nickel to steel; the added Cr and Ni form oxide coatings on the steel surface. f. Cathodic protection: a more easily oxidized metal is placed in electrical contact with the metal we are trying to protect. It is oxidized in preference to the protected metal. The protected metal becomes the cathode electrode, thus, "cathodic protection." **85.** It is easier to oxidize Zn than Fe, so the Zn will be oxidized, protecting the iron of the *Monitor*'s hull. **87.** The potential oxidizing agents are $NO_3^-$ and $H^+$. Hydrogen ion cannot oxidize Pt under either condition. Nitrate cannot oxidize Pt unless there is $Cl^-$ in the solution. Aqua regia has both $Cl^-$ and $NO_3^-$. The overall reaction is $12Cl^-(aq) + 3Pt(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3PtCl_4^{2-}(aq) + 2NO(g) + 4H_2O(l)$; $\mathscr{E}^\circ_{cell} = 0.21$ V **89.** a. ±0.02 pH units; $\pm 6 \times 10^{-6}$ *M* $H^+$; b. ±0.001 V **91.** a. decrease; b. increase; c. decrease; d. decrease; e. no effect **93.** osmium(IV) nitrate; copper, Cu **95.** a. 1.14 V; b. 1.09 V; c. 78 g Zn, 319 g Cu; d. 13.4 h **97.** a. $5.77 \times 10^{-10}$; b. 1.9 *M* **99.** $2.39 \times 10^{-7}$ **101.** a. 0.16 V; b. 8.6 mol **103.** 0.64 V **105.** a. yes; b. $3H_2O(l) + Zr(s) \rightarrow 2H_2(g) + ZrO_2 \cdot H_2O(s)$; c. $\mathscr{E}^\circ = 1.53$ V; $\Delta G^\circ = -590.$ kJ; $K \approx 10^{104}$; d. $4.42 \times 10^4$ g $H_2$; $2.3 \times 10^6$ L; e. Probably yes; less radioactivity overall was released by venting the $H_2$ than what would have been released if the $H_2$ had exploded inside the reactor (as happened at Chernobyl). Neither alternative is pleasant, but venting the radioactive hydrogen is the less unpleasant of the two alternatives.

## Chapter 12

**21.** $3.0 \times 10^{10}$ $s^{-1}$; $2.0 \times 10^{-23}$ J/photon; 12 J/mol **23.** a. $5.0 \times 10^{-6}$ m; b. infrared; **c.** $4.0 \times 10^{-20}$ J/photon; $2.4 \times 10^4$ J/mol; d. less **25.** 427.7 nm **27.** $4.36 \times 10^{-19}$ J **29.** The photoelectric effect refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes it. The light must have a certain minimum frequency (energy) in order to remove electrons from the surface of a metal. Light having a frequency below the minimum results in no electrons being emitted, whereas light at or higher than the minimum frequency does cause electrons to be emitted. For light having a frequency higher than the minimum frequency, the excess energy is transferred into kinetic energy for the emitted electron. Albert Einstein explained the photoelectric effect by applying quantum theory. **31.** a. $1.32 \times 10^{-13}$ m; b. $5.3 \times 10^3$ m/s **33.** Ca **35.** a. 656.7 nm, visible electromagnetic radiation (red light); b. 486.4 nm, visible electromagnetic radiation (green-blue light); c. 121.6 nm, ultraviolet electromagnetic radiation; d. 1876 nm, infrared electromagnetic radiation **37.** a. False; It takes less energy to ionize an electron from $n = 3$ than from the ground state. b. True; c. False; The energy difference between $n = 3$ and $n = 2$ is smaller than the energy difference between $n = 3$ and $n = 1$. Thus the wavelength of light emitted is longer for the $n = 3$ to $n = 2$ electronic transition than for the $n = 3$ to $n = 1$ transition. d. True; e. False; $n = 2$ is the first excited state and $n = 3$ is the second excited state. **39.** $n = 7$ **41.** $n = 4$ **43.** $n = 4$ **45.** a. $5.79 \times 10^{-4}$ m; b. $3.64 \times 10^{-33}$ m; c. The diameter of an H atom is roughly $1.0 \times 10^{-8}$ cm. The uncertainty in position is much larger than the size of the atom. d. The uncertainty is insignificant compared to the size of a baseball. **47.** 3.50 nm **49.** As $L$ increases, $E_n$ will decrease and the spacing between energy levels will also decrease. **51.** Since $E_n$ is inversely proportional to $L^2$, the electron in the larger box ($10^{-6}$ m) has the lowest ground-state energy. **53.** The 2*p* orbitals differ from each other in the direction in which they point in space. The 2*p* and 3*p* orbitals differ from each other in their size, energy, and number of nodes. A nodal surface in an atomic orbital is a surface in which the probability of finding an electron is zero. The 1*p*, 1*d*, 2*d*, 1*f*, 2*f*, and 3*f* orbitals are not allowed solutions to the Schrödinger equation. For $n = 1$, $\ell \neq 1, 2, 3$, etc., so 1*p*, 1*d*, and 1*f* orbitals are forbidden. For $n = 2$, $\ell \neq 2, 3, 4$, etc., so 2*d* and 2*f* orbitals are forbidden. For $n = 3$, $\ell \neq 3, 4, 5$, etc., so 3*f* orbitals are forbidden. The penetrating term refers to the fact that there is a higher probability of finding a 4*s* electron closer to the nucleus than a 3*d* electron. This leads to a lower energy for the 4*s* orbital relative to the 3*d* orbitals in polyelectronic atoms and ions. **55.** a. For $n = 3$, $\ell = 3$ is not possible. d. $m_s$ cannot equal −1. e. $\ell$ cannot be a negative number. f. For $\ell = 1$, $m_l$ cannot equal 2. **57.** 1*p*, 0 electrons ($\ell \neq 1$ when $n = 1$); $6d_{x^2-y^2}$, 2 electrons (specifies one atomic orbital); 4*f*, 14 electrons (7 orbitals have 4*f* designation); $7p_y$, 2 electrons (specifies one atomic orbital); 2*s*, 2 electrons (specifies one atomic orbital); $n = 3$, 18 electrons (3*s*, 3*p*, and 3*d* orbitals are possible; there are one 3*s* orbital, three 3*p* orbitals, and five 3*d* orbitals) **59.** The diagrams of the orbitals in the text give only 90% probabilities of where the electron may reside. We can never be 100% certain of the location of the electrons due to Heisenberg's uncertainty principle. **61.** $\theta = 0 : 2.46 \times 10^{28}$; $\theta = 90° : 0$ **63.** Valence electrons are the electrons in the outermost principal quantum level of an atom (those electrons in the highest $n$ value orbitals). The electrons in the lower $n$ value orbitals are all inner core or just core electrons. The key is that the outermost electrons are the valence electrons. When atoms interact with each other, it will be the outermost electrons that are involved in these interactions. In addition, how tightly the nucleus holds these outermost electrons determines atomic size, ionization energy, and other properties of atoms. Elements in the same group have similar valence electron configurations and, as a result, have similar chemical properties. **65.** a. 32; b. 8; c. 25; d. 10; e. 6; f. 0; g. 1; h. 9; i. 0; j. 2 **67.** Sc: $1s^22s^22p^63s^23p^64s^23d^1$; Fe: $1s^22s^22p^63s^23p^64s^23d^6$; P: $1s^22s^22p^63s^23p^3$; Cs: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^1$; Eu: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^65d^1$ (actual: $[Xe]6s^24f^7$); Pt: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^8$ (actual: $[Xe]6s^14f^{14}5d^9$); Xe: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$; Br: $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$ **69.** Cr, Cu, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Pt, Au **71.** Cr: $1s^22s^22p^63s^23p^64s^13d^5$; Cr has 6 unpaired electrons.



Cu: $1s^22s^22p^63s^23p^64s^13d^{10}$; Cu has 1 unpaired electron.



**73.** a. 32; b. 28; c. 23; d. 56 or 59 **75.** Li (1 unpaired electron), N (3 unpaired electrons), Ni (2 unpaired electrons), and Te (2 unpaired electrons) are paramagnetic. **77.** H, Li, Na, K, B, Al, Ga, F, Cl, Br, Sc, and Cu all have one unpaired electron in the ground state. **79.** O, 2; $O^+$, 3; $O^-$, 1; Os, 4; Zr, 2; S, 2; F, 1; Ar, 0 **81.** Ionization energy: $P(g) \rightarrow P^+(g) + e^-$; electron affinity: $P(g) + e^- \rightarrow P^-(g)$ **83.** As successive electrons are removed, the net positive charge on the resultant ion increases. This increase in positive charge binds the remaining electrons more firmly, and the ionization energy increases. The electron configuration for Si is $1s^22s^22p^63s^23p^2$. There is a large jump in ionization energy when going from the removal of valence electrons to the removal of core electrons. For silicon, this occurs when the fifth electron is removed since we go from the valence electrons in $n = 3$ to the core electrons in $n = 2$. There should be another big jump when the thirteenth electron is removed (i.e., when a 1*s* electron is removed). **85.** a. S < Se < Te; b. Br < Ni < K; c. F < Si < Ba; d. Be < Na < Rb; e. Ne < Se < Sr; f. O < P < Fe **87.** a. Ba; b. K; c. O; d. $S^{2-}$; e. Cs **89.** As: $[Ar]4s^2 3d^{10} 4p^3$; Se: $[Ar]4s^2 3d^{10} 4p^4$; The general ionization energy trend predicts that Se should have a higher ionization energy than As. Se is an exception to the general ionization energy trend. There are extra electron–electron repulsions in Se because two electrons are in the same 4*p* orbital, resulting in a lower ionization energy for Se than predicted. **91.** Size also decreases going across a period. Sc and Ti plus Y and Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller. **93.** a. $[Rn]7s^2 5f^{14} 6d^{10} 7p^5$; b. At; c. NaUus, $Mg(Uus)_2$, $C(Uus)_4$, $O(Uus)_2$; d. $UusO^-$, $UusO_2{}^-$, $UusO_3{}^-$, $UusO_4{}^-$ **95.** Electron–electron repulsions must be considered when adding an electron to an atom. Smaller atoms attract electrons more strongly yet have larger electron–electron repulsions. The two factors oppose one another, leading to relatively small variations in electron affinities. **97.** Electron–electron repulsions are much greater in $O^-$ than in $S^-$ because the electron goes into a smaller 2*p* orbital versus the larger 3*p* orbital in sulfur. This results in a more favorable (more exothermic) electron affinity for sulfur. **99.** a. −1445 kJ/mol; b. −580 kJ/mol; c. 348.7 kJ/mol; d. 1255 kJ/mol; e. −1255 kJ/mol **101.** Yes; ionization energy generally decreases down a group, and atomic radius generally increases down a group. The data in Table 12.9 confirm both of these general trends. **103.** a. $6Li(s) + N_2(g) \rightarrow 2Li_3N(s)$; b. $2Rb(s) + S(s) \rightarrow Rb_2S(s)$; c. $2Cs(s) + 2H_2O(l) \rightarrow 2CsOH(aq) + H_2(g)$; d. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$ **105.** For 589.0 nm: $5.090 \times 10^{14}\ s^{-1}$, $3.373 \times 10^{-19}$ J/photon, 203.1 kJ/mol; for 589.6 nm: $5.085 \times 10^{14}\ s^{-1}$, $3.369 \times 10^{-19}$ J/photon, 202.9 kJ/mol **107.** 119: $[Rn]7s^2 5f^{14} 6d^{10} 7p^6 8s^1$ **109.** a. *n*; b. *n* and $\ell$ **111.** Size decreases from left to right and increases going down the periodic table. So going one element right and one element down would result in a similar size for the two elements diagonal to each other. The ionization energies will be similar for the diagonal elements since the periodic trends also oppose each other. Electron affinities are harder to predict, but atoms with similar size and ionization energy should also have similar electron affinities. **113.** 200 s (about 3 minutes) **115.** greenish yellow light **117.** When the *p* and *d* orbital functions are evaluated at various points in space, the results sometimes have positive values and sometimes have negative values. The term "phase" is often associated with the + and − signs. For example, a sine wave has alternating positive and negative phases. This is analogous to the positive and negative values (phases) in the *p* and *d* orbitals. **119.** a. 146 kJ; b. 407 kJ; c. 1117 kJ; d. 1524 kJ **121.** alkaline earth metal family **123.** a. 24; b. 6; c. 12; d. 2; e. 26; f. 24.9 g; g. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ **125.** a. 4; b. four elements in the first period and 16 elements in the second period; c. 20; d. 28 **127.** At $x = 0$, the value of the square of the wave function must be zero. The particle must be inside the box. For $\psi = A\cos(Lx)$, at $x = 0$, $\cos(0) = 1$ and $\psi^2 = A^2$. This violates the boundary condition. **129.** a. Line A: 6 → 3; Line B: 5 → 3; b. 121.6 nm **131.** X = carbon; $m = 5(C^{5+})$ **133.** a. The quantum numbers are:

$$\begin{array}{ll} \text{ground state } (E_{11}) & \rightarrow n_x = 1, n_y = 1 \\ \text{first excited state } (E_{21}) & \rightarrow n_x = 2, n_y = 1 \\ \text{second excited state } (E_{12}) & \rightarrow n_x = 1, n_y = 2 \end{array}$$

b. $4.5 \times 10^{-5}$ m **135.** a. $2.2 \times 10^{-9}$; b. $1.5 \times 10^{-9}$; c. $2.9 \times 10^{-10}$; d. $1.9 \times 10^{-4}$; e. $1 \times 10^{-3}$ **137.** 2470 nm **139.** a. 43.33; b. $Z_{\text{eff}}$ is slightly less than *Z*. Electrons in other orbitals can penetrate the 1*s* orbital. Thus a 1*s* electron can be slightly shielded from the nucleus, giving a $Z_{\text{eff}}$ close to but less than *Z*.

## Chapter 13

**11.** Electronegativity is the ability of an atom in a molecule to attract electrons to itself. Electronegativity is a bonding term. Electron affinity is the energy change when an electron is added to a substance. Electron affinity deals with isolated atoms in the gas phase. A covalent bond is a sharing of an electron pair in a bond between two atoms. An ionic bond is a complete transfer of electrons from one atom to another to form ions. The electrostatic attraction of the oppositely charged ions is the ionic bond. A pure covalent bond is an equal sharing of a shared electron pair in a bond. A polar covalent bond is an unequal sharing. Ionic bonds form when there is a large difference in electronegativity between the two atoms bonding together. This usually occurs when a metal with a small electronegativity is bonded to a nonmetal having a large electronegativity. A pure covalent bond forms between atoms having identical or nearly identical electronegativities. A polar covalent bond forms when there is an intermediate electronegativity difference. In general, nonmetals bond together by forming covalent bonds, either pure covalent or polar covalent. Ionic bonds form due to the strong electrostatic attraction between two oppositely charged ions. Covalent bonds form because the shared electrons in the bond are attracted to two different nuclei, unlike the isolated atoms, in which electrons are attracted to only one nuclei. The attraction to another nuclei overrides the added electron–electron repulsions. **13.** a. C < N < O; b. Se < S < Cl; c. Sn < Ge < Si; d. Tl < Ge < S; e. Rb < K < Na; f. Ga < B < O **15.** a. C (2.6) < N (3.0) < O (3.4), same as predicted; b. Se (2.6) = S (2.6) < Cl (3.2), different; c. Si (1.9) < Ge (2.0) = Sn (2.0), different; d. Tl (2.0) = Ge (2.0) < S (2.6), different; e. Rb = K < Na, different; f. Ga < B < O, same; Most polar bonds in Exercise 14 using actual EN values: a. Si—F (Ge—F predicted); b. P—Cl (same as predicted); c. S—F (same as predicted); d. Ti—Cl (same as predicted); e. C—H (Sn—H predicted); f. Al—Br (Tl—Br predicted) **17.** Br—Br < N—O < C—F < Ca—O < K—F **19.** Anions are larger than the neutral atom, and cations are smaller than the neutral atom. For anions, the added electrons increase the electron–electron repulsions. To counteract this, the size of the electron cloud increases, placing the electrons further apart from one another. For cations, as electrons are removed, there are fewer electron–electron repulsions, and the electron cloud can be pulled closer to the nucleus. Isoelectronic: same number of electrons. Two variables, the number of protons and the number of electrons, determine the size of an ion. Keeping the number of electrons constant, we have to consider only the number of protons to predict trends in size. The ion with the most protons attracts the same number of electrons most strongly, resulting in a smaller size. **21.** a. $Cu > Cu^+ > Cu^{2+}$; b. $Pt^{2+} > Pd^{2+} > Ni^{2+}$; c. $O^{2-} > O^- > O$; d. $La^{3+} > Eu^{3+} > Gd^{3+} > Yb^{3+}$; e. $Te^{2-} > I^- > Cs^+ > Ba^{2+} > La^{3+}$ **23.** a. $Cs_2S$ is composed of $Cs^+$ and $S^{2-}$. $Cs^+$ has the same electron configuration as Xe, and $S^{2-}$ has the same configuration as Ar. b. $SrF_2$; $Sr^{2+}$ has the Kr electron configuration and $F^-$ has the Ne configuration. c. $Ca_3N_2$; $Ca^{2+}$ has the Ar electron configuration and $N^{3-}$ has the Ne configuration. d. $AlBr_3$; $Al^{3+}$ has the Ne electron configuration and $Br^-$ has the Kr configuration. **25.** $Se^{2-}$, $Br^-$, $Rb^+$, $Sr^{2+}$, $Y^{3+}$, and $Zr^{4+}$ are some ions that are isoelectronic with Kr (36 electrons). In terms of size, the ion with the most protons will hold the electrons tightest and will be the smallest. The size trend is

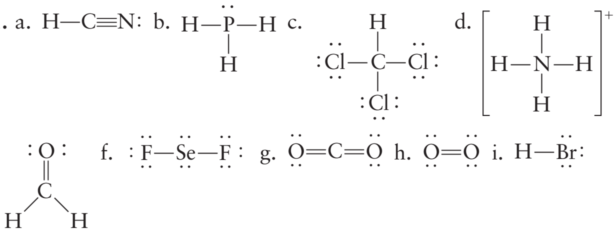
$$\begin{array}{lr} Zr^{4+} < Y^{3+} < Sr^{2+} < Rb^+ < Br^- < & Se^{2-} \\ \text{smallest} & \text{largest} \end{array}$$

**27.** a. $Al_2S_3$, aluminum sulfide; b. $K_3N$, potassium nitride; c. $MgCl_2$, magnesium chloride; d. CsBr, cesium bromide **29.** −437 kJ/mol **31.** 181 kJ/mol **33.** a. From the data given, less energy is required to produce $Mg^+(g) + O^-(g)$ than to produce $Mg^{2+}(g) + O^{2-}(g)$. However, the lattice energy for $Mg^{2+}O^{2-}$ will be much more exothermic than for $Mg^+O^-$ (because of the greater charges in $Mg^{2+}O^{2-}$). The favorable lattice energy term will dominate and $Mg^{2+}O^{2-}$ forms. b. $Mg^+$ and $O^-$ both have unpaired electrons. In $Mg^{2+}$ and $O^{2-}$, there are no unpaired electrons. Hence, $Mg^+O^-$ would be paramagnetic; $Mg^{2+}O^{2-}$ would be diamagnetic. Paramagnetism can be detected by measuring the mass of a sample in the presence and absence of a magnetic field. The apparent mass of a paramagnetic substance will be larger in a magnetic field because of the force between the unpaired electrons and the field. **35.** $Ca^{2+}$ has greater charge than $Na^+$, and $Se^{2-}$ is smaller than $Te^{2-}$. The effect of charge on the lattice energy is greater than the effect of size. We expect the trend from most exothermic to least exothermic to be

$$\underset{(-2862)}{\mathrm{CaSe}} > \underset{(-2721)}{\mathrm{CaTe}} > \underset{(-2130)}{\mathrm{Na_2Se}} > \underset{(-2095\ \mathrm{kJ/mol})}{\mathrm{Na_2Te}}$$

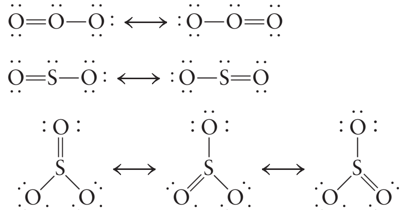
**37.** a. −183 kJ; b. −109 kJ; c. −158 kJ; d. −1169 kJ **39.** −42 kJ **41.** −1228 kJ **43.** −5681 kJ **45.** Since both reactions are highly exothermic, the high temperature is not needed to provide energy. It must be necessary for some other reason. This will be discussed in Chapter 15 on kinetics. **47.** a. 1549 kJ; b. 1390. kJ; c. 1312 kJ; d. 1599 kJ **49.** $D_{\text{calc}}$ = 389 kJ/mol as compared with 391 kJ/mol in the table.

**51.**



**53.** Molecules or ions that have the same number of valence electrons and the same number of atoms will have similar Lewis structures.

**55.**



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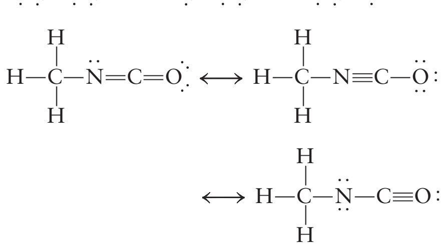
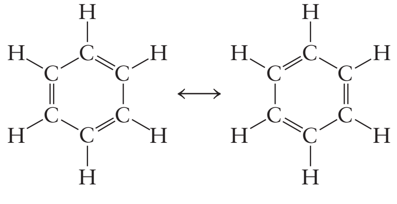
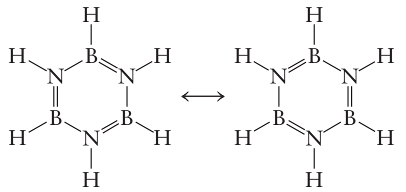


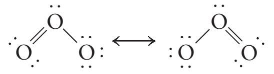
**59.**



**61.**

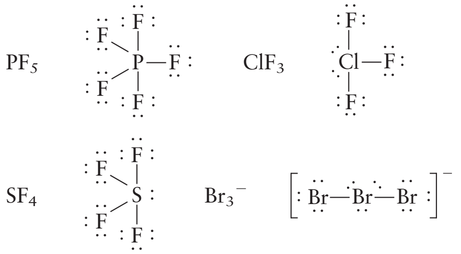


**63.** Statements a and c are true. For statement b, $SF_4$ has 5 electron pairs around the sulfur in the best Lewis structure; it is an exception to the octet rule. Because $OF_4$ has the same number of valence electrons as $SF_4$, $OF_4$ would also have to be an exception to the octet rule. However, Row 2 elements like O never have more than 8 electrons around them, so $OF_4$ does not exist. For statement d, two resonance structures can be drawn for ozone:

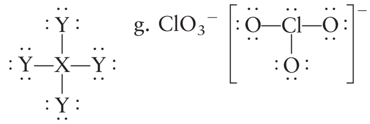


When resonance structures can be drawn, the actual bond lengths and strengths are all equal to each other. Even though each Lewis structure implies the two O—O bonds are different, this is not the case in real life. In real life, both of the O—O bonds are equivalent. When resonance structures can be drawn, you can think of the bonding as an average of all of the resonance structures.

**65.**



Row 3 and heavier nonmetals can have more than 8 electrons around them when they have to. Row 3 and heavier elements have empty *d* orbitals which are close in energy to the valence *s* and *p* orbitals. These empty *d* orbitals can accept extra electrons.
**67.** Three resonance structures can be drawn for $CO_3^{2-}$. The actual structure for $CO_3^{2-}$ is an average of these three resonance structures. That is, the three C—O bond lengths are all equivalent, with a length somewhere between a single bond and a double bond. The actual bond length of 136 pm is consistent with this resonance view of $CO_3^{2-}$. **69.** $N_2 < N_2F_2 < N_2F_4$ **71.** a–f and h all have similar Lewis structures:



Formal charges: a. +1; b. +2; c. +3; d. +1; e. +2; f. +4; g. +2; h. +1

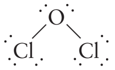
**73.**

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

**75.** [51] a. linear, 180°; b. trigonal pyramid, < 109.5°; c. tetrahedral, 109.5°; d. tetrahedral, 109.5°; e. trigonal planar, 120°; f. V-shaped, < 109.5°; g. linear, 180°; h. and i. linear, no bond angle in diatomic molecules; [52] a. All are tetrahedral, 109.5°; b. All are trigonal pyramid, < 109.5°; c. All are V-shaped, < 109.5°; [54] a. $NO_2^-$: V-shaped, ≈ 120°; $NO_3^-$: trigonal planar, 120°;

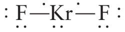
$N_2O_4$: trigonal planar about both nitrogens, 120°; b. All are linear; 180° **77.** $Br_3^-$ is linear; $ClF_3$ is T-shaped; $SF_4$ is see-saw. **79.** a. linear, 180°; b. T-shaped, ≈ 90°; c. see-saw, ≈ 120° and ≈ 90°; d. trigonal bipyramid, 120° and 90° **81.** $SeO_2$, $PCl_3$, and $SCl_2$ have net dipole moments (are polar). **83.** The two general requirements for a polar molecule are (1) polar bonds and (2) a structure such that the bond dipoles of the polar bonds do not cancel. In $CF_4$, the fluorines are symmetrically arranged about the central carbon atom. The net result is for all of the individual C—F bond dipoles to cancel each other out, giving a nonpolar molecule. In $XeF_4$ the 4 Xe—F bond dipoles are also symmetrically arranged and $XeF_4$ is also nonpolar. The individual bond dipoles cancel out when summed together. In $SF_4$ we also have 4 polar bonds. But in $SF_4$ the bond dipoles are not symmetrically arranged and they do not cancel each other out. $SF_4$ is polar. It is the positioning of the lone pair that disrupts the symmetry in $SF_4$. $CO_2$ is nonpolar because the individual bond dipoles cancel each other out, but COS is polar. By replacing an O with a less electronegative S atom, the molecule is not symmetric any more. The individual bond dipoles do not cancel since the C—S bond dipole is smaller than the C—O bond dipole, resulting in a polar molecule. **85.** Only statement c is true. The bond dipoles in $CF_4$ and $KrF_4$ are arranged in a manner that they all cancel each other out, making them nonpolar molecules ($CF_4$ has a tetrahedral molecular structure, while $KrF_4$ has a square planar molecular structure). In $SeF_4$ the bond dipoles in this see-saw molecule do not cancel each other out, so $SeF_4$ is polar. For statement a, all the molecules have either a trigonal planar geometry or a trigonal bipyramidal geometry, both of which have 120-degree bond angles. However, $XeCl_2$ has three lone pairs and two bonded chlorine atoms around it. $XeCl_2$ has a linear molecular structure with a 180-degree bond angle. With three lone pairs, we no longer have a 120-degree bond angle in $XeCl_2$. For statement b, $SO_2$ has a V-shaped molecular structure with a bond angle of about 120 degrees. $CS_2$ is linear with a 180-degree bond angle, and $SCl_2$ is V-shaped but with an approximately 109.5-degree bond angle. The three compounds do not have the same bond angle. For statement d, central atoms adopt a geometry to minimize electron repulsions, not maximize them. **87.** Element E must belong to the Group 6A elements because it has 6 valence electrons. E must also be a Period 3 or heavier element since this ion has more than 8 electrons around the central E atom (Period 2 elements never have more than 8 electrons around them). Some possible identities for E are S, Se, and Te. The ion has a T-shaped molecular structure with bond angles of ≈ 90°.

**89.** a. $OCl_2$



V-shaped, polar

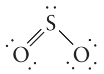
$KrF_2$



Linear, nonpolar

$BeH_2$ H—Be—H Linear, nonpolar

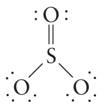
$SO_2$



V-shaped, polar

(One other resonance structure possible)

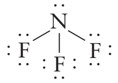
b. $SO_3$



Trigonal planar, nonpolar

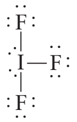
(Two other resonance structures possible)

$NF_3$



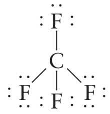
Trigonal pyramid, polar

$IF_3$



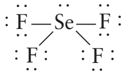
T-shaped, polar

c. $CF_4$



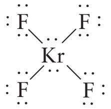
Tetrahedral, nonpolar

$SeF_4$



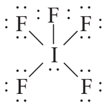
See-saw, polar

$KrF_4$



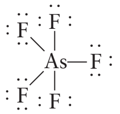
Square planar, nonpolar

d. $IF_5$



Square pyramid, polar

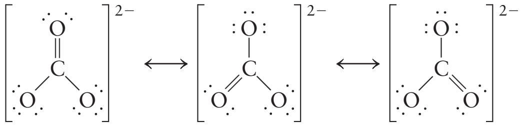
$AsF_5$

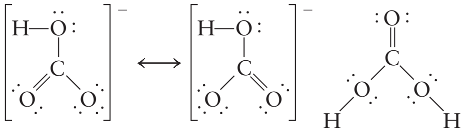


Trigonal bipyramid, nonpolar

**91.** All these molecules have polar bonds that are symmetrically arranged around the central atom. In each molecule, the individual bond dipoles cancel to give no net overall dipole moment.

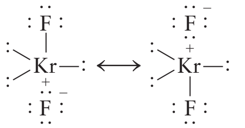
**93.**



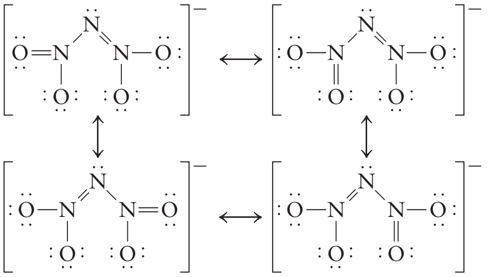


$\Delta H = -83$ kJ; the carbon–oxygen double bond is stronger than two carbon–oxygen single bonds; hence $CO_2$ and $H_2O$ are more stable than $H_2CO_3$. **95.** As the halogen atoms get larger, it becomes more difficult to fit three halogen atoms around the small nitrogen atom, and the $NX_3$ molecule becomes less stable. **97.** a. NaBr: In $NaBr_2$ the sodium ion would have a +2 charge assuming each bromine has a −1 charge. Sodium doesn't form stable $Na^{2+}$ compounds. b. $ClO_4^-$: $ClO_4$ has 31 valence electrons so it is impossible to satisfy the octet rule for all atoms in $ClO_4$. The extra electron from the −1 charge in $ClO_4^-$ allows for complete octets for all atoms. c. $XeO_4$: We can't draw a Lewis structure that obeys the octet rule for $SO_4$ (30 electrons), unlike with $XeO_4$ (32 electrons). d. $SeF_4$: Both compounds require the central atom to expand its octet. O is too small and doesn't have low-energy *d* orbitals to expand its octet (which is true for all Period 2 elements). **99.** a. radius: $N^+ < N < N^-$; IE: $N^- < N < N^+$; b. radius: $Cl^+ < Cl < Se < Se^-$; IE: $Se^- < Se < Cl < Cl^+$; c. radius: $Sr^{2+} < Rb^+ < Br^-$; IE: $Br^- < Rb^+ < Sr^{2+}$ **101.** Nonmetals, which form covalent bonds to each other, have valence electrons in the *s* and *p* orbitals. Since there are

4 total *s* and *p* orbitals, there is room for only 8 valence electrons (the octet rule). The valence shell for hydrogen is just the 1*s* orbital. This orbital can hold 2 electrons, so hydrogen follows the duet rule. **103.** I; square pyramid **105.** Yes; each structure has the same number of effective pairs around the central atom, giving the same predicted molecular structure for each compound/ion. (A multiple bond is counted as a single group of electrons.) **107.** From VSEPR, the molecular structure would be linear. Using hyperconjugation, the resonance structures are



**109.** −562 kJ **111.** a. The most likely structures are

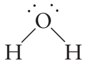


There are other possible resonance structures, but these are most likely. b. The NNN, ONN, and ONO bond angles should be about 120°. c. $NH_4N(NO_2)_2(s) \rightarrow 2N_2(g) + 2H_2O(g) + O_2(g)$, $\Delta H = -893$ kJ; d. To estimate $\Delta H$, we ignored the ionic interactions between $NH_4^+$ and $N(NO_2)_2^-$. In addition, we assumed the bond energies in Table 13.6 applied to the $N(NO_2)^-$ bonds in any one of the resonance structures above. This is a bad assumption since molecules that exhibit resonance generally have stronger overall bonds than predicted. All of these assumptions give an estimated $\Delta H$ value that is too negative. **113.** a. i. −2636 kJ; ii. −3471 kJ; iii. −3543 kJ; b. reaction iii, −8085 kJ/kg **115.** 17 kJ/mol

## Chapter 14

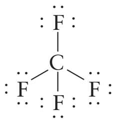
**9.** The valence orbitals of the nonmetals are the *s* and *p* orbitals. The lobes of the *p* orbitals are 90 degrees and 180 degrees apart from each other. If the *p* orbitals were used to form bonds, then all bond angels should be 90 degrees or 180 degrees. This is not the case. In order to explain the observed geometry (bond angles) that molecules exhibit, we need to make up (hybridize) orbitals that point to where the bonded atoms and lone pairs are located. We know the geometry; we hybridize orbitals to explain the geometry. Sigma bonds have shared electrons in the area centered on a line joining the atoms. The orbitals that overlap to form the sigma bonds must overlap head to head or end to end. The hybrid orbitals about a central atom always are directed at the bonded atoms. Hybrid orbitals will always overlap head to head to form sigma bonds. **11.** We use *d* orbitals when we have to; that is, we use *d* orbitals when the central atom on a molecule has more than eight electrons around it. The *d* orbitals are necessary to accommodate more than eight electrons. Row 2 elements never have more than eight electrons around them so they never hybridize *d* orbitals. We rationalize this by saying there are no *d* orbitals close in energy to the valence 2*s* and 2*p* orbitals (2*d* orbitals are forbidden energy levels). However, for Row 3 and heavier elements, there are 3*d*, 4*d*, 5*d*, etc. orbitals, which will be close in energy to the valence *s* and *p* orbitals. It is Row 3 and heavier nonmetals that hybridize *d* orbitals when they have to. For phosphorus, the valence electrons are in 3*s* and 3*p* orbitals. Therefore, 3*d* orbitals are closest in energy and are available for hybridization. Arsenic would hybridize 4*d* orbitals to go with the valence 4*s* and 4*p* orbitals, whereas iodine would hybridize 5*d* orbitals since the valence electrons are in $n = 5$.

**13.** $H_2O$ :

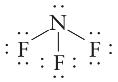


$H_2O$ has a tetrahedral arrangement of the electron pairs around the O atom that requires $sp^3$ hybridization. Two of the $sp^3$ hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two $sp^3$ hybrid orbitals hold the two lone pairs on oxygen. The two O—H bonds are formed from overlap of the $sp^3$ hybrid orbitals from oxygen with the 1*s* atomic orbitals from the hydrogen atoms. **15.** For ethane, the carbon atoms are $sp^3$ hybridized. The six C—H sigma bonds are formed from overlap of the $sp^3$ hybrid orbitals on C with the 1*s* atomic orbitals from the hydrogen atoms. The carbon–carbon sigma bond is formed from overlap of an $sp^3$ hybrid orbital on each C atom. For ethanol, the two C atoms and the O atom are $sp^3$ hybridized. All bonds are formed from overlap with these $sp^3$ hybrid orbitals. The C—H and O—H sigma bonds are formed from overlap of $sp^3$ hybrid orbitals with hydrogen 1*s* atomic orbitals. The C—C and C—O sigma bonds are formed from overlap of the $sp^3$ hybrid orbitals on each atom. **17.** [51] a. *sp*; b. $sp^3$; c. $sp^3$; d. $sp^3$; e. $sp^2$; f. $sp^3$; g. *sp*; h. each O is $sp^2$ hybridized; i. Br is $sp^3$ hybridized [52] a. All are $sp^3$ hybridized. b. All are $sp^3$ hybridized. c. All are $sp^3$ hybridized. [54] a. $NO_2^-$, $sp^2$; $NO_3^-$, $sp^2$; $N_2O_4$, $sp^2$ for both nitrogens; b. All are *sp* hybridized.

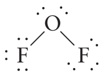
**19.** a. Tetrahedral, 109.5°, $sp^3$, nonpolar



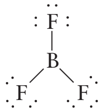
b. Trigonal pyramid, <109.5°, $sp^3$, polar



c. V-shaped, <109.5°, $sp^3$, polar



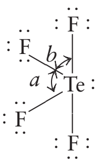
d. Trigonal planar, 120°, $sp^2$, nonpolar



e. Linear, 180°, *sp*, nonpolar

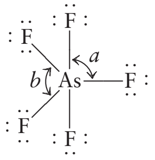
H— Be— H

f.



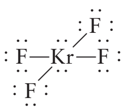
$a \approx 120°$, see-saw, $dsp^3$, polar
$b \approx 90°$

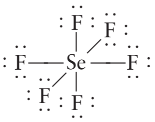
g.

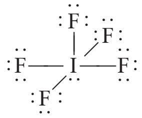


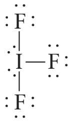
$a = 90°$, trigonal bipyramid, $dsp^3$, nonpolar
$b = 120°$

h. : F—Kr—F : Linear, 180°, $dsp^3$, nonpolar

i.  Square planar, 90°, $d^2sp^3$, nonpolar

j.  Octahedral, 90°, $d^2sp^3$, nonpolar

k. 

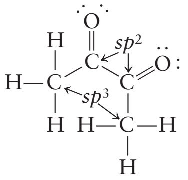
l. 

Square pyramid, ≈90°; $d^2sp^3$, polar

T-shaped, ≈90°, $dsp^3$, polar

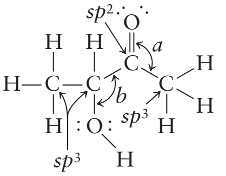
**21.** For the $p$ orbitals to properly line up to form the $\pi$ bond, all six atoms are forced into the same plane. If the atoms are not in the same plane, then the $\pi$ bond could not form since the $p$ orbitals would no longer be parallel to each other.

**23.** Biacetyl



All CCO angles are 120°. The six atoms are not forced to lie in the same plane because of free rotation around the carbon–carbon single ($\sigma$) bonds. 11 $\sigma$ and 2 $\pi$ bonds.

Acetoin



Angle $a$ = 120°, angle $b$ = 109.5°, 13 $\sigma$ bonds and 1 $\pi$ bond
**25.** To complete the Lewis structure, add lone pairs to complete octets for each atom. a. 6; b. 4; c. The center N in —N=N=N group; d. 33 $\sigma$; e. 5 $\pi$; f. 180°; g. ≈109.5°; h. $sp^3$

**27.** CO :C≡O:   $CO_2$ O=C=O   $C_3O_2$ O=C=C=C=O

There is no molecular structure for the diatomic CO molecule. The carbon in CO is $sp$ hybridized. $CO_2$ is a linear molecule, and the central carbon atom is $sp$ hybridized. $C_3O_2$ is a linear molecule with all of the central carbon atoms exhibiting $sp$ hybridization. **29.** Bonding and antibonding molecular orbitals are both solutions to the quantum mechanical treatment of the molecule. Bonding orbitals form when in-phase orbitals combine to give constructive interference. This results in enhanced electron probability located between the two nuclei. The end result is that a bonding MO is lower in energy than the atomic orbitals from which it is composed. Antibonding orbitals form when out-of-phase orbitals combine. The mismatched phases produce destructive interference leading to a node of electron probability between the two nuclei. With electron distribution pushed to the outside, the energy of an antibonding orbital is higher than the energy of the atomic orbitals from which it is composed. **31.** a. $H_2$ has two valence electrons to put in the MO diagram whereas $He_2$ has 4 valence electrons.

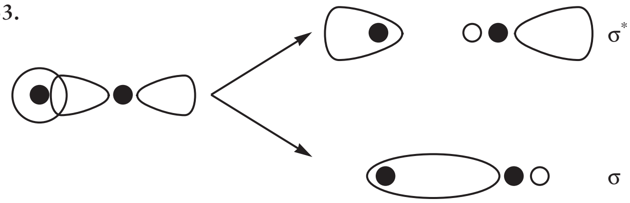
$H_2$: $(\sigma_{1s})^2$   Bond order = B.O. = (2 − 0)/2 = 1
$He_2$: $(\sigma_{1s})^2(\sigma_{1s}{}^*)^2$   B.O. = (2 − 2)/2 = 0

$H_2$ has a nonzero bond order, so MO theory predicts it will exist. The $H_2$ molecule is stable with respect to the two free H atoms. $He_2$ has a bond order of zero, so it should not form. The $He_2$ molecule is not more stable than the two free He atoms. b. See Fig. 14.41 for the MO energy-level diagrams of $B_2$, $C_2$, $N_2$, $O_2$, and $F_2$. $B_2$ and $O_2$ have unpaired electrons in their electron configurations, so they are predicted to be paramagnetic. $C_2$, $N_2$, and $F_2$ have no unpaired electrons in their MO diagrams; they are all diamagnetic. c. From the MO energy diagram in Fig. 14.41, $N_2$ maximizes the number of electrons in the lower-energy bonding orbitals and has no electrons in the antibonding $2p$ molecular orbitals. $N_2$ has the highest possible bond order of 3, so it should be a very strong (stable) bond. d. $NO^+$ has 5 + 6 − 1 = 10 valence electrons to place in the MO diagram and $NO^-$ has 5 + 6 + 1 = 12 valence electrons. The MO diagram for these two ions is assumed to be the same as that used for $N_2$.

$NO^+$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$   B.O. = (8 − 2)/2 = 3
$NO^-$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^2$   B.O. = (8 − 4)/2 = 2

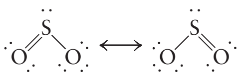
$NO^+$ has a larger bond order than $NO^-$, so $NO^+$ should be more stable than $NO^-$.

**33.**

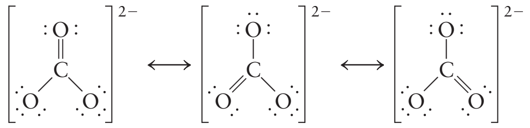


These MOs are $\sigma$ MOs since the electron density is cylindrically symmetric around the internuclear axis. **35.** $N_2{}^+$ and $N_2{}^-$ both have a bond order of 2.5.
**37.** CN: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$;
NO: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}{}^*)^1$;
$O_2{}^{2+}$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2p})^2(\pi_{2p})^4$;
$N_2{}^{2+}$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4$; If the added electron goes into a bonding orbital, the bond order would increase, making the species more stable and more likely to form. Between CN and NO, CN would most likely form $CN^-$ since the bond order increases (unlike $NO^-$, in which the added electron goes into an antibonding orbital). Between $O_2{}^{2+}$ and $N_2{}^{2+}$, $N_2{}^+$ would most likely form since the bond order increases (unlike $O_2{}^+$). **39.** The $\pi$ bonds between S atoms and between C and S atoms are not as strong. The atomic orbitals do not overlap with each other as well as the smaller atomic orbitals of C and O overlap. **41.** $\pi$ molecular orbital **43.** a. The electron density would be closer to F on the average. The F atom is more electronegative than the H atom, and the $2p$ orbital of F is lower in energy than the $1s$ orbital of H; b. The bonding MO would have more fluorine $2p$ character because it is closer in energy to the fluorine $2p$ atomic orbital; c. The antibonding MO would place more electron density closer to H and would have a greater contribution from the higher-energy hydrogen $1s$ atomic orbital. **45.** Molecules that exhibit resonance have delocalized $\pi$ bonding. This is a fancy way of saying that the $\pi$ electrons are not permanently stationed between two specific atoms but instead can roam about over the surface of a molecule. We use the concept of delocalized $\pi$ electrons to explain why molecules that exhibit resonance have equal bonds in terms of strength. Because the $\pi$ electrons can roam about over the entire surface of the molecule, the $\pi$ electrons are shared by all of the

atoms in the molecule, giving rise to equal bond strengths. The classic example of delocalized $\pi$ electrons is benzene ($C_6H_6$). Figure 14.50 shows the $\pi$ molecular orbital system for benzene. Each carbon in benzene is $sp^2$ hybridized, leaving one unhybridized $p$ atomic orbital. All six of the carbon atoms in benzene have an unhybridized $p$ orbital pointing above and below the planar surface of the molecule. Instead of just two unhybridized $p$ orbitals overlapping, we say all six of the unhybridized $p$ orbitals overlap, resulting in delocalized $\pi$ electrons roaming about above and below the entire surface of the benzene molecule.

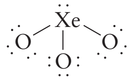


In $SO_2$ the central sulfur atom is $sp^2$ hybridized. The unhybridized $p$ atomic orbital on the central sulfur atom will overlap with parallel $p$ orbitals on each adjacent O atom. All three of these $p$ orbitals overlap together, resulting in the $\pi$ electrons moving about above and below the surface of the $SO_2$ molecule. With the delocalized $\pi$ electrons, the S—O bond lengths in $SO_2$ are equal (and not different as each individual Lewis structure indicates). **47.** The Lewis structures for $CO_3^{2-}$ (24 $e^-$) are:



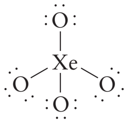
In the localized electron view, the central carbon atom is $sp^2$ hybridized; the $sp^2$ hybrid orbitals are used to form the three sigma bonds in $CO_3^{2-}$. The central C atom also has one unhybridized $p$ atomic orbital that overlaps with another $p$ atomic orbital from one of the oxygen atoms to form the $\pi$ bond in each resonance structure. This localized $\pi$ bond moves (resonates) from one position to another. In the molecular orbital model for $CO_3^{2-}$, all four atoms in $CO_3^{2-}$ have a $p$ atomic orbital that is perpendicular to the plane of the ion. All four of these $p$ orbitals overlap at the same time to form a delocalized $\pi$ bonding system where the $\pi$ electrons can roam above and below the entire surface of the ion. The $\pi$ molecular orbital system for $CO_3^{2-}$ is analogous to that for $NO_3^-$, which is shown in Fig. 14.51 of the text. **49.** 411.7 N $m^{-1}$ **51.** a. 113 pm; b. $3.45 \times 10^{11}$ $s^{-1}$ **53.** a. quadruplet in iv; b. singlet in i; c. triplet in iii; d. doublet in ii

**55.** a.



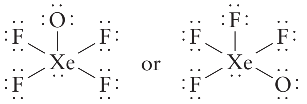
Trigonal pyramid; $sp^3$

b.



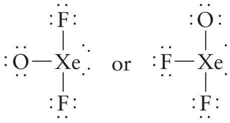
Tetrahedral; $sp^3$

c.



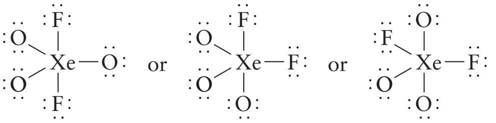
Square pyramid; $d^2sp^3$

d.



T-shaped; $dsp^3$

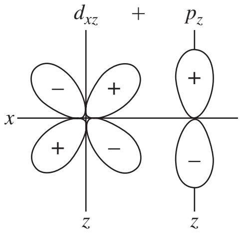
e.



Trigonal bipyramid; $dsp^3$

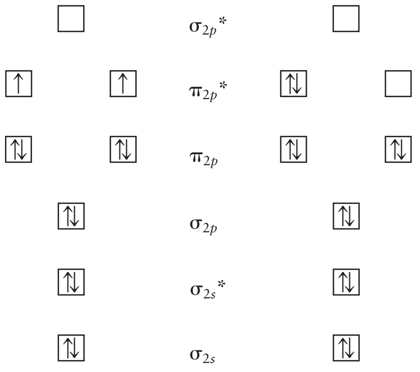
**57.** a. No, some atoms are in different places. Thus these are not resonance structures; they are different compounds. b. For the first Lewis structure, all nitrogens are $sp^3$ hybridized and all carbons are $sp^2$ hybridized. In the second Lewis structure, all nitrogens and carbons are $sp^2$ hybridized. c. The first structure with the carbon–oxygen double bonds is slightly more stable.

**59.**



The two orbitals overlap side to side, so when the orbitals are in phase, a $\pi$ bonding molecular orbital would form.

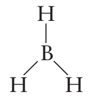
**61.**



Ground state Excited state

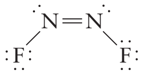
Lewis structure shows no unpaired electrons. The ground-state MO diagram for $O_2$ has two unpaired electrons. It takes energy to pair electrons in the same orbital. The MO diagram with no unpaired electrons is at a higher energy and is an excited state.

**63.** a.

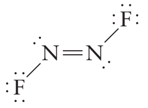


Trigonal planar; nonpolar; 120°; $sp^2$

b.



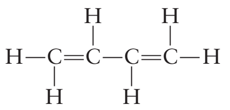
Can also be:



Polar Nonpolar

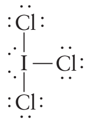
V-shaped about both N atoms; ≈120°; $sp^2$.
These are distinctly different molecules.

c.



Trigonal planar about each carbon; nonpolar; 120°; $sp^2$ for all carbons

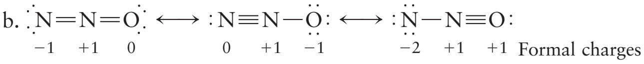
d.



T-shaped; polar; ≈90°; $dsp^3$

**65.** 6 C and N atoms are $sp^2$ hybridized; 6 C and N atoms are $sp^3$ hybridized; 0 C and N atoms are $sp$ hybridized (linear geometry); 25 $\sigma$ bonds and 4 $\pi$ bonds **67.** a. The NNO structure is correct.

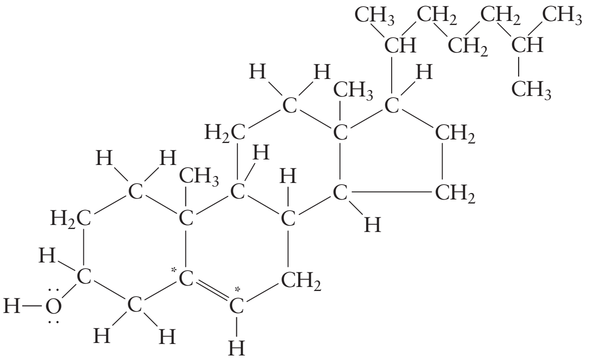
From the Lewis structures we would predict both NNO and NON to be linear, but NON would be nonpolar. NNO is polar.

b. 
$:\ddot{N}=N=\ddot{O}: \longleftrightarrow :N\equiv N-\ddot{\underset{..}{O}}: \longleftrightarrow :\ddot{\underset{..}{N}}-N\equiv O:$

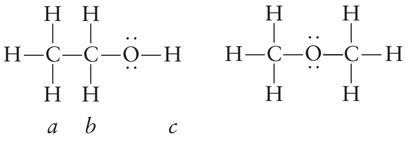
The central N is *sp* hybridized. We can probably ignore the third resonance structure on the basis of formal charge. c. *sp* hybrid orbitals from the center N overlap with atomic orbitals (or hybrid orbitals) from the other two atoms to form the two sigma bonds. The remaining *p* orbitals from the center N overlap with *p* orbitals from the other N to form the two $\pi$ bonds. 69. a. 116 kJ/mol;

b. $F_2$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}{}^*)^4$ B.O. = (8 − 6)/2 = 1
$F_2{}^-$: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}{}^*)^4(\sigma_{2p}{}^*)^1$ B.O. = (8 − 7)/2 = 0.5

MO theory predicts that $F_2$ should have a stronger bond than $F_2{}^-$ because $F_2$ has the larger bond order. The calculated $F_2{}^-$ bond energy is indeed smaller than the $F_2$ bond energy (154 kJ/mol). **71.** a. $N_2$, $N_2{}^+$, N, and $N^+$ will all be present, assuming excess $N_2$. b. Light with wavelengths in the range of 85.33 nm $< \lambda \leq$ 127 nm will produce N but no ions. c. Consider the MO energy-level diagram for $N_2$ (see Figs. 14.40 and 14.41). The electron removed from $N_2$ is in the $\sigma_{2p}$ MO, which is lower in energy than the 2*p* atomic orbital from which the electron in atomic nitrogen is removed. Since the electron removed from $N_2$ is lower in energy than the electron in N, the ionization energy of $N_2$ is greater than for N. **73.** The complete Lewis structure follows. All but two of the carbon atoms are $sp^3$ hybridized. The two carbon atoms that contain the double bond are $sp^2$ hybridized (see*).



No; most of the carbons are not in the same plane since a majority of carbon atoms exhibit a tetrahedral structure. *Note:* CH, $CH_2$, and $CH_3$ are shorthand for carbon atoms singly bonded to hydrogen atoms. **75.** a. The CO bond is polar with the negative end around the more electronegative oxygen atom. We would expect metal cations to be attracted to and bond to the oxygen end of CO on the basis of electronegativity. b. :C≡O: FC (carbon) = −1; FC (oxygen) = +1. From formal charge, we would expect metal cations to bond to the carbon (with the negative formal charge). c. In MO theory, only orbitals with proper symmetry overlap to form bonding orbitals. The metals that form bonds to CO are usually transition metals, all of which have outer electrons in the *d* orbitals. The only MOs of CO that have proper symmetry to overlap with *d* orbitals are the $\pi_{2p}{}^*$ orbitals, whose shape is similar to the *d* orbitals (see Fig. 14.36). Since the antibonding MOs have more carbon character, one would expect the bond to form through carbon. **77.** $\Delta H_f^\circ$ = 237 kJ/mol (calculated); there is a 154 kJ discrepancy. Benzene is more stable (lower in energy) by 154 kJ than we expect from bond energies. Two equivalent Lewis structures can be drawn for benzene. The $\pi$ bonding system implied by each Lewis structure consists of three localized $\pi$ bonds. This, however, does not adequately explain the six equivalent C—C bonds in benzene. To explain the equivalent C—C bonds, the $\pi$ electrons are said to be delocalized over the entire surface of the molecule (see Section 14.5). The large discrepancy between the $\Delta H_f^\circ$ values is due to the effect of a delocalized $\pi$ bonding system that was not considered when calculating $\Delta H_f^\circ$. The extra stability associated with benzene can be called resonance stabilization. **79.** The two isomers having the formula $C_2H_6O$ are



The first structure has three types of hydrogens (*a*, *b*, and *c*), so the signals should be seen in three different regions of the NMR spectrum. The overall relative areas of the three signals should be in a 3:2:1 ratio due to the number of *a*, *b*, and *c* hydrogens. The signal for the *a* hydrogens will be split into a triplet signal due to the two neighboring *b* hydrogens. The signal for the *b* hydrogens will be split into a quartet signal due to the three neighboring *a* hydrogens. In theory, the *c* hydrogen should be split into a triplet signal due to the two neighboring *b* hydrogens. In practice, the *c* hydrogen signal is usually not split (which you could not predict). In the second structure, all 6 hydrogens are equivalent, so only one signal will appear in the NMR spectrum. This signal will be a singlet signal because the hydrogens in the two —$CH_3$ groups are more than three sigma bonds apart from each other (no splitting occurs).

## Chapter 15

**11.** A possible balanced equation is 2A + 3B → 4C.

**13.** $\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$ **15.** $L^{1/2}\ mol^{-1/2}\ s^{-1}$

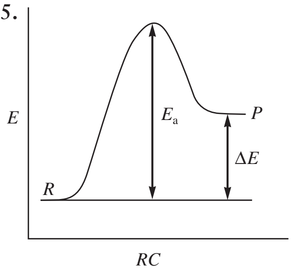
**17.** a. Rate = $k[NO]^2[Cl_2]$; b. $k_{mean} = 1.8 \times 10^2\ L^2\ mol^{-2}\ min^{-1}$ **19.** a. rate = $k[NOCl]^2$; b. $k_{mean} = 6.6 \times 10^{-29}\ cm^3\ molecules^{-1}\ s^{-1}$; c. $4.0 \times 10^{-8}\ L\ mol^{-1}\ s^{-1}$ **21.** a. Rate = $k[ClO_2]^2[OH^-]$; $k_{mean} = 2.30 \times 10^2\ L^2\ mol^{-2}\ s^{-1}$; b. 0.594 mol $L^{-1}\ s^{-1}$ **23.** Rate = $k[N_2O_5]$; $k_{mean} = 1.19 \times 10^{-2}\ s^{-1}$ **25.** Rate = $\frac{k[I^-][OCl^-]}{[OH^-]}$; $k_{mean} = 60.\ s^{-1}$ **27.** The first-order half-life is independent of concentration, the zero-order half-life is directly related to the concentration, and the second-order half-life is inversely related to concentration. For a first-order reaction, if the first half-life equals 20. s, the second half-life will also be 20. s because the half-life for a first-order reaction is concentration-independent. The second half-life for a zero-order reaction will be 1/2(20.) = 10. s. This is so because the half-life for a zero-order reaction has a direct relationship with concentration (as the concentration decreases by a factor of 2, the half-life decreases by a factor of 2). Because a second-order reaction has an inverse relationship between $t_{1/2}$ and $[A]_0$, the second half-life will be 40. s (twice the first half-life value). **29.** a. Rate = $k[A]$; $\ln[A] = -kt + \ln[A]_0$; $k = 2.97 \times 10^{-2}\ min^{-1}$; b. 23.3 min; c. 69.9 min **31.** $\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$; Rate = $k[H_2O_2]$; $k = 8.3 \times 10^{-4}\ s^{-1}$; 0.037 *M* **33.** $\frac{1}{[NO_2]} = kt + \frac{1}{[NO_2]_0}$; Rate = $k[NO_2]^2$; $k = 2.08 \times 10^{-4}\ L\ mol^{-1}\ s^{-1}$; 0.131 *M* **35.** The rate law and integrated rate law are Rate = $k$ = $1.7 \times 10^{-4}$ atm/s;

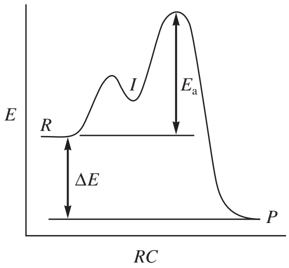
$P_{C_2H_5OH} = -kt + 250.\ \text{torr}\left(\dfrac{1\ \text{atm}}{760\ \text{torr}}\right) = -kt + 0.329\ \text{atm}$;
At 900. s, $P_{C_2H_5OH} = 130$ torr **37.** a. The reaction is first order with respect to NO and first order with respect to $O_3$. b. Rate = $k[NO][O_3]$; c. $k' = 1.8\ s^{-1}$; $k'' = 3.6\ s^{-1}$; d. $1.8 \times 10^{-14}\ cm^3\ molecules^{-1}\ s^{-1}$ **39.** 150. s **41.** 12.5 s **43.** a. 160. s for both; b. 532 s **45.** a. $[A] = -kt + [A]_0$ where $k = 5.0 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$ and $[A]_0 = 1.00 \times 10^{-3}\ M$; b. $1.0 \times 10^{-2}$ s; c. $2.5 \times 10^{-4}\ M$ **47.** a. $1.15 \times 10^2\ L^3\ mol^{-3}\ s^{-1}$; b. 87.0 s; c. [B] = 1.00 *M*; [A] = $1.27 \times 10^{-5}\ M$ **49.** In a unimolecular reaction, a single-reactant molecule decomposes to products. In a bimolecular reaction, two molecules collide to give products. The probability of the simultaneous collision of three molecules with enough energy and proper orientation is very small, making termolecular steps very unlikely. **51.** a. Rate = $k[CH_3NC]$; b. Rate = $k[O_3][NO]$; c. Rate = $k[O_3]$; d. Rate = $k[O_3][O]$; e. Rate = $k[^{14}_{6}C]$ or rate = $kN$ where $N$ = the number of $^{14}_{6}C$ atoms **53.** Rate = $k[C_4H_9Br]$; $C_4H_9Br + 2H_2O \rightarrow C_4H_9OH + Br^- + H_3O^+$; the intermediates are $C_4H_9^+$ and $C_4H_9OH_2^+$ **55.** mechanism b **57.** Rate = $\dfrac{k_3k_2k_1}{k_{-2}k_{-1}}[Br^-][BrO_3^-][H^+]^2 = k[Br^-][BrO_3^-][H^+]^2$ **59.** Rate = $\dfrac{k_2k_1[I^-][OCl^-]}{k_{-1}[OH^-]} = \dfrac{k[I^-][OCl^-]}{[OH^-]}$

**61.** a. $MoCl_5^-$; b. Rate = $\dfrac{d[NO_2^-]}{dt} = \dfrac{k_1k_2[NO_3^-][MoCl_6^{2-}]}{k_{-1}[Cl^-] + k_2[NO_3^-]}$

**63.** a. Rate = $\dfrac{d[E]}{dt} = \dfrac{k_1k_2[B]^2}{k_{-1}[B] + k_2}$; b. When $k_2 << k_{-1}[B]$, then the reaction is first order in B. c. Collisions between B molecules only transfer energy from one B to another. This occurs at a much faster rate than the decomposition of an energetic B molecule (B*). **65.** Two reasons are: a. The collision must involve enough energy to produce the reaction; that is, the collision energy must be equal to or exceed the activation energy. b. The relative orientation of the reactants when they collide must allow formation of any new bonds necessary to produce products. **67.** $9.5 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$ **69.** 51°C **71.** a. 91.5 kJ/mol; b. $3.54 \times 10^{14}\ s^{-1}$; c. $3.24 \times 10^{-2}\ s^{-1}$ **73.** A plot of ln(*k*) versus $\dfrac{1}{T}$ gives a straight line with negative slope equal to $-E_a/R$ (see *Solutions Guide* for plot). $E_a = 11.2$ kJ/mol

**75.**





d. See plot for the intermediate plateau, which represents the energy of the intermediate. The two steps in the mechanism are $R \rightarrow I$ and $I \rightarrow P$. In a mechanism, the rate of the slowest step determines the rate of the reaction. The activation energy for the slowest step will be the largest energy barrier that the reaction must overcome. Since the second hump in the diagram is at the highest energy, then the second step ($I \rightarrow P$) has the largest activation energy and will be the rate-determining step (the slow step). **77.** positive Δ*E* value **79.** A metal-catalyzed reaction is dependent on the number of adsorption sites on the metal surface. Once the metal surface is saturated with reactant, the rate of reaction becomes independent of concentration. **81.** a. W, because it has a lower activation energy than the Os catalyst. b. The W-catalyzed reaction is approximately $10^{30}$ times faster than the uncatalyzed reaction. c. Because $[H_2]$ is in the denominator of the rate law, the presence of $H_2$ decreases the rate of the reaction. For the decomposition to occur, $NH_3$ molecules must be adsorbed on the surface of the catalyst. If $H_2$ is also adsorbed on the catalyst surface, then there are fewer sites for $NH_3$ molecules to be adsorbed, and the rate decreases. **83.** Since the chlorine atom–catalyzed reaction has a lower activation energy, then the Cl-catalyzed rate is faster. Hence, Cl is a more effective catalyst. **85.** At high [S], the enzyme is completely saturated with substrate. Once the enzyme is completely saturated, the rate of decomposition of ES can no longer increase and the overall rate remains constant. **87.** ~1 second **89.** The most common method to experimentally determine the differential rate law is the method of initial rates. Once the differential rate law is determined experimentally, the integrated rate law can be derived. However, sometimes it is more convenient and more accurate to collect concentration versus time data for a reactant. When this is the case, then we do "proof" plots to determine the integrated rate law. Once the integrated rate law is determined, the differential rate law can be determined. Either experimental procedure allows determination of both the integrated and the differential rate; which rate law is determined by experiment and which is derived is usually decided by which data is easiest and most accurately collected. **91.** a. untreated: $k = 0.465\ day^{-1}$; deacidifying agent: $k = 0.659\ day^{-1}$; antioxidant: $k = 0.779\ day^{-1}$; b. No, the silk degrades more rapidly with the additives; c. untreated: $t_{1/2} = 1.49$ day; deacidifying agent: $t_{1/2} = 1.05$ day; antioxidant: $t_{1/2} = 0.890$ day **93.** Carbon cannot form the fifth bond necessary for the transition state because of the small atomic size of carbon and because carbon doesn't have low-energy *d* orbitals available to expand the octet. **95.** a. Second order; b. 17.1 s ≈ 20 s; c. 34.6 s ≈ 30 s; d. 847 s; e. 31 kJ/mol **97.** 29.8 kJ/mol **99.** a. 53.9 kJ/mol; b. 83 chirps per minute per insect;

c.

| *T* (°C) | *T* (°F) | *k* (min$^{-1}$) | 42 + 0.80 (*k*/4) |
|---|---|---|---|
| 25.0 | 77.0 | 178 | 78°F |
| 20.3 | 68.5 | 126 | 67°F |
| 17.3 | 63.1 | 100. | 62°F |
| 15.0 | 59.0 | 83 | 59°F |

The rule of thumb appears to be fairly accurate, about ±1°F.

**101.** Rate = $\dfrac{d[Cl_2]}{dt} = \dfrac{k_1k_2[NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$ **103.** a. Rate = $k[CH_3X]$, $k = 0.93\ h^{-1}$; b. $8.80 \times 10^{-10}$ h; c. $3.0 \times 10^2$ kJ/mol; d. The activation energy is close to the C—X bond energy. A plausible mechanism is

$$CH_3X \longrightarrow CH_3 + X \qquad \text{(slow)}$$
$$CH_3 + Y \longrightarrow CH_3Y \qquad \text{(fast)}$$

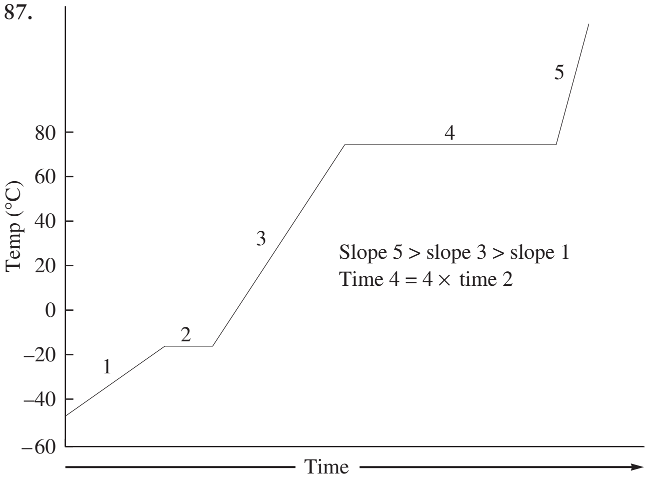
**105.** 10. s **107.** Rate = $k[A][B]^2$, $k = 1.4 \times 10^{-2}\ L^2\ mol^{-2}\ s^{-1}$

**109.** Rate = $\dfrac{-d[N_2O_5]}{dt} = \dfrac{2k_1k_2[M][N_2O_5]}{k_{-1}[M] + 2k_2}$ **111.** a. Both are first order. b. $k_1 = 0.82\ L\ mol^{-1}\ min^{-1}$; $k_2 = 9.5\ L^2\ mol^{-2}\ min^{-1}$ c. There are two pathways, one involving $H^+$ with rate = $k_2[H^+][I^-][H_2O_2]$ and another pathway not involving $H^+$ with rate = $k_1[I^-][H_2O_2]$. The overall rate of reaction depends on which of these two pathways dominates, and this depends on the $H^+$ concentration.

## Chapter 16

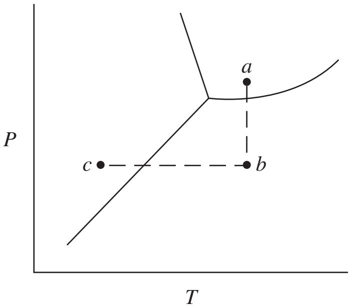
**11.** Intermolecular forces are the relatively weak forces between molecules that hold the molecules together in the solid and liquid phases. Intramolecular forces are the forces within a molecule. These are the covalent bonds in a molecule. Intramolecular forces (covalent bonds) are much stronger than intermolecular forces. Dipole forces are the forces that act between polar molecules. The electrostatic attraction between the partial positive end of one polar molecule and the partial negative end of another is the dipole force. Dipole forces are generally weaker than hydrogen bonding. Both of these forces are due to dipole moments in molecules. Hydrogen bonding is given a separate name from dipole forces because hydrogen bonding is a particularly strong dipole force. Any neutral molecule that has a hydrogen covalently bonded to N, O, or F exhibits the relatively strong hydrogen-bonding intermolecular forces. London dispersion forces are accidental or induced dipole forces. Like dipole forces, London dispersion forces are electrostatic in nature. Dipole forces are the electrostatic forces between molecules having a permanent dipole. London dispersion forces are the electrostatic forces between molecules having an accidental or induced dipole. All covalent molecules (polar and nonpolar) have London dispersion forces, but only polar molecules (those with permanent dipoles) exhibit dipole forces. **13.** *Fusion* refers to a solid converting to a liquid and *vaporization* refers to a liquid converting to a gas. Only a fraction of the hydrogen bonds are broken in going from the solid phase to the liquid phase. Most of the hydrogen bonds are still present in the liquid phase and must be broken during the liquid-to-gas transition. The enthalpy of vaporization is much larger than the enthalpy of fusion because more intermolecular forces are broken during the vaporization process. **15.** a. LD (London dispersion); b. dipole, LD; c. hydrogen bonding, LD; d. ionic; e. LD; f. dipole, LD; g. ionic; h. ionic; i. LD mostly; C—F bonds are polar, but polymers like Teflon are so large that LD forces are the predominant intermolecular forces. j. LD; k. dipole, LD; l. hydrogen bonding, LD; m. dipole, LD; n. LD **17.** a. $H_2NCH_2CH_2NH_2$; More extensive hydrogen bonding is possible since two $NH_2$ groups are present. b. $H_2CO$; $H_2CO$ has dipole forces in addition to LD forces. $CH_3CH_3$ has only LD forces; c. $CH_3OH$; $CH_3OH$ can form hydrogen-bonding interactions; $H_2CO$ does not. d. HF; HF is capable of forming hydrogen-bonding interactions; HBr is not. **19.** a. Neopentane is more compact than *n*-pentane. There is less surface area contact between neopentane molecules. This leads to weaker LD forces and a lower boiling point. b. HF is capable of hydrogen bonding; HCl is not. c. LiCl is ionic and HCl is a molecular solid with only dipole forces and LD forces. Ionic forces are much stronger than the forces for molecular solids. d. *n*-Hexane is a larger molecule so it has stronger LD forces. **21.** Ar exists as individual atoms that are held together in the condensed phases by London dispersion forces. The molecule that will have a boiling point closest to Ar will be a nonpolar substance with about the same molar mass as Ar (39.95 g/mol); this same size nonpolar substance will have about the equivalent strength of London dispersion forces. Of the choices, only $Cl_2$ (70.90 g/mol) and $F_2$ (38.00 g/mol) are nonpolar. Because $F_2$ has a molar mass closest to that of Ar, one would expect the boiling point of $F_2$ to be close to that of Ar. **23.** ethanol, 78.5°C; dimethyl ether, −23°C; propane, −42.1°C **25.** 46.7 kJ/mol; 90.% **27.** a. Surface tension: the resistance of a liquid to an increase in its surface area. b. Viscosity: the resistance of a liquid to flow. c. Melting point: the temperature (at constant pressure) where a solid converts entirely to a liquid as long as heat is applied. A more detailed definition is the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is constant. d. Boiling point: the temperature (at constant pressure) where a liquid converts entirely to a gas as long as heat is applied. The detailed definition is the temperature at which the vapor pressure of the liquid is exactly equal to the external pressure. e. Vapor pressure: the pressure of the vapor over a liquid at equilibrium. As the strengths of intermolecular forces increase, surface tension, viscosity, melting point, and boiling point increase, while vapor pressure decreases. **29.** Water is a polar substance and wax is a nonpolar substance. A molecule at the surface of a drop of water is subject to attractions only by molecules below it and to each side. The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and causes the droplet to assume the shape that has the minimum surface area, a sphere. **31.** The structure of $H_2O_2$ is H—O—O—H, which produces greater hydrogen bonding than in water. **33.** a. crystalline solid: regular, repeating structure; amorphous solid: irregular arrangement of atoms or molecules; b. ionic solid: made up of ions held together by ionic bonding; molecular solid: Made up of discrete covalently bonded molecules held together in the solid phase by weaker forces (LD, dipole, or hydrogen bonds); c. molecular solid: discrete, individual molecules; covalent network solid: no discrete molecules; A covalent network solid is one large molecule. The interparticle forces are the covalent bonds between atoms. d. metallic solid: completely delocalized electrons, conductor of electricity (ions in a sea of electrons); covalent network solid: localized electrons; insulator or semiconductor **35.** a. Both forms of carbon are network solids. In diamond, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule. Each carbon atom is covalently bonded to four other carbon atoms. The structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings. Each carbon atom in a particular layer of graphite is surrounded by three other carbons in a trigonal planar arrangement. This requires $sp^2$ hybridization. Each carbon has an unhybridized $p$ atomic orbital; all of these $p$ orbitals in each six-membered ring overlap with each other to form a delocalized $\pi$ electron system. b. Silica is a network solid having an empirical formula of $SiO_2$. The silicon atoms are singly bonded to four oxygens. Each silicon atom is at the center of a tetrahedral arrangement of oxygen atoms that are shared with other silicon atoms. The structure of silica is based on a network of $SiO_4$ tetrahedra with shared oxygen atoms rather than discrete $SiO_2$ molecules. Silicates closely resemble silica. The structure is based on interconnected $SiO_4$ tetrahedra. However, in contrast to silica, where the O/Si ratio is 2:1, silicates have O/Si ratios greater than 2:1 and contain silicon–oxygen anions. To form a neutral solid silicate, metal cations are needed to balance the charge. In other words, silicates are salts containing metal cations and polyatomic silicon–oxygen anions. When silica is heated above its melting point and cooled rapidly, an amorphous (disordered) solid called glass results. Glass more closely resembles a very viscous solution than it does a crystalline solid. To affect the properties of glass, several different additives are thrown into the mixture. Some of these additives are $Na_2CO_3$, $B_2O_3$, and $K_2O$, with each compound serving a specific purpose relating to the properties of the glass. **37.** A crystalline solid will have the simpler diffraction pattern because a regular, repeating arrangement is necessary to produce planes of atoms that will diffract the X rays in regular patterns. An amorphous solid does not have a regular repeating arrangement and will produce a complicated diffraction pattern. **39.** 0.704 Å **41.** 3.13 Å = 313 pm **43.** 1.54 g/cm$^3$ **45.** 136 pm **47.** edge length of unit cell = 328 pm; radius = 142 pm **49.** The measured density is consistent with the calculated density, assuming a face-centered cubic structure. **51.** Conductor: The energy difference between the filled and unfilled molecular orbitals is minimal. We call this energy difference the band gap. Because the band gap is minimal, electrons can easily move into the conduction bands (the unfilled molecular orbitals). Insulator: Large band gap; electrons do not move from the filled molecular orbitals to the conduction bands since the energy difference is large. Semiconductor: Small band gap; the energy difference between the filled and unfilled molecular orbitals is smaller than in insulators, so some electrons can jump into the conduction bands. The band gap, however, is not as small as with conductors, so semiconductors have intermediate conductivity. a. As the temperature is increased, more electrons in the filled molecular orbitals have sufficient kinetic energy to jump into the conduction bands (the unfilled molecular orbitals). b. A photon of light is absorbed by an electron, which then has sufficient energy to jump into the conduction bands. c. An impurity either adds electrons at an energy near that of the conduction bands (n-type) or creates holes (unfilled energy levels) at energies in the previously filled molecular orbitals (p-type). Both n-type and p-type semiconductors increase conductivity by creating an easier path for electrons to jump from filled to unfilled energy levels. In conductors, electrical conductivity is inversely proportional to temperature. Increases in temperature increase the motions of the atoms, which gives rise to increased resistance (decreased conductivity). In a semiconductor, electrical conductivity is directly proportional to temperature. An increase in temperature provides more electrons with enough kinetic energy to jump from the filled molecular orbitals to the conduction bands, increasing conductivity. **53.** A rectifier is a device that produces a current that flows in one direction from an alternating current, which flows in both directions. In a p–n junction, a p-type and an n-type semiconductor are connected. The natural flow of electrons in a p–n junction is for the excess electrons in the n-type semiconductor to move to the empty energy levels (holes) of the p-type semiconductor. Only when an external electric potential is connected so that electrons flow in this natural direction will the current flow easily (forward bias). If the external electric potential is connected in reverse of the natural flow of electrons, no current flows through the system (reverse bias). A p–n junction transmits a current only under forward bias, thus converting the alternating current to direct current. **55.** In has fewer valence electrons than Se; thus Se doped with In would be a p-type semiconductor. **57.** $5.0 \times 10^2$ nm **59.** The structures of most binary ionic solids can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements and the smaller cations fit into holes among the closest packed anions. There are different types of holes within the closest packed anions that are determined by the number of spheres that form them. Which of the three types of holes are filled usually depends on the relative size of the cation to the anion. Ionic solids will always try to maximize electrostatic attractions among oppositely charged ions and minimize the repulsions among ions with like charges. The structure of sodium chloride can be described in terms of a cubic closest packed array of $Cl^-$ ions with $Na^+$ ions in all of the octahedral holes. An octahedral hole is formed between 6 $Cl^-$ anions. The number of octahedral holes is the same as the number of packed ions. So, in the face-centered unit cell of sodium chloride, there are 4 net $Cl^-$ ions and 4 net octahedral holes. Because the stoichiometry dictates a 1:1 ratio between the number of $Cl^-$ anions and $Na^+$ cations, all of the octahedral holes must be filled with $Na^+$ ions. In zinc sulfide, the sulfide anions also occupy the lattice points of a cubic closest packing arrangement. But instead of having the cations in octahedral holes, the $Zn^{2+}$ cations occupy tetrahedral holes. A tetrahedral hole is the empty space created when four spheres are packed together. There are twice as many tetrahedral holes as packed anions in the closest packed structure. Therefore, each face-centered unit cell of sulfide anions contains 4 net $S^{2-}$ ions and 8 net tetrahedral holes. For the 1:1 stoichiometry to work out, only half the tetrahedral holes are filled with $Zn^{2+}$ ions. This gives 4 $S^{2-}$ ions and 4 $Zn^{2+}$ ions per unit cell for an empirical formula of ZnS. **61.** $CoF_2$ **63.** +3 **65.** From density data, 358 pm; from ionic radii data, 350. pm. The two values differ by less than 2.5%. **67.** CsBr: $r_+/r_- = 0.867$; From the radius ratio, $Cs^+$ should occupy cubic holes. The structure should be the CsCl structure. The actual structure is the CsCl structure. KF: $r_+/r_- = 0.978$; Again, we would predict a structure similar to CsCl, i.e., cations in the middle of a simple cubic array of anions. The actual structure is the NaCl structure. The rule fails for KF. Exceptions are common for crystal structures. **69.** a. $XeF_2$; b. 4.29 g/cm$^3$ **71.** The formula is $Al_2MgO_4$. Half of the octahedral holes are filled with $Al^{3+}$ ions, and one-eighth of the tetrahedral holes are filled with $Mg^{2+}$ ions. **73.** a. $YBa_2Cu_3O_9$; b. The structure of this superconductor material follows the alternative perovskite structure described in Exercise 72b. The $YBa_2Cu_3O_9$ structure is three of these cubic perovskite unit cells stacked on top of each other. The atoms are in the same places, Cu takes the place of Ti, two of the Ca atoms are replaced by two Ba atoms, and one Ca is replaced by Y. c. $YBa_2Cu_3O_7$ **75.** A volatile liquid is one that evaporates relatively easily. Volatile liquids have large vapor pressures because the intermolecular forces that prevent evaporation are relatively weak. **77.** a. As the strength of the intermolecular forces increases, the rate of evaporation decreases. b. As temperature increases, the rate of evaporation increases. c. As surface area increases, the rate of evaporation increases. **79.** $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ is an endothermic process. Heat is absorbed when liquid ethanol vaporizes; the internal heat from the body provides this heat, which results in the cooling of the body. **81.** If one plots $\ln(P_{vap})$ versus $1/T$ with temperature in kelvin, the slope of the straight line is $-\Delta H_{vap}/R$. Because $\Delta H_{vap}$ is always positive, the slope of the straight line will be negative. **83.** 77°C **85.** The plots of $\ln(P_{vap})$ versus $1/T$ are linear with negative slope equal to $-\Delta H_{vap}/R$ (see *Solutions Guide* for plot). For Li, $\Delta H_{vap}$ = 158 kJ/mol; for Mg, $\Delta H_{vap}$ = 139 kJ/mol. The bonding is stronger in Li since $\Delta H_{vap}$ is larger for Li.

**87.**



**89.** 1680 kJ **91.** The reaction doesn't release enough heat to melt all the ice. The temperature will remain at 0°C. **93.** 1490 g **95.** See Figs. 16.55 and 16.58 for the phase diagrams of $H_2O$ and $CO_2$. Most substances exhibit only three different phases: solid, liquid, and gas. This is true for $H_2O$ and $CO_2$. Also typical of phase diagrams is the positive slopes for both the liquid/gas equilibrium line and the solid/gas equilibrium line. This is also true for both $H_2O$ and $CO_2$. The solid/liquid equilibrium line also generally has a positive slope. This is true for $CO_2$ but not for $H_2O$. In the $H_2O$ phase diagram, the slope of the solid/liquid line is negative. The determining factor for the slope of the solid/liquid line is the relative densities of the solid and liquid phases. The solid phase is denser than the liquid phase in most substances; for these substances, the slope of the solid/liquid equilibrium line is positive. For water, the liquid phase is denser than the solid phase, which corresponds to a negative-sloping solid/liquid equilibrium line. Another difference between $H_2O$ and $CO_2$ is the normal melting points and normal boiling points. The term "normal" just dictates a pressure of 1 atm. $H_2O$ has a normal melting point (0°C) and a normal boiling point (100°C), but $CO_2$ does not. At 1 atm pressure, $CO_2$ only sublimes (goes from the solid phase directly to the gas phase). There are no temperatures at 1 atm for $CO_2$ where the solid and liquid phases are in equilibrium or where the liquid and gas phases are in equilibrium. There are other differences, but those discussed above are the major ones. The relationship between melting point and pressure is determined by the slope of the solid/liquid equilibrium line. For most substances ($CO_2$ included), the positive slope of the solid/liquid line shows a direct relationship between the melting point and pressure. As pressure increases, the melting point increases. Water is just the opposite since the slope of the solid/liquid line in water is negative. Here the melting point of water is inversely related to the pressure. For boiling points, the positive slope of the liquid/gas equilibrium line indicates a direct relationship between the boiling point and pressure. This direct relationship is true for all substances including $H_2O$ and $CO_2$. The critical temperature for a substance is defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical temperature, like the boiling-point temperature, is directly related to the strength of the intermolecular forces. Since $H_2O$ exhibits relatively strong hydrogen-bonding interactions and $CO_2$ exhibits only London dispersion forces, one would expect a higher critical temperature for $H_2O$ than for $CO_2$. **97.** The critical temperature is the temperature above which the vapor cannot be liquefied no matter what pressure is applied. Since $N_2$ has a critical temperature below room temperature (~22°C), it cannot be liquefied at room temperature. $NH_3$, with a critical temperature above room temperature, can be liquefied at room temperature. **99.** A: solid; B: liquid; C: vapor; D: solid + vapor; E: solid + liquid + vapor (triple point); F: liquid + vapor; G: liquid + vapor (critical point); H: vapor; the first dashed line (at the lower temperature) is the normal melting point, and the second dashed line is the normal boiling point. The solid phase is denser because of the positive slope of the solid/liquid equilibrium line. **101.** a. two; b. Higher-pressure triple point: graphite, diamond, and liquid; lower-pressure triple point: graphite, liquid, and vapor; c. It is converted to diamond (the more dense solid form). d. Diamond is more dense, which is why graphite can be converted to diamond by applying pressure. **103.** Because the density of the liquid phase is greater than the density of the solid phase, the slope of the solid/liquid boundary line is negative (as in $H_2O$). With a negative slope, the melting points increase with a decrease in pressure, so the normal melting point of X should be greater than 225°C.

**105.**



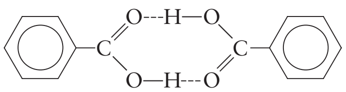
As *P* is lowered, we go from *a* to *b* on the phase diagram. The water boils. The evaporation of the water is endothermic and the water is cooled ($b \rightarrow c$), forming some ice. If the pump is left on, the ice will sublime until none is left. This is the basis of freeze drying. **107.** If $TiO_2$ conducts electricity as a liquid, then it is an ionic solid; if not, then $TiO_2$ is a network solid. **109.** $B_2H_6$, molecular solid; $SiO_2$, network solid; CsI, ionic solid; W, metallic solid **111.** The cation must have a radius that is 0.155 times the radius of the spheres to just fit into the trigonal hole. **113.** 1.71 g/cm$^3$ **115.** The formula is $TiO_{1.182}$ or $Ti_{0.8462}O$. 63.7% of the titanium is $Ti^{2+}$ and 36.3% is $Ti^{3+}$. **117.** 57.8 torr **119.** 92.47% of the energy goes to increase the internal energy of the water. The remainder of the energy (7.53%) goes to do work against the atmosphere. **121.** The empirical formula is $AB_2$. Each A atom is in a cubic hole of B atoms so 8 B atoms surround each A atom. This will also be true in the extended lattice. The structure of B atoms in the unit cell is a cubic arrangement with B atoms at every face, edge, corner, and center of the cube. **123.** 46.5 pm **125.** Rh; 12.42 g/cm$^3$ **127.** distance (liquid)/distance (vapor) = 0.03123 **129.** a. structure (a), $TlBa_2CuO_5$; structure (b), $TlBa_2CaCu_2O_7$; structure (c), $TlBa_2Ca_2Cu_3O_9$; structure (d), $TlBa_2Ca_3Cu_4O_{11}$; b. (a) < (b) < (c) < (d); c. structure (a), only $Cu^{3+}$ is present; structure (b), each formula unit contains 1 $Cu^{2+}$ ion and 1 $Cu^{3+}$ ion; structure (c), each formula unit contains 2 $Cu^{2+}$ ions and 1 $Cu^{3+}$ ion; structure (d), each formula unit contains 3 $Cu^{2+}$ ions and 1 $Cu^{3+}$ ion; d. This superconductor material achieves variable copper oxidation states by varying the numbers of Ca, Cu, and O in each unit cell. The mixtures of copper oxidation states are discussed in part c. The superconductor material in Exercise 73 achieves variable copper oxidation states by omitting oxygen at various sites in the lattice. **131.** Calculated $Li^+$ radius = 75 pm; calculated $Cl^-$ radius = 182 pm; From Fig. 13.8, the $Li^+$ radius is 60 pm and the $Cl^-$ radius is 181 pm. The $Li^+$ ion is much smaller than calculated. This probably means that the ions are not actually in contact with each other. The octahedral holes are larger than the $Li^+$ ions.

## Chapter 17

**13.** a. $HNO_3(l) \rightarrow H^+(aq) + NO_3^-(aq)$; b. $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$; c. $Al(NO_3)_3(s) \rightarrow Al^{3+}(aq) + 3NO_3^-(aq)$; d. $SrBr_2(s) \rightarrow Sr^{2+}(aq) + 2Br^-(aq)$; e. $KClO_4(s) \rightarrow K^+(aq) + ClO_4^-(aq)$; f. $NH_4Br(s) \rightarrow NH_4^+(aq) + Br^-(aq)$; g. $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$; h. $CuSO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$; i. $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$ **15.** 10.7 mol/kg; 6.77 mol/L; 0.162 **17.** 35%; 0.39; 7.3 mol/kg; 3.1 mol/L **19.** 23.9%; 1.6 mol/kg; 0.028 **21.** 1.06 g/cm$^3$; 0.0180; 0.981 mol/L; 1.02 mol/kg **23.** "Like dissolves like" refers to the nature of the intermolecular forces. Polar solutes and ionic solutes dissolve in polar solvents because the types of intermolecular forces present in solute and solvent are similar. When they dissolve, the strengths of the intermolecular forces in solution are about the same as in pure solute and pure solvent. The same is true for nonpolar solutes in nonpolar solvents. The strengths of the intermolecular forces (London dispersion forces) are about the same in solution as in pure solute and pure solvent. In all cases of like dissolves like, the magnitude of $\Delta H_{\text{soln}}$ is either a small positive number (endothermic) or a small negative number (exothermic). For polar solutes in nonpolar solvents and vice versa, $\Delta H_{\text{soln}}$ is a very large, unfavorable value (very endothermic). Because the energetics are so unfavorable, polar solutes do not dissolve in nonpolar solvents and vice versa. **25.** $NaI(s) \rightarrow Na^+(aq) + I^-(aq)$, $\Delta H_{\text{soln}} = -8$ kJ/mol **27.** Both $Al(OH)_3$ and NaOH are ionic compounds. Since the lattice energy is proportional to the charge of the ions, the lattice energy of aluminum hydroxide is greater than that of sodium hydroxide. The attraction of water molecules for $Al^{3+}$ and $OH^-$ cannot overcome the larger lattice energy and $Al(OH)_3$ is insoluble. For NaOH, the favorable hydration energy is large enough to overcome the smaller lattice energy and NaOH is soluble. **29.** Water is a polar molecule capable of hydrogen bonding. Polar molecules, especially molecules capable of hydrogen bonding, and ions are all attracted to water. For covalent compounds, as polarity increases, the attraction to water increases. For ionic compounds, as the charge of the ions increases and/or the size of the ions decreases, the attraction to water increases. a. $CH_3CH_2OH$; $CH_3CH_2OH$ is polar, whereas $CH_3CH_2CH_3$ is nonpolar. b. $CHCl_3$; $CHCl_3$ is polar, whereas $CCl_4$ is nonpolar. c. $CH_3CH_2OH$; $CH_3CH_2OH$ is much more polar than $CH_3(CH_2)_{14}CH_2OH$. **31.** As the length of the hydrocarbon chain increases, the solubility decreases. The —OH end of the alcohols can hydrogen-bond with water. The hydrocarbon chain, however, is basically nonpolar and interacts poorly with water. As the hydrocarbon chain gets longer, a greater portion of the molecule cannot interact with the water molecules and the solubility decreases; i.e., the effect of the —OH group decreases as the alcohols get larger. **33.** Structure effects refer to solute and solvent having similar polarities in order for solution formation to occur. Hydrophobic solutes are mostly nonpolar substances that are "water-fearing." Hydrophilic solutes are mostly polar or ionic substances that are "water-loving." Pressure has little effect on the solubilities of solids or liquids; it does significantly affect the solubility of a gas. Henry's law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution ($C = kP$). The equation for Henry's law works best for dilute solutions of gases that do not dissociate in or react with the solvent. HCl(*g*) does not follow Henry's law because it dissociates into $H^+(aq)$ and $Cl^-(aq)$ in solution (HCl is a strong acid). For $O_2$ and $N_2$, Henry's law works well since these gases do not react with the water solvent. An increase in temperature can either increase or decrease the solubility of a solid solute in water. It is true that a solute dissolves more rapidly with an increase in temperature, but the amount of solid solute that dissolves to form a saturated solution can either decrease or increase with temperature. The temperature effect is difficult to predict for solid solutes. However, the temperature effect for gas solutes is easier to predict as the solubility of a gas typically decreases with increasing temperature. **35.** 962 L atm/mol; $1.14 \times 10^{-3}$ mol/L **37.** As the temperature increases, the gas molecules will have a greater average kinetic energy. A greater fraction of the gas molecules in solution will have kinetic energy greater than the attractive forces between the gas molecules and the solvent molecules. More gas molecules escape to the vapor phase and the solubility of the gas decreases. **39.** 136 torr **41.** solution d **43.** $3.0 \times 10^2$ g/mol **45.** a. 290 torr; b. 0.69 **47.** $\chi_{\text{meth}} = \chi_{\text{prop}} = 0.500$ **49.** $P_{\text{ideal}} = 188.6$ torr; $\chi_{\text{acetone}} = 0.512$, $\chi_{\text{methanol}} = 0.488$; since the actual vapor pressure of the solution is smaller than the ideal vapor pressure, this solution exhibits a negative deviation from Raoult's law. This occurs when solute–solvent attractions are stronger than for the pure substances. **51.** No, the solution is not ideal. For an ideal solution, the strength of the intermolecular forces in the solution is the same as in pure solute and pure solvent. This results in $\Delta H_{\text{soln}} = 0$ for an ideal solution. $\Delta H_{\text{soln}}$ for methanol/water is not zero. Since $\Delta H_{\text{soln}} < 0$, this solution exhibits a negative deviation from Raoult's law. **53.** Solutions of A and B have vapor pressures less than ideal (see Fig. 17.11), so this plot shows negative deviations from Raoult's law. Negative deviations occur when the intermolecular forces are stronger in solution than in pure solvent and solute. This results in an exothermic enthalpy of solution. The only statement that is false is e. A substance boils when the vapor pressure equals the external pressure. Since $\chi_B = 0.6$ has a lower vapor pressure at the temperature of the plot than either pure A or pure B, one would expect this solution to require the highest temperature for the vapor pressure to reach the external pressure. Therefore, the solution with $\chi_B = 0.6$ will have a higher boiling point than either pure A or pure B. (Note that since $P^\circ_B > P^\circ_A$, then B is more volatile than A.) **55.** Osmotic pressure: the pressure that must be applied to a solution to stop osmosis; osmosis is the flow of solvent into the solution through a semipermeable membrane. The equation to calculate osmotic pressure $\pi$ is

$$\pi = MRT$$

where $M$ is the molarity of the solution, $R$ is the gas constant, and $T$ is the Kelvin temperature. The molarity of a solution approximately equals the molality of the solution when 1 kg solvent ≈ 1 L solution. This occurs for dilute solutions of water since $d_{H_2O} = 1.00$ g/cm$^3$. **57.** 101.5°C **59.** −29.9°C; 108.2°C **61.** 100.08°C **63.** 498 g/mol **65.** 776 g/mol **67.** $2.0 \times 10^{-5}$ °C; 0.20 torr **69.** ∼30 m **71.** With addition of salt or sugar, the osmotic pressure inside the fruit cells (and bacteria) is less than outside the cell. Water will leave the cells, which will dehydrate any bacteria present, causing them to die. **73.** 0.0880; 59.2 torr **75.** a. 0.010 *m* $Na_3PO_4$ and 0.020 *m* KCl; b. 0.020 *m* HF; c. 0.020 *m* $CaBr_2$ **77.** The van't Hoff factor *i* is the number of moles of particles (ions) produced for every mole of solute dissolved. For NaCl, $i = 2$ since $Na^+$ and $Cl^-$ are produced in water; for $Al(NO_3)_3$, $i = 4$ since $Al^{3+}$ and 3 $NO_3^-$ ions are produced when $Al(NO_3)_3$ dissolves in water. In real life, the van't Hoff factor is rarely the value predicted by the number of ions a salt dissolves into; *i* is generally something less than the predicted number of ions. This is due to a phenomenon called ion pairing, where at any instant a small percentage of oppositely charged ions pair up and act like a single solute particle. Ion pairing occurs most when the concentration of ions is large. Therefore, dilute solutions behave most ideally; here *i* is close to that determined by the number of ions in a salt. **79.** A pressure greater than 4.8 atm should be applied. **81.** a. −0.25°C; 100.069°C; b. −0.32°C; 100.087°C **83.** 97.8 g/mol **85.** Both solutions and colloids have suspended particles in some medium. The major difference between the two is the size of the particles. A colloid is a suspension of relatively large particles as compared with a solution. Because of this, colloids will scatter light, whereas solutions will not. The scattering of light by a colloidal suspension is called the Tyndall effect. **87.** Coagulation is the destruction of a colloid by the aggregation of many suspended particles to form a large particle that settles out of solution. **89.** 7.9 *M* **91.** a. 100.77°C; b. 23.1 mm Hg; c. We assumed ideal behavior in solution formation and assumed $i = 1$ (no ions form). **93.** Benzoic acid is capable of hydrogen bonding, but a significant part of benzoic acid is the nonpolar benzene ring, which is composed of only carbon and hydrogen. In benzene, a hydrogen-bonded dimer forms:

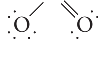


The dimer is relatively nonpolar and thus more soluble in benzene than in water. Since benzoic acid forms dimers in benzene, the effective solute particle concentration will be less than 1.0 molal. Therefore, the freezing-point depression would be less than 5.12°C ($\Delta T_f = K_f m$). **95.** a. 26.6 kJ/mol; b. −657 kJ/mol **97.** 0.050 **99.** $C_7H_4O$; $C_{14}H_8O_2$ **101.** a. 303 ± 9 g/mol; b. No, codeine could not be eliminated since its molar mass is in the possible range including the uncertainty; c. We would like the uncertainty to be ±1 g/mol. We need the freezing-point depression to be about 10 times what it was in this problem. Two possibilities are (1) make the solution ten times more concentrated (may be solubility problem) or (2) use a solvent with a larger $K_f$ value, e.g., camphor. **103.** $5.08 \times 10^{-17}$ **105.** $1.0 \times 10^{-3}$ **107.** 72% $MgCl_2$ **109.** $\chi_{CCl_4} = 0.554$, $\chi_{C_6H_6} = 0.446$ **111.** 0.286 **113.** a. If we assume $MgCO_3$ does not dissociate, 46 L of water must be processed. If $MgCO_3$ does dissociate, then 47 L of water must be processed. b. No; A reverse osmosis system that applies 8.0 atm can only purify water with a solute concentration less than 0.32 mol/L. Salt water has a solute concentration of $2(0.60\ M) = 1.2$ mol/L ions. The solute concentration of salt water is much too high for this reverse osmosis unit to work. **115.** a. 6.11 atm; b. $8.3 \times 10^{-3}$ **117.** a. 0.25 or 25%; b. −0.562°C

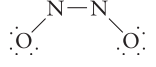
### Chapter 18

**1.** The gravity of the earth is not strong enough to keep $H_2$ in the atmosphere. **3.** a. $\Delta H° = -92$ kJ; $\Delta S° = -199$ J/K; $\Delta G° = -33$ kJ; b. yes; c. $T < 460$ K **5.** Ionic, covalent, and metallic (or interstitial); The ionic and covalent hydrides are true compounds obeying the law of definite proportions and differ from each other in the type of bonding. The interstitial hydrides are more like solid solutions of hydrogen with a transition metal, and do not obey the law of definite proportions. **7.** Alkali metals have an $ns^1$ valence shell electron configuration. Alkali metals lose this valence electron with relative ease to form $M^+$ cations when in ionic compounds. They all are easily oxidized. Therefore, in order to prepare the pure metals, alkali metals must be produced in the absence of materials ($H_2O$, $O_2$) that are capable of oxidizing them. The method of preparation is electrochemical processes, specifically, electrolysis of molten chloride salts and reduction of alkali salts with Mg and $H_2$. In all production methods, $H_2O$ and $O_2$ must be absent. **9.** Hydrogen forms many compounds in which the oxidation state is +1, as do the Group 1A elements. Consider, for example, $H_2SO_4$ and HCl compared with $Na_2SO_4$ and NaCl. On the other hand, hydrogen forms diatomic $H_2$ molecules and is a nonmetal, while the Group 1A elements are metals. Hydrogen also forms compounds with a −1 oxidation state, which is not characteristic of Group 1A metals, e.g., NaH. **11.** $4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$; $16Li(s) + S_8(s) \rightarrow 8Li_2S(s)$; $2Li(s) + Cl_2(g) \rightarrow 2LiCl(s)$; $12Li(s) + P_4(s) \rightarrow 4Li_3P(s)$; $2Li(s) + H_2(g) \rightarrow 2LiH(s)$; $2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$; $2Li(s) + 2HCl(aq) \rightarrow 2LiCl(aq) + H_2(g)$ **13.** $MgCl_2$ **15.** The alkaline earth ions that give water the hard designation are $Ca^{2+}$ and $Mg^{2+}$. These ions interfere with the action of detergents and form unwanted precipitates with soaps. Large-scale water softeners remove $Ca^{2+}$ by precipitating out the calcium ions as $CaCO_3$. In homes, $Ca^{2+}$ and $Mg^{2+}$ (plus other cations) are removed by ion exchange. See Fig. 18.6 for a schematic of a typical cation exchange resin. **17.** $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$ **19.** $CaF_2(s)$ will precipitate when $[Ca^{2+}]_0 > 2 \times 10^{-2}\ M$. Therefore, hard water should have a calcium ion concentration of less than $2 \times 10^{-2}\ M$ to avoid precipitate formation. **21.** The valence electron configuration of Group 3A elements is $ns^2np^1$. The lightest Group 3A element, boron, is a nonmetal because most of its compounds are covalent. Aluminum, although commonly thought of as a metal, does have some nonmetallic properties because its bonds to other nonmetals have significant covalent character. The other Group 3A elements have typical metal characteristics; their compounds formed with nonmetals are ionic. From this discussion, metallic character increases as the Group 3A elements get larger. As mentioned previously, boron is a nonmetal in both properties and compounds formed. However, aluminum has physical properties of metals such as high thermal and electrical conductivities and a lustrous appearance. The compounds of aluminum with other nonmetals, however, do have some nonmetallic properties because the bonds have significant covalent character. **23.** $B_2H_6(g) + 3O_2(g) \rightarrow 2B(OH)_3(s)$ **25.** $2Ga(s) + 3F_2(g) \rightarrow 2GaF_3(s)$; $4Ga(s) + 3O_2(g) \rightarrow 2Ga_2O_3(s)$; $16Ga(s) + 3S_8(s) \rightarrow 8Ga_2S_3(s)$; $2Ga(s) + 6HCl(aq) \rightarrow 2GaCl_3(aq) + 3H_2(g)$ **27.** The valence electron configuration of Group 4A elements is $ns^2np^2$. The two most important elements on earth are both Group 4A elements. They are carbon, found in all biologically important molecules, and silicon, found in most of the compounds that make up the earth's crust. They are important because they are so prevalent in compounds necessary for life and the geologic world. As with Group 3A, Group 4A shows an increase in metallic character as the elements get heavier. Carbon is a typical nonmetal, silicon and germanium have properties of both metals and nonmetals, so they are classified as semimetals, whereas tin and lead have typical metallic characteristics. **29.** White tin is stable at normal temperatures. Gray tin is stable at temperatures below 13.2°C. Thus for the phase change Sn(gray) → Sn(white), $\Delta G$ is negative at $T > 13.2°C$ and $\Delta G$ is positive at $T < 13.2°C$. This is possible only if $\Delta H$ is positive and $\Delta S$ is positive. Thus gray tin has the more ordered structure (has the smaller positional probability). **31.** $Sn(s) + 2F_2(g) \rightarrow SnF_4(s)$, tin(IV) fluoride; $Sn(s) + F_2(g) \rightarrow SnF_2(s)$, tin(II) fluoride. **33.** In each formula unit of $Pb_3O_4$, two atoms are Pb(II) and one atom is Pb(IV) (2:1 ratio). **35.** Both $NO_4^{3-}$ and $PO_4^{3-}$ have 32 valence electrons, so both have similar Lewis structures. From the Lewis structure for $NO_4^{3-}$, the central N atom has a tetrahedral arrangement of electron pairs. N is small. There is probably not enough room for all 4 oxygen atoms around N. P is larger; thus $PO_4^{3-}$ is stable. $PO_3^-$ and $NO_3^-$ both have 24 valence electrons, so both have similar Lewis structures. From the Lewis structure for $PO_3^-$, $PO_3^-$ has a trigonal arrangement of electron pairs around the central P atom (two single bonds and one double bond). P═O bonds are not particularly stable, whereas N═O bonds are stable. Thus $NO_3^-$ is stable. **37.** N: $1s^22s^22p^3$; the extremes of the oxidation states for N can be rationalized by examining the electron configuration of N. Nitrogen is three electrons short of the stable Ne electron configuration of $1s^22s^22p^6$. Having an oxidation state of −3 makes sense. The +5 oxidation state corresponds to N "losing" its 5 valence electrons. In compounds with oxygen, the N—O bonds are polar covalent, with N having the partial positive end of the bond dipole. In the world of oxidation states, electrons in polar covalent bonds are assigned to the more electronegative atom; this is oxygen in N—O bonds. N can form enough bonds to oxygen to give it a +5 oxidation state. This loosely corresponds to losing all of the valence electrons. **39.** This is due to nitrogen's ability to form strong $\pi$ bonds, whereas heavier Group 5A elements do not form strong $\pi$ bonds. Therefore, $P_2$, $As_2$, and $Sb_2$ do not form since two $\pi$ bonds are required to form these diatomic substances.

**41.** a.

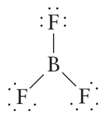


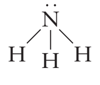
plus other resonance structures;

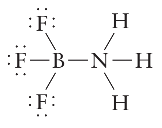


plus other resonance structures;

b.







In reaction a, $NO_2$ has an odd number of electrons so it is impossible to satisfy the octet rule. By dimerizing to form $N_2O_4$, the odd electrons on two $NO_2$ molecules can pair up, giving a species whose Lewis structure can satisfy the octet rule. In general odd-electron species are very reactive. In reaction b, $BF_3$ can be considered electron-deficient. Boron has only six electrons around it. By forming $BF_3NH_3$, the boron atom satisfies the octet rule by accepting a lone pair of electrons from $NH_3$ to form a fourth bond. **43.** exothermic **45.** $N_2H_4(l) + 2F_2(g) \longrightarrow 4HF(g) + N_2(g)$; $\Delta H° = -1169$ kJ

**47.** $2Bi_2S_3(s) + 9O_2(g) \longrightarrow 2Bi_2O_3(s) + 6SO_2(g)$; $2Bi_2O_3(s) + 3C(s) \longrightarrow 4Bi(s) + 3CO_2(g)$

$2Sb_2S_3(s) + 9O_2(g) \longrightarrow 2Sb_2O_3(s) + 6SO_2(g)$; $2Sb_2O_3(s) + 3C(s) \longrightarrow 4Sb(s) + 3CO_2(g)$

**49.** TSP = $Na_3PO_4$; $PO_4^{3-}$ is the conjugate base of the weak acid $HPO_4^{2-}$ ($K_a = 4.8 \times 10^{-13}$). All conjugate bases of weak acids are effective bases ($K_b = K_w/K_a = 1.0 \times 10^{-14}/4.8 \times 10^{-13} = 2.1 \times 10^{-2}$). The weak-base reaction of $PO_4^{3-}$ with $H_2O$ is $PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$ $K_b = 2.1 \times 10^{-2}$.

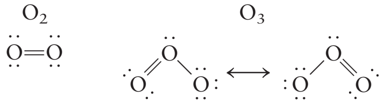
**51.**

$4As(s) + 3O_2(g) \longrightarrow As_4O_6(s)$; $4As(s) + 5O_2(g) \longrightarrow As_4O_{10}(s)$;

$As_4O_6(s) + 6H_2O(l) \longrightarrow 4H_3AsO_3(aq)$; $As_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3AsO_4(aq)$

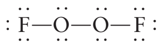
**53.** $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$, $\Delta G° = \Delta G°_{f,\,NO} = 87$ kJ/mol; By definition, $\Delta G°_f$ for a compound equals the free energy change that would accompany the formation of 1 mol of that compound from its elements in their standard states. NO (and some other oxides of nitrogen) have weaker bonds as compared to the triple bond of $N_2$ and the double bond of $O_2$. Because of this, NO (and some other oxides of nitrogen) have higher (positive) free energies of formation as compared to the relatively stable $N_2$ and $O_2$ molecules.

**55.** The pollution provides nitrogen and phosphorus nutrients so the algae can grow. The algae consume oxygen, causing fish to die. **57.** −4594 kJ **59.** Hydrazine also can hydrogen bond because it has covalent N—H bonds as well as a lone pair of electrons on each N. The high boiling point for hydrazine's relatively small size supports this. **61.** The two allotropic forms of oxygen are $O_2$ and $O_3$.



The MO electron configuration of $O_2$ has two unpaired electrons in the degenerate pi antibonding ($\pi_{2p}{}^*$) orbitals. A substance with unpaired electrons is paramagnetic (see Fig. 14.41). Ozone has a V-shape molecular structure with a bond angle of 117°, slightly less than the predicted 120° trigonal planar bond angle. **63.** In the upper atmosphere, $O_3$ acts as a filter for UV radiation: $O_3 \xrightarrow{h\nu} O_2 + O$; $O_3$ is also a powerful oxidizing agent. It irritates the lungs and eyes, and at high concentration it is toxic. The smell of a "fresh spring day" is $O_3$ formed during lightning discharges. Toxic materials don't necessarily smell bad. For example, HCN smells like almonds. **65.** +6 oxidation state: $SO_4^{2-}$, $SO_3$, $SF_6$; +4 oxidation state: $SO_3^{2-}$, $SO_2$, $SF_4$; +2 oxidation state: $SCl_2$; 0 oxidation state: $S_8$ and all other elemental forms of sulfur; −2 oxidation state: $H_2S$, $Na_2S$ **67.** $H_2SeO_4(aq) + 3SO_2(g) \rightarrow Se(s) + 3SO_3(g) + H_2O(l)$

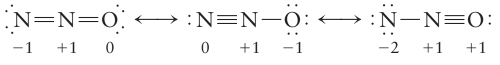
**69.**



| | | | | |
|---|---|---|---|---|
| Formal Charge | 0 | 0 | 0 | 0 |
| Oxidation State | −1 | +1 | +1 | −1 |

Oxidation states are more useful. We are forced to assign +1 as the oxidation state for oxygen. Oxygen is very electronegative and +1 is not a stable oxidation state for this element. **71.** Fluorine is the most reactive of the halogens because it is the most electronegative atom and the bond in the $F_2$ molecule is very weak. **73.** $ClO^-(aq) + 2NH_3(aq) \rightarrow Cl^-(aq) + N_2H_4(aq) + H_2O(l)$, $\mathscr{E}°_{cell} = 1.00$ V; Since $\mathscr{E}°_{cell}$ is positive for this reaction, then at standard conditions $ClO^-$ can spontaneously oxidize $NH_3$ to the somewhat toxic $N_2H_4$. **75.** a. $AgCl(s) \xrightarrow{h\nu} Ag(s) + Cl$; the reactive chlorine atom is trapped in the crystal. When light is removed, Cl reacts with silver atoms to re-form AgCl; that is, the reverse reaction occurs. In pure AgCl, the Cl atoms escape, making the reverse reaction impossible. b. Over time, chlorine is lost, and the dark silver metal is permanent. **77.** Helium is unreactive and doesn't combine with any other elements. It is a very light gas and would easily escape the earth's gravitational pull as the planet was formed **79.** $2 \times 10^4$ g; $2 \times 10^{26}$ atoms in room; $5 \times 10^{20}$ atoms in one breath; Since Ar and Rn are both noble gases, both species will be relatively unreactive. However, all nuclei of Rn are radioactive, unlike most nuclei of Ar. The radioactive decay products of Rn can cause biological damage when inhaled. **81.** One would expect $RnF_2$ and $RnF_4$ to form in fashion similar to $XeF_2$ and $XeF_4$. The chemistry of radon is difficult to study because all radon isotopes are radioactive. The hazards of dealing with radioactive materials are immense. **83.** Solids have stronger intermolecular forces than liquids. In order to maximize the hydrogen bonding in the solid phase, ice is forced into an open structure. This open structure is why $H_2O(s)$ is less dense than $H_2O(l)$. **85.** Strontium and calcium are both alkaline earth metals, so both have similar chemical properties. Since milk is a good source of calcium, strontium could replace some calcium in milk without much difficulty. **87.** In solution $Tl^{3+}$ can oxidize $I^-$ to $I_3^-$. Thus we expect $TlI_3$ to be thallium(I) triiodide. **89.** The inert pair effect refers to the difficulty of removing the pair of *s* electrons from some of the elements in the fifth and sixth periods of the periodic table. As a result, multiple oxidation states are exhibited for the heavier elements of Groups 3A and 4A. $In^+$, $In^{3+}$, $Tl^+$, and $Tl^{3+}$ oxidation states are all important to the chemistry of In and Tl. **91.** $5.4 \times 10^4$ kJ (Hall–Heroult process) versus $4.0 \times 10^2$ kJ; it is feasible to recycle Al by melting the metal because, in theory, it takes less than 1% of the energy required to produce the same amount of Al by the Hall–Heroult process. **93.** Carbon cannot form the fifth bond necessary for the transition state since carbon doesn't have low-energy *d* orbitals available to expand the octet. **95.** a. The NNO structure is correct. From the Lewis structures we would predict both NNO and NON to be linear. However, we would predict NNO to be polar and NON to be nonpolar. Since experiments show $N_2O$ to be polar, then NNO is the correct structure.

b.



The formal charges for the atoms in the various resonance structures appear below each atom. The central N is *sp* hybridized in all of the resonance structures. We can probably ignore the third resonance structure on the basis of the relatively large formal charges as compared to the first two resonance structures. c. The *sp* hybrid orbitals on the center N overlap with atomic orbitals (or hybrid orbitals) on the other two atoms to form the two $\sigma$ bonds. The remaining two unhybridized *p* orbitals on the center N overlap with two *p* orbitals on the peripheral N to form the two $\pi$ bonds. **97.** $\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{1}{0.9} = 1.1 \approx 1$; a best buffer has approximately equal concentrations of weak acid and conjugate base so that pH ≈ $\mathrm{p}K_a$ for a best buffer. The $\mathrm{p}K_a$ value for a $H_3PO_4/H_2PO_4^-$ buffer is $-\log(7.5 \times 10^{-3}) = 2.12$. A pH of 7.1 is too high for a $H_3PO_4/H_2PO_4^-$ buffer to be effective. At this high a pH, there would be so little $H_3PO_4$ present that we could hardly consider it a buffer. This solution would not be effective in resisting pH changes, especially when a strong base is added. **99.** $4.8 \times 10^{-11}\ M$ **101.** $\Delta H° = 286$ kJ; $\Delta G° = 326$ kJ; $K_p = 7.22 \times 10^{-58}$; $P_{O_3} = 3.3 \times 10^{-41}$ atm; The volume occupied by one molecule of ozone at 230. K is $9.5 \times 10^{17}$ L. Equilibrium is probably not maintained under these conditions. When only two ozone molecules are in a volume of $9.5 \times 10^{17}$ L, the reaction is not at equilibrium. Under these conditions, $Q > K$ and the reaction shifts to the left. But with only two ozone molecules in this huge volume, it is extremely unlikely that they will collide with each other. Under these conditions, the concentration of ozone is not large enough to maintain equilibrium. **103.** a. NO is the catalyst; b. $NO_2$ is an intermediate; c. $k_{\text{cat}}/k_{\text{uncat}} = 2.3$; d. The proposed mechanism for the chlorine-catalyzed destruction of ozone is:

$$\begin{array}{lll} O_3 + Cl \longrightarrow O_2 + ClO & & \text{Slow} \\ \underline{ClO + O \longrightarrow O_2 + Cl} & & \text{Fast} \\ O_3 + O \longrightarrow 2O_2 & & \end{array}$$

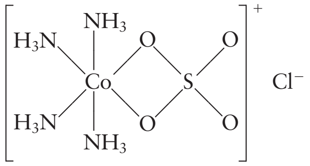
e. $k_{Cl}/k_{NO} = 52$; At 25°C, the Cl-catalyzed reaction is roughly 52 times faster (more efficient) than the NO-catalyzed reaction, assuming the frequency factor $A$ is the same for each reaction and assuming similar rate laws. **105.** $2.0 \times 10^{-37}\ M$ **107.** a. 8.8 kJ; b. Other ions will have to be transported to maintain electroneutrality. Either anions must be transported into the cells or cations ($Na^+$) in the cell must be transported to the blood. The latter is what happens: $[Na^+]$ in blood is greater than $[Na^+]$ in cells as a result of this pumping. c. 0.28 mol.

## Chapter 19

**7.** a. Cr: $[Ar]4s^13d^5$, $Cr^{2+}$: $[Ar]3d^4$, $Cr^{3+}$: $[Ar]3d^3$; b. Cu: $[Ar]4s^13d^{10}$, $Cu^+$: $[Ar]3d^{10}$, $Cu^{2+}$: $[Ar]3d^9$; c. V: $[Ar]4s^23d^3$, $V^{2+}$: $[Ar]3d^3$, $V^{3+}$: $[Ar]3d^2$ **9.** The lanthanide elements are located just before the 5*d* transition metals. The lanthanide contraction is the steady decrease in the atomic radii of the lanthanide elements when going from left to right across the periodic table. As a result of the lanthanide contraction, the sizes of the 4*d* and 5*d* elements are very similar (see the following exercise). This leads to a greater similarity in the chemistry of the 4*d* and 5*d* elements in a given vertical group. **11.** a. molybdenum(IV) sulfide; molybdenum(VI) oxide; b. $MoS_2$, +4; $MoO_3$, +6; $(NH_4)_2Mo_2O_7$, +6; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, +6 **13.** $TiF_4$: Ionic compound containing $Ti^{4+}$ ions and $F^-$ ions. $TiCl_4$, $TiBr_4$, and $TiI_4$: Covalent compounds containing discrete, tetrahedral $TiX_4$ molecules. As these molecules get larger, the bp and mp increase because the London dispersion forces increase. $TiF_4$ has the highest bp since the interparticle forces are stronger in ionic compounds as compared with those in covalent compounds. **15.** $H^+ + OH^- \rightarrow H_2O$; Sodium hydroxide (NaOH) will react with the $H^+$ on the product side of the reaction. This effectively removes $H^+$ from the equilibrium, which will shift the reaction to the right to produce more $H^+$ and $CrO_4^{2-}$. Since more $CrO_4^{2-}$ is produced, the solution turns yellow. **17.** Because transition metals form bonds to species that donate lone pairs of electrons, transition metals are Lewis acids (electron-pair acceptors). The Lewis bases in coordination compounds are the ligands, all of which have an unshared pair of electrons to donate. The coordinate covalent bond between the ligand and the transition metal just indicates that both electrons in the bond originally came from one of the atoms in the bond. Here, the electrons in the bond come from the ligand.

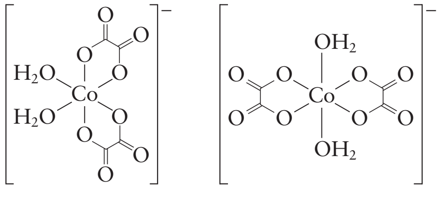
**19.** $Fe_2O_3(s) + 6H_2C_2O_4(aq) \rightarrow 2Fe(C_2O_4)_3^{3-}(aq) + 3H_2O(l) + 6H^+(aq)$; the oxalate anion forms a soluble complex ion with iron in rust ($Fe_2O_3$), which allows rust stains to be removed. **21.** a. The correct name is tetraamminecopper(II) chloride. The complex ion is named incorrectly in several ways. b. The correct name is bis(ethylenediamine)nickel(II) sulfate. The ethylenediamine ligands are neutral and sulfate has a 2– charge. Therefore, $Ni^{2+}$ is present, not $Ni^{4+}$. c. The correct name is potassium diaquatetrachlorochromate(III). Because the complex ion is an anion, the *-ate* suffix ending is added to the name of the metal. Also, the ligands were not in alphabetical order (*a* in aqua comes before *c* in chloro). d. The correct name is sodium tetracyanooxalatocobaltate(II). The only error is that *tetra* should be omitted in front of sodium. That four sodium ions are needed to balance charge is deduced from the name of the complex ion. **23.** a. pentaamminechlororuthenium(III) ion; b. hexacyanoferrate(II) ion; c. tris(ethylenediamine)manganese(II) ion; d. pentaamminenitrocobalt(III) ion **25.** a. $K_2[CoCl_4]$; b. $[Pt(H_2O)(CO)_3]Br_2$; c. $Na_3[Fe(CN)_2(C_2O_4)_2]$; d. $[Cr(NH_3)_3Cl(H_2NCH_2CH_2NH_2)]I_2$

**27.**



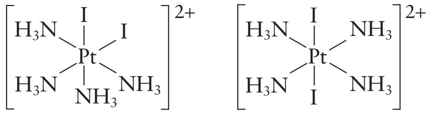
**29.** Three moles of AgI will precipitate per mole of $[Co(NH_3)_6]I_3$, 2 moles of AgI will precipitate per mole of $[Pt(NH_3)_4I_2]I_2$, 0 moles of AgI will precipitate per mole of $Na_2[PtI_6]$, and 1 mole of AgI will precipitate per mole of $[Cr(NH_3)_4I_2]I$. **31.** a. Isomers: Species with the same formulas but different properties. See text for examples of the following types of isomers. b. Structural isomers: Isomers that have one or more bonds that are different. c. Stereoisomers: Isomers that contain the same bonds but differ in how the atoms are arranged in space. d. Coordination isomers: Structural isomers that differ in the atoms that make up the complex ion. e. Linkage isomers: Structural isomers that differ in how one or more ligands are attached to the transition metal. f. Geometric isomers: (*cis–trans* isomerism); stereoisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other. g. Optical isomers: Stereoisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different.

**33.** a.



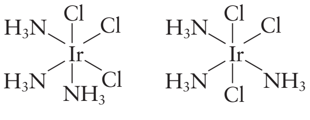
*cis* *trans*

b.



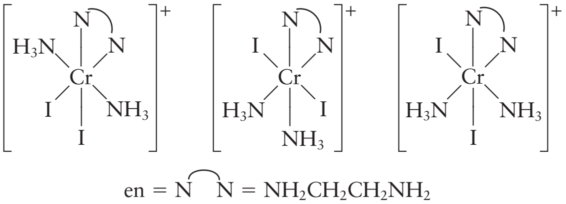
*cis* *trans*

c.



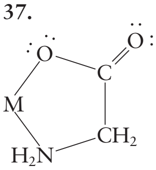
*cis* *trans*

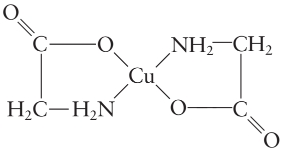
d.



**35.** No; both the *trans* and the *cis* forms of $Co(NH_3)_4Cl_2^+$ have mirror images that are superimposable. For the *cis* form, the mirror image needs only a 90° rotation to produce the original structure. Hence neither the *trans* nor *cis* form is optically active.

**37.**





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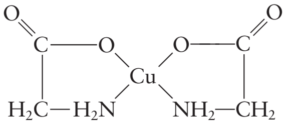
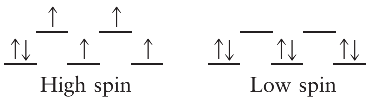
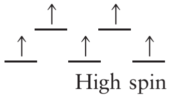


**39.** Linkage isomers differ in the way that the ligand bonds to the metal. $SCN^-$ can bond through the sulfur or through the nitrogen atom. $NO_2^-$ can bond through the nitrogen or through the oxygen atom. $OCN^-$ can bond through the oxygen or through the nitrogen atom. $N_3^-$, $NH_2CH_2CH_2NH_2$, and $I^-$ are not capable of linkage isomerism. **41.** $Cr(acac)_3$ and *cis*-$Cr(acac)_2(H_2O)_2$ are optically active. **43.** a. ligand that will give complex ions with the maximum number of unpaired electrons; b. ligand that will give complex ions with the minimum number of unpaired electrons; c. complex with a minimum number of unpaired electrons (low spin = strong field); d. complex with a maximum number of unpaired electrons (high spin = weak field) **45.** $Sc^{3+}$ has no electrons in *d* orbitals. $Ti^{3+}$ and $V^{3+}$ have *d* electrons present. The color of transition metal complexes results from electron transfer between split *d* orbitals. If no *d* electrons are present, no electron transfer can occur and the compounds are not colored.

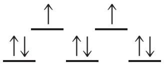
**47.** a. $Fe^{2+}$



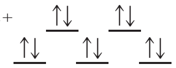
b. $Fe^{3+}$



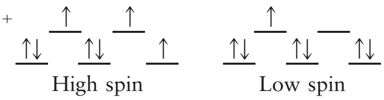
c. $Ni^{2+}$



d. $Zn^{2+}$

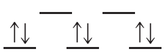


e. $Co^{2+}$



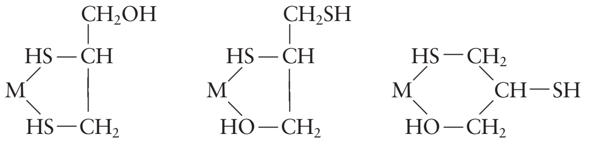
**49.** a. 0; b. 2; c. 2 **51.** Replacement of water ligands by ammonia ligands resulted in shorter wavelengths of light being absorbed. Energy and wavelength are inversely related, so the presence of the $NH_3$ ligands resulted in a larger *d*-orbital splitting (larger Δ). Therefore, $NH_3$ is a stronger field ligand than $H_2O$. **53.** The violet complex ion absorbs yellow-green light ($\lambda \approx 570$ nm) and is $Cr(H_2O)_6^{3+}$. The yellow complex ion absorbs blue light ($\lambda \approx 450$ nm) and is $Cr(NH_3)_6^{3+}$. The green complex ion absorbs red light ($\lambda \approx 650$ nm) and is $Cr(H_2O)_4Cl_2^+$.

**55.** a. optical isomerism; b.



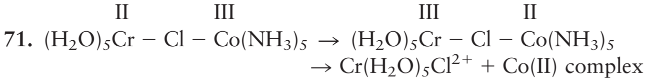
**57.** The crystal field diagrams are different because the geometries of where the ligands point is different. The tetrahedrally oriented ligands point differently in relationship to the *d*-orbitals than do the octahedrally oriented ligands. Plus, there are more ligands in an octahedral complex. The *d*-orbital splitting in tetrahedral complexes is less than one-half the *d*-orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case; hence all tetrahedral complexes are weak-field or high-spin. **59.** $CoBr_6^{4-}$ has an octahedral structure and $CoBr_4^{2-}$ has a tetrahedral structure (as do most $Co^{2+}$ complexes with four ligands). Coordination complexes absorb electromagnetic radiation (EMR) of energy equal to the energy difference between the split *d* orbitals. Since the tetrahedral *d*-orbital splitting is less than one-half of the octahedral *d*-orbital splitting, tetrahedral complexes will absorb lower-energy EMR, which corresponds to longer-wavelength EMR ($E = hc/\lambda$). Therefore, $CoBr_6^{4-}$ will absorb EMR having a wavelength shorter than $3.4 \times 10^{-6}$ m. **61.** $Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$, orange ppt.; $HgI_2(s) + 2I^-(aq) \rightarrow HgI_4^{2-}(aq)$, soluble complex ion; $Hg^{2+}$ is a $d^{10}$ ion. Color is the result of electron transfer between split *d* orbitals. This cannot occur for the filled *d* orbitals in $Hg^{2+}$. Therefore, we would not expect $Hg^{2+}$ complex ions to form colored solutions. **63.** zero (carbon monoxide is a neutrally charged ligand) **65.** $Cr(NH_3)_5I_3$ is the empirical formula. Cr(III) forms octahedral complexes. So compound A is made of the octahedral $[Cr(NH_3)_5I]^{2+}$ complex ion and two $I^-$ ions; that is, $[Cr(NH_3)_5I]I_2$.

**67.**



where M = metal ion **69.** No; in all three cases, six bonds are formed between $Ni^{2+}$ and nitrogen, so $\Delta H$ values should be similar. $\Delta S°$ for formation of the complex ion is most negative for six $NH_3$ molecules reacting with a metal ion (seven independent species become one). For penten reacting with a metal ion, two independent species become one, so $\Delta S°$ is least negative of all three of the reactions. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the more favorable $\Delta S°$ is for the formation of the complex ion and the larger the formation constant.

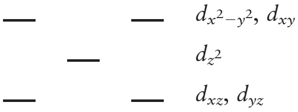
**71.**



$$(H_2O)_5\overset{II}{Cr} - Cl - \overset{III}{Co}(NH_3)_5 \rightarrow (H_2O)_5\overset{III}{Cr} - Cl - \overset{II}{Co}(NH_3)_5 \rightarrow Cr(H_2O)_5Cl^{2+} + \text{Co(II) complex}$$

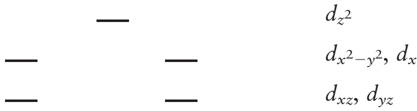
Yes, this is consistent. After the oxidation, the ligands on Cr(III) won't exchange. Since $Cl^-$ is in the coordination sphere, then it must have formed a bond to Cr(II) before the electron transfer occurred (as proposed through the formation of the intermediate). **73.** a. 1.66; b. Because of the lower charge, $Fe^{2+}(aq)$ will not be as strong an acid as $Fe^{3+}(aq)$. A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate. **75.** a. In the lungs, there is a lot of $O_2$, and the equilibrium favors $Hb(O_2)_4$. In the cells, there is a deficiency of $O_2$, and the equilibrium favors $HbH_4^{4+}$. b. $CO_2$ is a weak acid in water, $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$. Removing $CO_2$ essentially decreases $H^+$. $Hb(O_2)_4$ is then favored, and $O_2$ is not released by hemoglobin in the cells. Breathing into a paper bag increases $[CO_2]$ in the blood, thus increasing $[H^+]$ and shifting the reaction to the left. c. $CO_2$ builds up in the blood, and it becomes too acidic, driving the equilibrium to the left. Hemoglobin can't bind $O_2$ as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.

**77.**

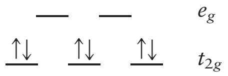


The $d_{x^2-y^2}$ and $d_{xy}$ orbitals are in the plane of the three ligands and should be destabilized the most. The amount of destabilization should be about equal when all the possible interactions are considered. The $d_{z^2}$ orbital has some electron density in the *xy* plane (the doughnut) and should be destabilized a lesser amount as compared to the $d_{x^2-y^2}$ and $d_{xy}$ orbitals. The $d_{xz}$ and $d_{yz}$ orbitals have no electron density in the plane and should be lowest in energy.

**79.**



The $d_{z^2}$ orbital will be destabilized much more than in the trigonal planar case (see Exercise 19.77). The $d_{z^2}$ orbital has electron density on the *z*-axis directed at the two axial ligands. The $d_{x^2-y^2}$ and $d_{xy}$ orbitals are in the plane of the three trigonal planar ligands and should be destabilized a lesser amount as compared to the $d_{z^2}$ orbital; only a portion of the electron density in the $d_{x^2-y^2}$ and $d_{xy}$ orbitals is directed at the ligands. The $d_{xz}$ and $d_{yz}$ orbitals will be destabilized the least since the electron density is directed between the ligands. **81.** a. −0.26 V; b. The stronger oxidizing agent is the species more easily reduced. From the reduction potentials, $Co^{3+}$ ($\mathscr{E}° = 1.82$ V) is a much stronger oxidizing agent than $Co(en)_3^{3+}$ ($\mathscr{E}° = -0.26$ V). c. In aqueous solution, $Co^{3+}$ forms the hydrated transition metal complex $Co(H_2O)_6^{3+}$. In both complexes, $Co(H_2O)_6^{3+}$ and $Co(en)_3^{3+}$, cobalt exists as $Co^{3+}$, which has 6 *d* electrons. Assuming a strong-field case, the *d*-orbital splitting diagram for each is



When each complex gains an electron, the electron enters the higher-energy $e_g$ orbitals. Since en is a stronger field ligand than $H_2O$, the *d*-orbital splitting is larger for $Co(en)_3^{3+}$ and it takes more energy to add an electron to $Co(en)_3^{3+}$ than to $Co(H_2O)_6^{3+}$. Therefore, it is more favorable for $Co(H_2O)_6^{3+}$ to gain an electron than for $Co(en)_3^{3+}$ to gain an electron. **83.** a. $7.1 \times 10^{-7}$ mol/L; b. $8.7 \times 10^{-3}$ mol/L; c. The presence of $NH_3$ increases the solubility of AgBr. Added $NH_3$ removes $Ag^+$ from solution by forming the complex ion $Ag(NH_3)_2^+$. As $Ag^+$ is removed, more AgBr(*s*) will dissolve to replenish the $Ag^+$ concentration. d. 0.41g; e. Added $HNO_3$ will have no effect on the AgBr(*s*) solubility in pure water. Neither $H^+$ nor $NO_3^-$ reacts with $Ag^+$ or $Br^-$ ions. $Br^-$ is the conjugate base of the strong acid HBr, so it is a terrible base. Added $H^+$ will not react with $Br^-$ to any great extent. However, added $HNO_3$ will reduce the solubility of AgBr(*s*) in the ammonia solution. $NH_3$ is a weak base ($K_b = 1.8 \times 10^{-5}$). Added $H^+$ will react with $NH_3$ to form $NH_4^+$. As $NH_3$ is removed, a smaller amount of the $Ag(NH_3)_2^+$ complex ion will form, resulting in a smaller amount of AgBr(*s*) which will dissolve.

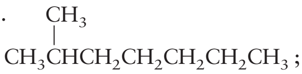
## Chapter 20

**1.** a. Thermodynamic stability: the potential energy of a particular nucleus as compared to the sum of the potential energies of its component protons and neutrons. b. Kinetic stability: the probability that a nucleus will undergo decomposition to form a different nucleus. c. Radioactive decay: a spontaneous decomposition of a nucleus to form a different nucleus. d. *β*-particle production: a decay process for radioactive nuclides where an electron is produced; the mass number remains constant and the atomic number changes. e. *α*-particle production: a common mode of decay for heavy radioactive nuclides where a helium nucleus is produced causing the atomic number and the mass number to change. f. Positron production: a mode of nuclear decay in which a particle is formed having the same mass as an electron but opposite in charge. g. Electron capture: a process in which one of the inner-orbital electrons in an atom is captured by the nucleus. h. *γ*-ray emissions: the production of high-energy photons called *γ* rays that frequently accompany nuclear decays and particle reactions. **3.** a. ${}^{51}_{24}Cr + {}^{0}_{-1}e \rightarrow {}^{51}_{23}V$; b. ${}^{131}_{53}I \rightarrow {}^{0}_{-1}e + {}^{131}_{54}Xe$; c. ${}^{32}_{15}P \rightarrow {}^{0}_{-1}e + {}^{32}_{16}S$; d. ${}^{235}_{92}U \rightarrow {}^{4}_{2}He + {}^{231}_{90}Th$ **5.** a. ${}^{68}_{31}Ga + {}^{0}_{-1}e \rightarrow {}^{68}_{30}Zn$; b. ${}^{62}_{29}Cu \rightarrow {}^{0}_{+1}e + {}^{62}_{28}Ni$; c. ${}^{212}_{87}Fr \rightarrow {}^{4}_{2}He + {}^{208}_{85}At$; d. ${}^{129}_{51}Sb \rightarrow {}^{0}_{-1}e + {}^{129}_{52}Te$ **7.** 10 *α* particles and 5 *β* particles **9.** Refer to Table 20.2 for potential radioactive decay processes. ${}^{17}F$ and ${}^{18}F$ contain too many protons or too few neutrons. Electron capture or positron production are both possible decay mechanisms that increase the neutron-to-proton ratio. *α*-particle production also increases the neutron-to-proton ratio, but it is not likely for these light nuclei. ${}^{21}F$ contains too many neutrons or too few protons. *β*-particle production lowers the neutron-to-proton ratio, so we expect ${}^{21}F$ to be a *β*-emitter. **11.** a. ${}^{249}_{98}Cf + {}^{18}_{8}O \rightarrow {}^{263}_{106}Sg + 4{}^{1}_{0}n$; b. ${}^{259}_{104}Rf$ **13.** $6.35 \times 10^{11}$ **15.** a. $6.27 \times 10^{-7}$ s$^{-1}$; b. $1.65 \times 10^{14}$ decays/s; c. 25.6 days **17.** 0.219 or 21.9% of the ${}^{90}Sr$ remains. **19.** 6.22 mg ${}^{32}P$ **21.** Plants take in $CO_2$ in the photosynthesis process, which incorporates carbon, including ${}^{14}C$, into its molecules. As long as the plant is alive, the ${}^{14}C/{}^{12}C$ ratio in the plant will equal the ratio in the atmosphere. When the plant dies, ${}^{14}C$ is not replenished, and ${}^{14}C$ decays by *β*-particle production. By measuring the ${}^{14}C$ activity today in the artifact and comparing this to the assumed ${}^{14}C$ activity when the plant died to make the artifact, an age can be determined for the artifact. The assumptions are that the ${}^{14}C$ level in the atmosphere is constant or that the ${}^{14}C$ level at the time the plant died can be calculated. A constant ${}^{14}C$ level is a pure assumption, and accounting for variation is complicated. Another problem is that some of the material must be destroyed to determine the ${}^{14}C$ level. **23.** No; from ${}^{14}C$ dating, the painting was produced (at the earliest) during the late 1800s. **25.** 1975 **27.** $3.8 \times 10^9$ yr **29.** $4.3 \times 10^6$ kg/s **31.** $1.408 \times 10^{-12}$ J/nucleon **33.** ${}^{12}C$, $1.230 \times 10^{-12}$ J/nucleon; ${}^{235}U$, $1.2154 \times 10^{-12}$ J/nucleon; Since ${}^{26}Fe$ is the most stable known nucleus, the binding energy per nucleon for ${}^{56}Fe$ ($1.41 \times 10^{-12}$ J/nucleon) will be larger than that for ${}^{12}C$ or ${}^{235}U$ (see Fig. 20.9). **35.** 26.9830 amu **37.** $-2.820 \times 10^{-12}$ J/nucleus; $-1.698 \times 10^{12}$ J/mol **39.** The Geiger-Müller tube has a certain response time. After the gas in the tube ionizes to produce a "count," some time must elapse for the gas to return to an electrically neutral state. The response of the tube levels because at high activities, radioactive particles are entering the tube faster than the tube can respond to them. **41.** Fission: Splitting of a heavy nucleus into two (or more) lighter nuclei. Fusion: Combining two light nuclei to form a heavier nucleus. The maximum binding energy per nucleon occurs at Fe. Nuclei smaller than Fe become more stable by fusing to form heavier nuclei closer in mass to Fe. Nuclei larger than Fe form more stable nuclei by splitting to form lighter nuclei closer in mass to Fe. **43.** The moderator slows the neutrons to increase the efficiency of the fission reaction. The control rods absorb neutrons to slow or halt the fission reaction. **45.** In order to sustain a nuclear chain reaction, the neutrons produced by the fission must be contained within the fissionable material so that they can go on to cause other fissions. The fissionable material must be closely packed together to ensure that neutrons are not lost to the outside. The critical mass is the mass of material in which exactly one neutron from each fission event causes another fission event so that the process sustains itself. A supercritical situation occurs when more than one neutron from each fission event causes another fission event. In this case the process rapidly escalates and the heat build-up causes a violent explosion. **47.** A nonradioactive substance can be put in equilibrium with a radioactive substance. The two materials can then be checked to see whether all the radioactivity remains in the original material or if it has been scrambled by the equilibrium. **49.** All evolved oxygen in $O_2$ comes from water and not from carbon dioxide. **51.** Some factors for the biological effects of radiation exposure are as follows: a. The energy of the radiation. The higher the energy, the more damage it can cause. b. The penetrating ability of radiation. The ability of specific radiation to penetrate human tissue and cause damage must be considered. c. The ionizing ability of the radiation. When biomolecules are ionized, their function is usually disturbed. d. The chemical properties of the radiation source. Specifically, the radioactive substance either is readily incorporated into the body or is inert chemically and passes through the body relatively quickly. $^{90}Sr$ will be incorporated into the body by replacing calcium in the bones. Once incorporated, $^{90}Sr$ can cause leukemia and bone cancer. Krypton is chemically inert so it will not be incorporated into the body. **53.** (i) and (ii) mean that Pu is not a significant threat outside the body. Our skin is sufficient to keep out the $\alpha$ particles. If Pu gets inside the body, it is easily oxidized to $Pu^{4+}$ (iv), which is chemically similar to $Fe^{3+}$ (iii). Thus $Pu^{4+}$ will concentrate in tissues where $Fe^{3+}$ is found, including the bone marrow, where red blood cells are produced. Once inside the body, $\alpha$ particles cause considerable damage. **55.** ~900 g $^{235}U$ (assuming that all $^{235}U$ present undergoes fission) **57.** $\frac{1}{9}$ of the $NO_2$ is $N^{16}O_2$, $\frac{4}{9}$ of the $NO_2$ is $N^{18}O_2$, and $\frac{4}{9}$ of the $NO_2$ is $N^{16}O^{18}O$. **59.** Assuming that (1) the radionuclide is long-lived enough that no significant decay occurs during the time of the experiment, and (2) the total activity is uniformly distributed only in the rat's blood; $V = 10.$ mL. **61.** $5 \times 10^9$ K **63.** $4.3 \times 10^{-29}$ **65.** a. $^{235}UF_6$; At constant temperature, average velocity is proportional to $(1/M)^{1/2}$. Therefore, the lighter the molecule, the faster the average velocity. b. In theory, 345 stages (steps) are required. c. $^{235}U/^{238}U = 1.01 \times 10^{-2}$

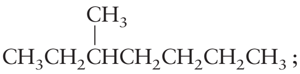
## Chapter 21

**1.** A hydrocarbon is a compound composed of only carbon and hydrogen. A saturated hydrocarbon has only carbon–carbon single bonds in the molecule. An unsaturated hydrocarbon has one or more carbon–carbon multiple bonds but may also contain carbon–carbon single bonds. A normal hydrocarbon has one chain of consecutively bonded carbon atoms. A branched hydrocarbon has at least one carbon atom not bonded to the end carbon of a chain of consecutively bonded carbon atoms. Instead, at least one carbon atom forms a bond to an inner carbon atom in the chain of consecutively bonded carbon atoms. **3.** In order to form, cyclopropane and cyclobutane are forced to form bond angles much smaller than the preferred 109.5° bond angles. Cyclopropane and cyclobutane easily react in order to obtain the preferred 109.5° bond angles.

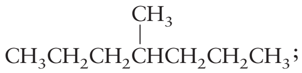
**5.** a.


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_2CH_3$ ;

2-Methylheptane

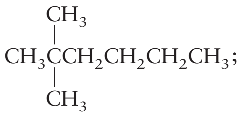

$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$ ;

3-Methylheptane

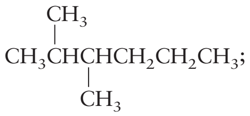

$CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$;

4-Methylheptane

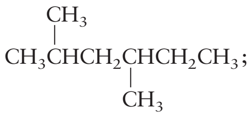
b.


$CH_3\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_2CH_2CH_2CH_3$;

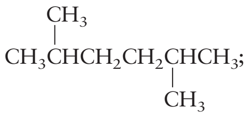
2,2-Dimethylhexane


$CH_3\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$;

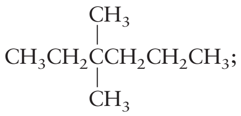
2,3-Dimethylhexane


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$ ;

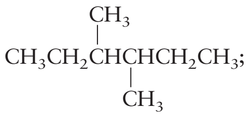
2,4-Dimethylhexane


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$;

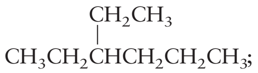
2,5-Dimethylhexane


$CH_3CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}CH_2CH_2CH_3$;

3,3-Dimethylhexane

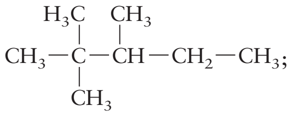

$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$;

3,4-Dimethylhexane

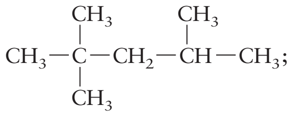

$CH_3CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$;

3-Ethylhexane

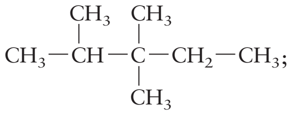
c.


$CH_3-\overset{H_3C}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_3$;

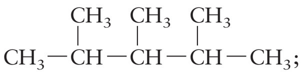
2,2,3-Trimethylpentane


$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_3$;

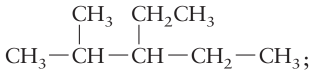
2,2,4-Trimethylpentane


$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-CH_3$;

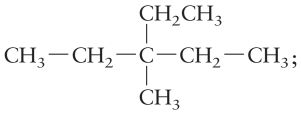
2,3,3-Trimethylpentane


$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_3}{\overset{|}{C}}H-CH_3$;

2,3,4-Trimethylpentane

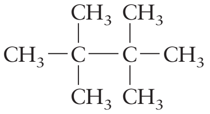

$CH_3-\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2CH_3}{\overset{|}{C}}H-CH_2-CH_3$;

3-Ethyl-2-methylpentane


$CH_3-CH_2-\overset{CH_2CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-CH_3$;

3-Ethyl-3-methylpentane

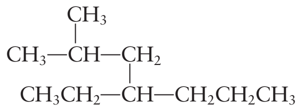
d.


$CH_3-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$

2,2,3,3-Tetramethylbutane

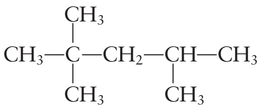
**7.** London dispersion (LD) forces are the primary intermolecular forces exhibited by hydrocarbons. The strength of the LD forces depends on the surface area contact among neighboring molecules. As branching increases, there is less surface area contact among neighboring molecules, leading to weaker LD forces and lower boiling points.

**9.** a.



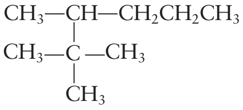
$CH_3CH_2-\overset{\overset{\displaystyle CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2}{|}}{CH}-CH_2CH_2CH_3$

b.



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

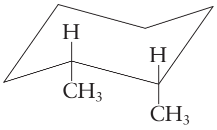
c.



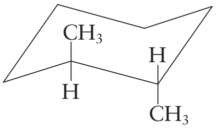
$CH_3-\underset{\underset{\displaystyle CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3}{|}}{CH}-CH_2CH_2CH_3$

d. 4-ethyl-2-methylheptane, 2,2,3-trimethylhexane **11.** a. 2,2,4-trimethylhexane; b. 5-methylnonane; c. 2,2,4,4-tetramethylpentane; d. 3-ethyl-3-methyloctane **13.** a. 1-butene; b. 2-methyl-2-butene; c. 2,5-dimethyl-3-heptene; d. 2,3-dimethyl-1-pentene; e. 1-ethyl-3-methylcyclopentene; f. 4-ethyl-3-methylcyclopentene; g. 4-methyl-2-pentyne **15.** a. 1,3-dichlorobutane; b. 1,1,1-trichlorobutane; c. 2,3-dichloro-2,4-dimethylhexane; d. 1,2-difluoroethane; e. 3-iodo-1-butene; f. 2-bromotoluene (or 1-bromo-2-methylbenzene); g. 1-bromo-2-methylcyclohexane; h. 4-bromo-3-methylcyclohexene **17.** isopropylbenzene or 2-phenylpropane **19.** All six of these compounds are the same. They differ from each other only by rotations about one or more carbon–carbon single bonds. Only one isomer of $C_7H_{16}$ is present in all of these names, 3-methylhexane. **21.** Compounds c and f exhibit *cis–trans* isomerism. See Exercise 25 for an example of *cis–trans* isomerism in ring compounds. **23.** a. Compounds ii and iii are identical compounds, so they would have the same physical properties. b. Compound i is a *trans* isomer because the bulkiest groups bonded to the carbon atoms in the $C_3{=}C_4$ double bond are as far apart as possible. c. Compound iv does not have carbon atoms in a double bond that each have two different groups attached. Compound iv does not exhibit *cis–trans* isomerism.

**25.**

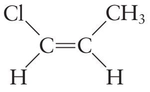


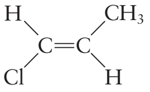
*cis*

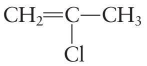


*trans*

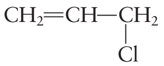
**27.**





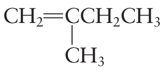


$CH_2{=}\underset{\underset{\displaystyle Cl}{|}}{C}-CH_3$

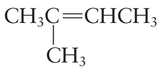


$CH_2{=}CH-\underset{\underset{\displaystyle Cl}{|}}{CH_2}$

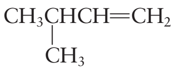
**29.** $CH_2{=}CHCH_2CH_2CH_3$ $CH_3CH{=}CHCH_2CH_3$



$CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2CH_3$

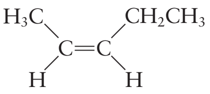


$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_3$

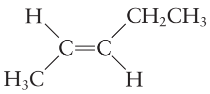


$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH{=}CH_2$

Only 2-pentene exhibits *cis–trans* isomerism. The isomers are



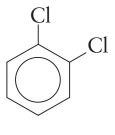
*cis*



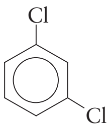
*trans*

**31.** a. *cis*-1-bromo-1-propene; b. *cis*-4-ethyl-3-methyl-3-heptene; c. *trans*-1,4-diiodo-2-propyl-1-pentene

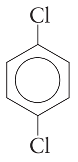
**33.** a.



*ortho*



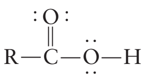
*meta*



*para*

b. There are three trichlorobenzenes (1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene). c. The *meta* isomer will be very difficult to synthesize. d. 1,3,5-trichlorobenzene will be the most difficult to synthesize since all Cl groups are *meta* to each other in this compound.

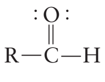
**35.** Carboxylic acid



$R-\overset{\overset{\displaystyle :\!O\!:}{\|}}{C}-\underset{..}{\overset{..}{O}}-H$

RCOOH

Aldehyde

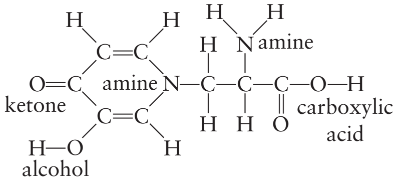


$R-\overset{\overset{\displaystyle :\!O\!:}{\|}}{C}-H$

RCHO

The R designation refers to the rest of the organic molecule beyond the specific functional group indicated in the formula. The R group may sometimes be a hydrogen, but is usually a hydrocarbon fragment. The major point in the R group designation is that if the R group is an organic fragment, then the first atom in the R group is a carbon atom. What the R group has after the first carbon is not important to the functional group designation. **37.** a. ketone; b. aldehyde; c. carboxylic acid; d. amine

**39.** a.

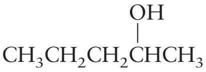


b. 5 carbons in ring and the carbon in $-CO_2H$: $sp^2$, the other two carbons: $sp^3$; c. 24 $\sigma$ bonds, 4 $\pi$ bonds **41.** a. 3-chloro-1-butanol, primary alcohol; b. 3-methyl-3-hexanol, tertiary alcohol; c. 2-methylcyclopentanol, secondary alcohol

**43.**

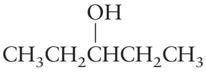
$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{CH_2}$

1-Pentanol



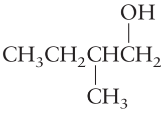
$CH_3CH_2CH_2\overset{\overset{\displaystyle OH}{|}}{CH}CH_3$

2-Pentanol



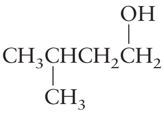
$CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{CH}CH_2CH_3$

3-Pentanol



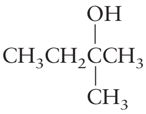
$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}\overset{\overset{\displaystyle OH}{|}}{CH_2}$

2-Methyl-1-butanol



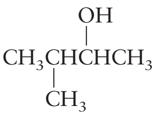
$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2\overset{\overset{\displaystyle OH}{|}}{CH_2}$

3-Methyl-1-butanol



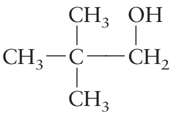
$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}CH_3$

2-Methyl-2-butanol



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}\overset{\overset{\displaystyle OH}{|}}{CH}CH_3$

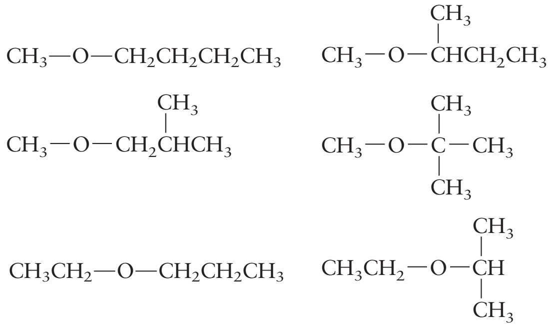
3-Methyl-2-butanol



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle OH}{|}}{CH_2}$

2,2-Dimethyl-1-propanol

There are six isomeric ethers with the formula $C_5H_{12}O$. The structures follow.



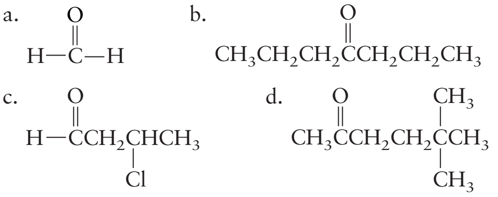
$CH_3-O-CH_2CH_2CH_2CH_3$ $\quad CH_3-O-\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

$CH_3-O-CH_2\overset{CH_3}{\overset{|}{C}}HCH_3$ $\quad CH_3-O-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

$CH_3CH_2-O-CH_2CH_2CH_3$ $\quad CH_3CH_2-O-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}H$

**45.** a. 4,5-dichloro-3-hexanone; b. 2,3-dimethylpentanal; c. 3-methylbenzaldehyde or *m*-methylbenzaldehyde

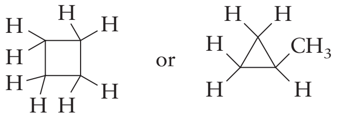
**47.**



a. $H-\overset{O}{\overset{\|}{C}}-H$ b. $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

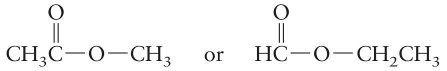
c. $H-\overset{O}{\overset{\|}{C}}CH_2\underset{Cl}{\underset{|}{C}}HCH_3$ d. $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_3$

**49.** a.



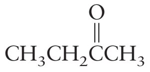
or

b.



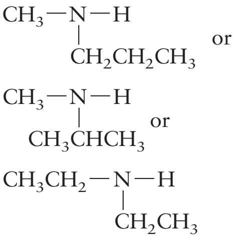
$CH_3\overset{O}{\overset{\|}{C}}-O-CH_3$ or $H\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

c.



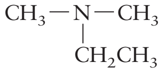
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$

d.



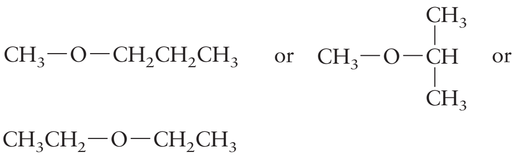
$CH_3-\underset{CH_2CH_2CH_3}{\underset{|}{N}}-H$ or $CH_3-\underset{CH_3CHCH_3}{\underset{|}{N}}-H$ or $CH_3CH_2-\underset{CH_2CH_3}{\underset{|}{N}}-H$

e.



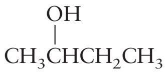
$CH_3-\underset{CH_2CH_3}{\underset{|}{N}}-CH_3$

f.



$CH_3-O-CH_2CH_2CH_3$ or $CH_3-O-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}H$ or $CH_3CH_2-O-CH_2CH_3$

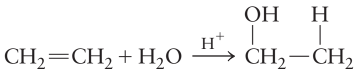
g.



$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$

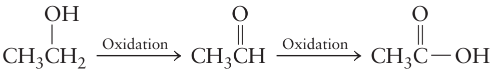
**51.** a. 2-Chloro-2-butyne would have 5 bonds to the second carbon. Carbon never expands its octet. b. 2-Methyl-2-propanone would have 5 bonds to the second carbon. c. Carbon-1 in 1,1-dimethylbenzene would have 5 bonds. d. You cannot have an aldehyde functional group bonded to a middle carbon in a chain. Aldehyde groups can only be at the beginning and/or the end of a chain of carbon atoms. e. You cannot have a carboxylic acid group bonded to a middle carbon in a chain. Carboxylic groups must be at the beginning and/or the end of a chain of carbon atoms. f. In cyclobutanol, the 1 and 5 positions refer to the same carbon atom. 5,5-Dibromo-1-cyclobutanol would have five bonds to carbon-1. This is impossible; carbon never expands its octet. **53.** Substitution: An atom or group is replaced by another atom or group; e.g., H in benzene is replaced by Cl. $C_6H_6 + Cl_2 \xrightarrow{\text{Catalyst}} C_6H_5Cl + HCl$ Addition: Atoms or groups are added to a molecule; e.g., $Cl_2$ adds to ethene. $CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2Cl-CH_2Cl$

**55.** a.



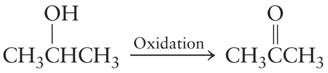
$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} \overset{OH}{\overset{|}{C}}H_2-\overset{H}{\overset{|}{C}}H_2$

b.



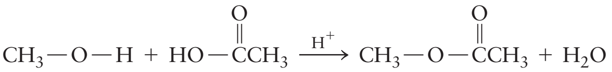
$CH_3\overset{OH}{\overset{|}{C}}H_2 \xrightarrow{\text{Oxidation}} CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{\text{Oxidation}} CH_3\overset{O}{\overset{\|}{C}}-OH$

c.



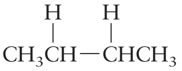
$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{\text{Oxidation}} CH_3\overset{O}{\overset{\|}{C}}CH_3$

d.



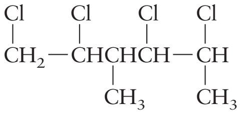
$CH_3-O-H + HO-\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{H^+} CH_3-O-\overset{O}{\overset{\|}{C}}CH_3 + H_2O$

**57.** a.



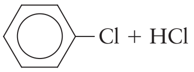
$CH_3\overset{H}{\overset{|}{C}}H-\overset{H}{\overset{|}{C}}HCH_3$

b.



$\overset{Cl}{\overset{|}{C}}H_2-\overset{Cl}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}H\overset{Cl}{\overset{|}{C}}H-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}H$

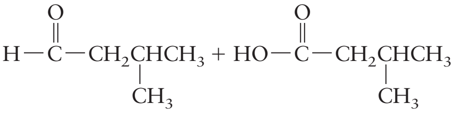
c.



d. $C_4H_8(g) + 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(g)$

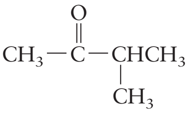
**59.** When $CH_2{=}CH_2$ reacts with HCl, there is only one possible product, chloroethane. When $Cl_2$ is reacted with $CH_3CH_3$ (in the presence of light), there are six possible products because any number of the six hydrogens in ethane can be substituted for by Cl. The light-catalyzed substitution reaction is very difficult to control; hence it is not a very efficient method of producing monochlorinated alkanes.

**61.** a.



$H-\overset{O}{\overset{\|}{C}}-CH_2\underset{CH_3}{\underset{|}{C}}HCH_3 + HO-\overset{O}{\overset{\|}{C}}-CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$

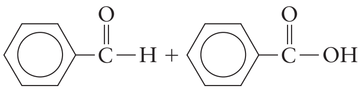
b.



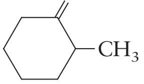
$CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{C}}HCH_3$

c. no reaction

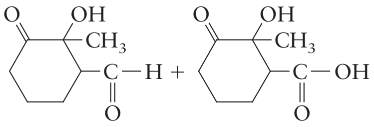
d.



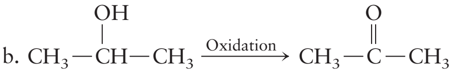
e.



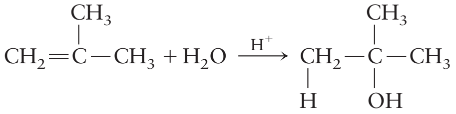
f.



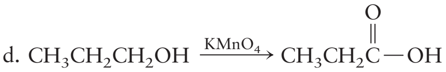
**63.** The products of the reactions with excess $KMnO_4$ are 2-propanone and propanoic acid. **65.** a. $CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$ (Addition reaction of $Br_2$ with propene)

b.

$$\mathrm{CH_3{-}\overset{OH}{\overset{|}{C}}H{-}CH_3 \xrightarrow{\text{Oxidation}} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

Oxidation of 2-propanol yields acetone (2-propanone).

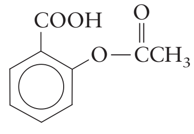
c.

$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 + H_2O \xrightarrow{H^+} \underset{H}{\underset{|}{CH_2}}{-}\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}CH_3}$$

Addition of $H_2O$ to 2-methylpropene would yield *tert*-butyl alcohol (2-methyl-2-propanol) as the major product.

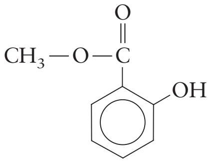
d.

$$\mathrm{CH_3CH_2CH_2OH \xrightarrow{KMnO_4} CH_3CH_2\overset{O}{\overset{\|}{C}}{-}OH}$$

Oxidation of 1-propanol would eventually yield propanoic acid. Propanal is produced first in this reaction and is then oxidized to propanoic acid.

**67.**

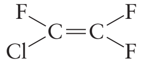


Acetylsalicylic acid (aspirin)

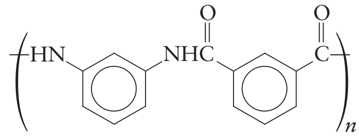


Methyl salicylate

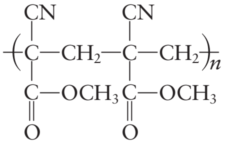
**69.** a. Addition polymer: a polymer that forms by adding monomer units together (usually by reacting double bonds). Teflon, polyvinyl chloride, and polyethylene are examples of addition polymers.
b. Condensation polymer: a polymer that forms when two monomers combine by eliminating a small molecule (usually $H_2O$ or HCl). Nylon and Dacron are examples of condensation polymers.
c. Copolymer: a polymer formed from more than one type of monomer. Nylon and Dacron are copolymers. d. Homopolymer: a polymer formed from the polymerization of only one type of monomer. Polyethylene, Teflon, and polystyrene are examples of homopolymers. e. Polyester: a condensation polymer whose monomers link together by formation of the ester functional group. Dacron is a polyester. f. Polyamide: a condensation polymer whose monomers link together by formation of the amide functional group. Nylon is a polyamide as are proteins in the human body.
**71.** a. A polyester forms when an alcohol functional group reacts with a carboxylic acid functional group. The monomer for a homopolymer polyester must have an alcohol functional group and a carboxylic acid functional group present in the structure.
b. A polyamide forms when an amine functional group reacts with a carboxylic acid functional group. For a copolymer polyamide, one monomer would have at least two amine functional groups present, and the other monomer would have at least two carboxylic acid functional groups present. For polymerization to occur, each monomer must have two reactive functional groups present.
c. To form a typical addition polymer, a carbon–carbon double bond must be present. To form a polyester, the monomer would need the alcohol and carboxylic acid functional groups present. To form a polyamide, the monomer would need the amine and carboxylic acid functional groups present. The two possibilities are for the monomer to have a carbon–carbon double bond, an alcohol functional group, and a carboxylic acid functional group present or to have a carbon–carbon double bond, an amine functional group, and a carboxylic acid functional group present.

**73.**


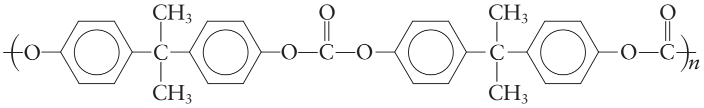
**75.** a.


b. Repeating unit:


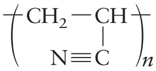
The two polymers differ in the substitution pattern on the benzene rings. The Kevlar chain is straighter, and there is more efficient hydrogen bonding between Kevlar chains than between Nomex chains.

**77.**

$$\mathrm{\left(\overset{CN}{\overset{|}{C}}\underset{\underset{O}{\overset{\|}{C}}{-}OCH_3}{\underset{|}{}}{-}CH_2{-}\overset{CN}{\overset{|}{C}}\underset{\underset{O}{\overset{\|}{C}}{-}OCH_3}{\underset{|}{}}{-}CH_2\right)_n}$$

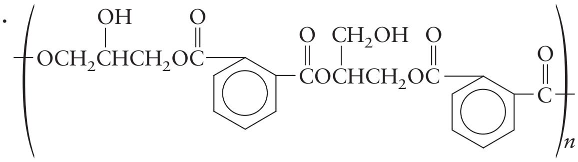
**79.** Divinylbenzene (a crosslinking agent) has two reactive double bonds, which are both reacted when divinylbenzene inserts itself into two adjacent polymer chains. The chains cannot move past each other because the crosslinks bond adjacent polymer chains together making the polymer more rigid.

**81.** a.


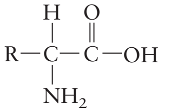
b. Condensation; HCl is eliminated when the polymer bonds form.

**83.** Polyacrylonitrile:

$$\mathrm{\left(CH_2{-}\underset{N\equiv C}{\underset{|}{CH}}\right)_n}$$

The CN triple bond is very strong and will not easily break in the combustion process. A likely combustion product is the toxic gas hydrogen cyanide [$HCN(g)$].

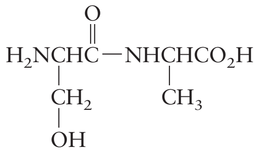
**85.**


Two linkages are possible with glycerol. A possible repeating unit with both types of linkages is shown above. With either linkage, there are free OH groups on the polymer chains. These unreacted OH groups on adjacent polymer chains can react with the acid groups of phthalic acid to form crosslinks between various polymer chains.

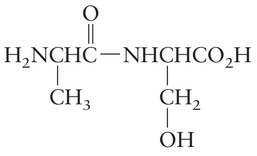
**87.**

$$\mathrm{R{-}\overset{H}{\overset{|}{\underset{NH_2}{\underset{|}{C}}}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

Hydrophilic (water-loving) and hydrophobic (water-fearing) refer to the polarity of the R groups. When the R group consists of a polar group, then the amino acid is hydrophilic. When the R group consists of a nonpolar group, then the amino acid is hydrophobic.

**89.** Denaturation changes the three-dimensional structure of a protein. Once the structure is affected, the function of the protein will also be affected. **91.** a. serine, tyrosine, and threonine; b. aspartic acid and glutamic acid; c. histidine, lysine, arginine, and tryptophan; d. glutamine and asparagine **93.** a. aspartic acid and phenylalanine; b. Aspartame contains the methyl ester of phenylalanine. This ester can hydrolyze to form methanol, $R—CO_2CH_3 + H_2O \rightleftharpoons RCO_2H + CH_3OH$.

**95.**

$\mathrm{H_2N\underset{\underset{OH}{|}}{\underset{CH_2}{\underset{|}{CH}}}\overset{O}{\overset{\|}{C}}-NH\underset{CH_3}{\underset{|}{CH}}CO_2H}$

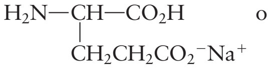
ser-ala


$\mathrm{H_2N\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}-NH\underset{\underset{OH}{|}}{\underset{CH_2}{\underset{|}{CH}}}CO_2H}$

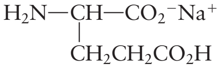
ala-ser

**97.** a. Six tetrapeptides are possible. From $NH_2$ to $CO_2H$ end:
phe-phe-gly-gly, gly-gly-phe-phe, gly-phe-phe-gly,
phe-gly-gly-phe, phe-gly-phe-gly, gly-phe-gly-phe;
b. Twelve tetrapeptides are possible. From $NH_2$ to $CO_2H$ end:
phe-phe-gly-ala, phe-phe-ala-gly, phe-gly-phe-ala,
phe-gly-ala-phe, phe-ala-phe-gly, phe-ala-gly-phe,
gly-phe-phe-ala, gly-phe-ala-phe, gly-ala-phe-phe,
ala-phe-phe-gly, ala-phe-gly-phe, ala-gly-phe-phe

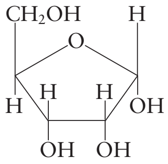
**99.** a. covalent; b. hydrogen bonding; c. ionic; d. London dispersion **101.** Glutamic acid: $R = —CH_2CH_2CO_2H$; Valine: $R = —CH(CH_3)_2$; A polar side chain is replaced by a nonpolar side chain. This could affect the tertiary structure of hemoglobin and the ability of hemoglobin to bind oxygen.

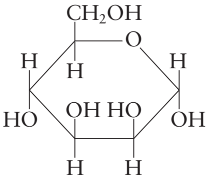
**103.**

$\mathrm{H_2N—\underset{CH_2CH_2CO_2^-Na^+}{\underset{|}{CH}}—CO_2H}$

or

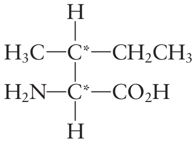

$\mathrm{H_2N—\underset{CH_2CH_2CO_2H}{\underset{|}{CH}}—CO_2^-Na^+}$

The first structure is MSG, which is impossible for you to predict.

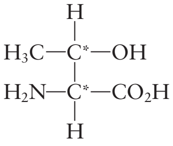
**105.**

D-Ribose


D-Mannose

**107.** The aldohexoses contain 6 carbons and the aldehyde functional group. Glucose, mannose, and galactose are aldohexoses. Ribose and arabinose are aldopentoses since they contain 5 carbons with the aldehyde functional group. The ketohexose (6 carbons + ketone functional group) is fructose, and the ketopentose (5 carbons + ketone functional group) is ribulose. **109.** A disaccharide is a carbohydrate formed by bonding two monosaccharides (simple sugars) together. In sucrose, the simple sugars are glucose and fructose, and the bond formed between these two monosaccharides is called a glycoside linkage. **111.** The $\alpha$ and $\beta$ forms of glucose differ in the orientation of a hydroxyl group on one specific carbon in the cyclic forms (see Fig. 21.31). Starch is a polymer composed of only $\alpha$-D-glucose, and cellulose is a polymer composed of only $\beta$-D-glucose.

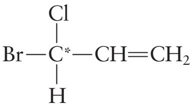
**113.**

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H_3C—C^*—CH_2CH_3} \\ | \\ \mathrm{H_2N—C^*—CO_2H} \\ | \\ \mathrm{H} \end{array}$$

Isoleucine

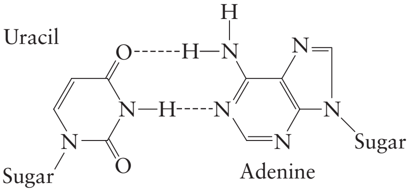

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H_3C—C^*—OH} \\ | \\ \mathrm{H_2N—C^*—CO_2H} \\ | \\ \mathrm{H} \end{array}$$

Threonine

The chiral carbons are marked with asterisks.

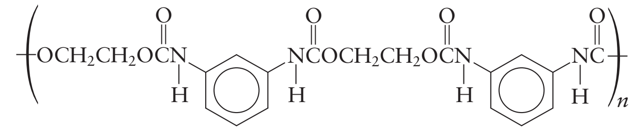
**115.**

$\mathrm{Br—\underset{H}{\underset{|}{\overset{Cl}{\overset{|}{C^*}}}}—CH{=}CH_2}$

is optically active. The chiral carbon is marked with an asterisk. **117.** They all contain nitrogen atoms with lone pairs of electrons. **119.** C-C-A-G-A-T-A-T-G **121.** Uracil will hydrogen-bond to adenine.

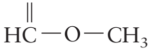


**123.** a. glu: CTT, CTC; val: CAA, CAG, CAT, CAC; met: TAC; trp: ACC; phe: AAA, AAG; asp: CTA, CTG; b. ACC-CTT-AAA-TAC;
or or
CTC AAG
c. Due to glu and phe, there is a possibility of four different DNA sequences; d. met-asp-phe; e. TAC-CTA-AAG; TAC-CTA-AAA; TAC-CTG-AAA **125.** A deletion may change the entire code for a protein, thus giving an entirely different sequence of amino acids. A substitution will change only one single amino acid in a protein. **127.** $CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH + OH^- \rightarrow CH_3-(CH_2)_6-COO^- + H_2O$; Octanoic acid is more soluble in 1 $M$ NaOH. Added $OH^-$ will remove the acidic proton from octanoic acid, creating a charged species. As is the case with any substance with an overall charge, solubility in water increases. When morphine is reacted with $H^+$, the amine group is protonated, creating a positive charge on morphine ($R_3N + H^+ \rightarrow R_3\overset{+}{N}H$). By treating morphine with HCl, an ionic compound results that is more soluble in water and in the bloodstream than is the neutral covalent form of morphine. **129.** To substitute for the benzene ring hydrogens, an iron(III) catalyst must be present. Without this special iron catalyst, the benzene ring hydrogens are unreactive. To substitute for an alkane hydrogen, light must be present. For toluene, the light-catalyzed reaction substitutes a chlorine for a hydrogen in the methyl group attached to the benzene ring. **131.** 1-butene **133.** a. The bond angles in the ring are about 60°. VSEPR predicts bond angles close to 109°. The bonding electrons are closer together than they prefer, resulting in strong electron–electron repulsions. Thus ethylene oxide is unstable (reactive). b. The ring opens up during polymerization; monomers link together through the formation of O—C bonds.

$$\left(\!-O—CH_2CH_2—O—CH_2CH_2—O—CH_2CH_2\!-\right)_n$$

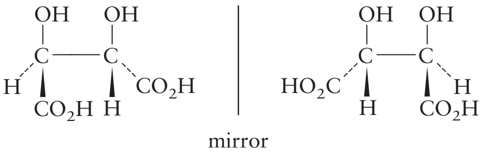
**135.**


**137.** $n$-hexane, 69°C; pentanal, 103°C; 1-pentanol, 137°C; butanoic acid, 164°C; the strength of the intermolecular forces increases when going from $n$-hexane to pentanal to 1-pentanol to butanoic acid. Hence the boiling points will increase in the same order.

**139.**

$\mathrm{H\overset{O}{\overset{\|}{C}}—O—CH_3}$

**141.** a. The longest chain is 4 carbons long. The correct name is 2-methylbutane. b. The longest chain is 7 carbons long, and we would start the numbering system at the other end for lowest possible numbers. The correct name is 3-iodo-3-methylheptane. c. This compound cannot exhibit *cis–trans* isomerism because one of the double-bonded carbons has the same two groups ($CH_3$) attached. The numbering system should also start at the other end to give the double bond the lowest possible number. 2-Methyl-2-pentene is correct. d. The OH functional group gets the lowest number. 3-Bromo-2-butanol is correct. **143.** For the reaction, we break a P—O and O—H bond and form a P—O and O—H bond, so $\Delta H \approx 0$. $\Delta S$ for this process should be negative since two molecules are reacting to form one molecule (positional probability decreases). Thus $\Delta G$ should be positive and the reaction is not expected to be spontaneous. **145.** a. No; the mirror image is superimposable.

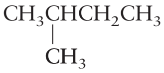
b.



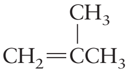
These two forms of tartaric acid are nonsuperimposable.

**147.** pH = 6.07 = isoelectric point **149.** 0.11% **151.** $C_2H_6$; ethane

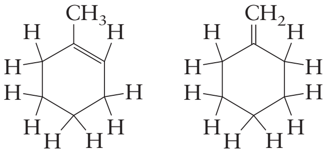
**153.** a.


$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$

b.

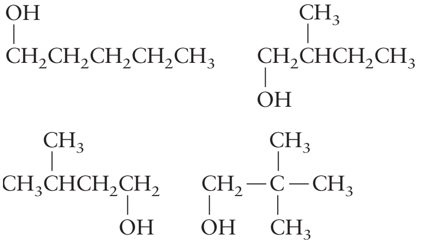

$CH_2{=}\overset{\substack{CH_3\\ |}}{C}CH_3$

c.



d. $CH_2{=}CHCH_3$

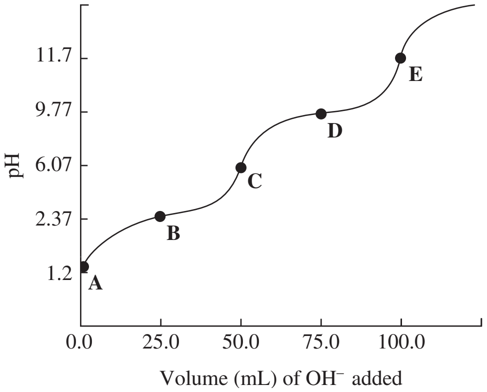
e.


$\overset{\substack{OH\\ |}}{C}H_2CH_2CH_2CH_2CH_3$ $\quad \underset{\substack{|\\ OH}}{C}H_2\overset{\substack{CH_3\\ |}}{C}HCH_2CH_3$

$CH_3\overset{\substack{CH_3\\ |}}{C}HCH_2\underset{\substack{|\\ OH}}{C}H_2$ $\quad \underset{\substack{|\\ OH}}{CH_2}-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_3$

**155.** a. 25.0 mL, 2.37; 50.0 mL, 6.07; 75.0 mL, 9.77

b.



The major amino acid species present are:

point A (0.0 mL $OH^-$): $H_3\overset{+}{N}CH_2COOH$

point B (25.0 mL $OH^-$): $H_3\overset{+}{N}CH_2COOH$, $H_3\overset{+}{N}CH_2COO^-$

point C (50.0 mL $OH^-$): $H_3\overset{+}{N}CH_2COO^-$

point D (75.0 mL $OH^-$): $H_3\overset{+}{N}CH_2COO^-$, $H_2NCH_2COO^-$

point E (100.0 mL $OH^-$): $H_2NCH_2COO^-$

c. 6.07; d. $+\frac{1}{2}$, 2.37; $-\frac{1}{2}$, 9.77