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 1

17. A law summarizes what happens, e.g., law of conservation of mass in a chemical reaction or the ideal gas law, $PV = nRT$. A theory (model) is an attempt to explain why something happens. Dalton's atomic theory explains why mass is conserved in a chemical reaction. The kinetic molecular theory explains why pressure and volume are inversely related at constant temperature and moles of gas. **19.** A qualitative observation expresses what makes something what it is; it does not involve a number; e.g., the air we breathe is a mixture of gases, ice is less dense than water, rotten milk stinks. The SI units are mass in grams, length in meters, and volume in the derived units of m^3. The assumed uncertainty in a number is ± 1 in the last significant figure of the number. The precision of an instrument is related to the number of significant figures associated with an experimental reading on that instrument. Different instruments for measuring mass, length, or volume have varying degrees of precision. Some instruments only give a few significant figures for a measurement while others will give more significant figures. **21.** Significant figures are the digits we associate with a number. They contain all of the certain digits and the first uncertain digit (the first estimated digit). What follows is one thousand indicated to varying numbers of significant figures: 1000 or 1×10^3 (1 S.F.); 1.0×10^3 (2 S.F.); 1.00×10^3 (3 S.F.); 1000. or 1.000×10^3 (4 S.F.). To perform the calculation, the addition/subtraction significant rule is applied to $1.5 - 1.0$. The result of this is the one significant figure answer of 0.5. Next, the multiplication/division rule is applied to 0.5/0.50. A one significant number divided by a two significant number yields an answer with one significant figure (answer = 1). **23.** The slope of the T_F vs. T_C plot is 1.8 (= 9/5) and the y-intercept is 32°F. The slope of T_C vs. T_K plot is one and the y-intercept is −273°C. **25. a.** exact; **b.** inexact; **c.** exact; **d.** inexact **27. a.** 3; **b.** 4; **c.** 4; **d.** 1; **e.** 7; **f.** 1; **g.** 3; **h.** 3 **29. a.** 3.42×10^{-4}; **b.** 1.034×10^4; **c.** 1.7992×10^1; **d.** 3.37×10^5 **31. a.** 641.0; **b.** 1.327; **c.** 77.34; **d.** 3215; **e.** 0.420 **33. a.** 188.1; **b.** 12.; **c.** 4×10^{-7}; **d.** 6.3×10^{-26}; **e.** 4.9; Uncertainty appears in the first decimal place. The average of several numbers can be only as precise as the least precise number. Averages can be exceptions to the significant figure rules. **f.** 0.22 **35. a.** 84.3 mm; **b.** 2.41 m; **c.** 2.945×10^{-5} cm; **d.** 14.45 km; **e.** 2.353×10^5 mm; **f.** 0.9033 μm **37. a.** 8 lb and 9.9 oz; $20\frac{1}{4}$ in; **b.** 4.0×10^4 km, 4.0×10^7 m; **c.** 1.2×10^{-2} m^3, 12 L, 730 in^3, 0.42 ft^3 **39. a.** 4.00×10^2 rods; 10.0 furlongs; 2.01×10^3 m; 2.01 km; **b.** 8390.0 rods; 209.75 furlongs; 42,195 m; 42.195 km **41. a.** 0.373 kg, 0.822 lb; **b.** 31.1 g, 156 carats; **c.** 19.3 cm^3 **43.** 2.95×10^9 knots; 3.36×10^9 mi/h **45.** To the proper number of significant figures, the car is traveling at 40. mi/h, which would not violate the speed limit. **47.** 0.68 Canadian/L **49. a.** −273°C, 0 K; **b.** −40.°C, 233 K; **c.** 20.°C, 293 K; **d.** 4×10^7 °C, 4×10^7 K **51. a.** 312.4 K; 102.6°F; **b.** 248 K; −13°F; **c.** 0 K; −459°F; **d.** 1074 K; 1470°F **53.** It will float (density = 0.80 g/cm^3). **55.** 1×10^6 g/cm^3 **57.** 0.28 cm^3 **59.** 3.8 g/cm^3 **61. a.** Both are the same mass; **b.** 1.0 mL mercury; **c.** Both are the same mass; **d.** 1.0 L benzene **63. a.** 1.0 kg feather; **b.** 100 g water; **c.** same **65.** 2.77 cm **67. a.** Picture iv represents a gaseous compound. Pictures ii and iii also contain a gaseous compound but have a gaseous element present. **b.** Picture vi represents a mixture of two elemental gases. **c.** Picture v represents a solid element. **d.** Pictures ii and iii both represent a mixture of a gaseous element and a gaseous compound. **69. a.** heterogeneous; **b.** homogeneous (hopefully); **c.** homogeneous; **d.** homogeneous (hopefully); **e.** heterogeneous; **f.** heterogeneous **71. a.** physical; **b.** chemical; **c.** physical; **d.** chemical **73.** 24 capsules **75.** 1.0×10^5 bags **77.** 56.56°C **79. a.** Volume × density = mass; the orange block is more dense. Since mass (orange) > mass (blue) and volume (orange) < volume (blue), then the density of the orange block must be greater to account for the larger mass of the orange block. **b.** Which block is more dense cannot be determined. Since mass (orange) > mass (blue) and volume (orange) > volume (blue), then the density of the orange block may or may not be larger than the blue block. If the blue block is more dense, then its density cannot be so large that the mass of the smaller blue block becomes larger than the orange block mass. **c.** The blue block is more dense. Since mass (blue) = mass (orange) and volume (blue) < volume (orange), then the density of the blue block must be larger to equate the masses. **d.** The blue block is more dense. Since mass (blue) > mass (orange) and the volumes are equal, then the density of the blue block must be larger to give the blue block the larger mass. **81.** 8.5 ± 0.5 g/cm^3 **83. a.** 2%; **b.** 2.2%; **c.** 0.2% **85.** d_{old} = 8.8 g/cm^3, d_{new} = 7.17 g/cm^3; $d_{new}/d_{old} = \text{mass}_{new}/\text{mass}_{old} = 0.81$; The difference in mass is accounted for by the difference in the alloy used (if the assumptions are correct). **87.** 7.0% **89. a.** One possibility is that rope B is not attached to anything and rope A and rope C are connected via a pair of pulleys and/or gears; **b.** Try to pull rope B out of the box. Measure the distance moved by C for a given movement of A. Hold either A or C firmly while pulling on the other rope. **91.** \$160/person; 3.20×10^3 nickels/person; 85.6 £/person **93.** 200.0°F = 93.33°C; −100.0°F = −73.3°C; 93.33°C = 366.48 K; −73.3°C = 199.9 K; difference of temperatures in °C = 166.6; difference of temperatures in K = 166.6; No, there is not a difference of 300 degrees in °C or K.

Chapter 2

15. A compound will always contain the same numbers (and types) of atoms. A given amount of hydrogen will react only with a specific amount of oxygen. Any excess oxygen will remain unreacted. **17.** Law of conservation of mass: mass is neither created nor destroyed. The mass before a chemical reaction always equals the mass after a chemical reaction. Law of definite proportion: a given compound always contains exactly the same proportion of elements by mass. Water is always 1 g H for every 8 g oxygen. Law of multiple proportions: When two elements form a series of compounds, the ratios of the mass of the second element that combine with one gram of the first element can always be reduced to small whole numbers. For CO_2 and CO discussed in section 2.2, the mass ratios of oxygen that react with 1 g of carbon in each compound are in a 2 : 1 ratio. **19.** J. J. Thomson's study of cathode-ray tubes led him to postulate the existence of negatively charged particles which we now call electrons. Ernest Rutherford and his alpha bombardment of metal foil experiments led him to postulate the nuclear atom—an atom with a tiny dense center of positive charge (the nucleus) with electrons moving about the nucleus at relatively large distances away; the distance is so large that an atom is mostly empty space. **21.** The number and arrangement of electrons in an atom determines how the atom will react with other atoms. The electrons determine the chemical properties of an atom. The number of neutrons present determine the isotope identity. **23.** Statements a and b are true. Counting over in the periodic table, element 118 will be the next noble gas (a nonmetal). For statement c, hydrogen has mostly nonmetallic properties. For statement d, a family of elements is also known as a group of elements. For statement e, two items are incorrect. When a metal reacts with a nonmetal, an ionic compound is produced and the formula of the compound would be AX_2 (since alkaline earth metals for +2 ions and halogens form −1 ions in ionic compounds). The correct statement would be: When alkaline earth metal, A reacts with a halogen, X, the formula of the ionic compound formed should be AX_2. **25. a.** The composition of a substance depends on the number of atoms of each element making up the compound (depends on the formula of the compound) and not on the composition of the mixture from which it was formed. **b.** Avogadro's hypothesis implies that volume ratios are equal to molecule ratios at constant temperature and pressure. $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$; from the balanced equation, the volume of HCl produced will be twice the volume of H_2 (or Cl_2) reacted. **27.** 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. **29.** 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. **31.** Using $r = 5 \times 10^{-14}$ cm, $d_{\text{nucleus}} = 3 \times 10^{15}$ g/cm^3; using $r = 1 \times 10^{-8}$ cm, $d_{\text{atom}} = 0.4$ g/cm^3 **33.** 37 **35.** sodium, Na; radium, Ra; iron, Fe; gold, Au; manganese, Mn; lead, Pb **37.** Sn, tin; Pt, platinum; Hg, mercury; Mg, magnesium; K, potassium; Ag, silver **39. a.** Metals: Mg, Ti, Au, Bi, Ge, Eu, Am; nonmetals: Si, B, At, Rn, Br; **b.** metalloids: Si, Ge, B, At. The elements at the boundary between the metals and the nonmetals are B, Si, Ge, As, Sb, Te, Po, and At. These elements are all considered metalloids. Aluminum has mostly properties of metals. **41. a.** 6; **b.** 5; **c.** 4; **d.** 6 **43. a.** 35 p, 44 n, 35 e; **b.** 35 p, 46 n, 35 e; **c.** 94 p, 145 n, 94 e; **d.** 55 p, 78 n, 55 e; **e.** 1 p, 2 n, 1 e; **f.** 26 p, 30 n, 26 e **45. a.** ${}^{17}_{8}O$; **b.** ${}^{37}_{17}Cl$; **c.** ${}^{60}_{27}Co$; **d.** ${}^{57}_{26}Fe$; **e.** ${}^{131}_{53}I$; **f.** ${}^{7}_{3}Li$ **47.** ${}^{151}_{63}Eu^{3+}$; ${}^{118}_{50}Sn^{2+}$ **49.** ${}^{238}_{92}U$, 92 p, 146 n, 92 e, 0; ${}^{40}_{20}Ca^{2+}$, 20 p, 20 n, 18 e, 2+; ${}^{51}_{23}V^{3+}$, 23 p, 28 n, 20 e, 3+; ${}^{89}_{39}Y$, 39 p, 50 n, 39 e, 0; ${}^{79}_{35}Br^-$, 35 p, 44 n, 36 e, 1−; ${}^{31}_{15}P^{3-}$, 15 p, 16 n, 18 e, 3− **51. a.** transition metals; **b.** alkaline earth metals; **c.** alkali metals; **d.** noble gases; **e.** halogens **53. 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^+ **55. a.** sodium bromide; **b.** rubidium oxide; **c.** calcium sulfide; **d.** aluminum iodide; **e.** SrF_2; **f.** Al_2Se_3; **g.** K_3N; **h.** Mg_3P_2 **57. a.** cesium fluoride; **b.** lithium nitride; **c.** silver sulfide (Silver forms only +1 ions so no Roman numerals are needed); **d.** manganese(IV) oxide; **e.** titanium(IV) oxide; **f.** strontium phosphide **59. a.** barium sulfite; **b.** sodium nitrite; **c.** potassium permanganate; **d.** potassium dichromate **61. a.** dinitrogen tetroxide; **b.** iodine trichloride; **c.** sulfur dioxide; **d.** diphosphorus pentasulfide **63. 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 **65. a.** SF_2; **b.** SF_6; **c.** NaH_2PO_4; **d.** Li_3N; **e.** $Cr_2(CO_3)_3$; **f.** SnF_2; **g.** $NH_4C_2H_3O_2$; **h.** NH_4HSO_4; **i.** $Co(NO_3)_3$; **j.** Hg_2Cl_2; Mercury(I) exists as $Hg_2{}^{2+}$ ions. **k.** $KClO_3$; **l.** NaH **67. a.** Na_2O; **b.** Na_2O_2; **c.** KCN; **d.** $Cu(NO_3)_2$; **e.** $SeBr_4$; **f.** HIO_2; **g.** PbS_2; **h.** CuCl; **i.** GaAs (from the positions in the periodic table, Ga^{3+} and As^{3-} are the predicted ions); **j.** CdSe; **k.** ZnS; **l.** HNO_2; **m.** P_2O_5 **69. 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 **71.** Yes, 1.0 g H would react with 37.0 g ${}^{37}Cl$ and 1.0 g H would react with 35.0 g ${}^{35}Cl$. No, the mass ratio of H/Cl would always be 1 g H/37 g Cl for ${}^{37}Cl$ and 1 g H/35 g Cl for ${}^{35}Cl$. As long as we had pure ${}^{35}Cl$ or pure ${}^{37}Cl$, these ratios will always hold. If we have a mixture (such as the natural abundance of chlorine), the ratio will also be constant as long as the composition of the mixture of the two isotopes does not change. **73.** Only statement a is true. For statement b, X has 34 protons. For statement c, X has 45 neutrons. For statement d, X is selenium. **75. 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) **77.** X = Ra, 142 neutrons **79. a.** Ca_3N_2; calcium nitride; **b.** K_2O; potassium oxide; **c.** RbF; rubidium fluoride; **d.** MgS; magnesium sulfide; **e.** BaI_2; barium iodide; **f.** Al_2Se_3; aluminum selenide; **g.** Cs_3P; cesium phosphide; **h.** $InBr_3$; indium(III) bromide (In forms compounds with +1 and +3 ions. You would predict a +3 ion from the position of In in the periodic table.) **81.** 116 g S; 230. g O **83.** Cu, Ag, and Au **85.** C:H = 8:18 or 4:9 **87.** 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 is the formula of the first compound. **89. a.** The compounds are isomers of each other. Isomers are compounds with the same formula but the atoms are attached differently, resulting in different properties. **b.** When wood burns, most of the solid material is converted to gases, which escape. **c.** Atoms are not an indivisible particle. Atoms are composed of electrons, neutrons, and protons. **d.** The two hydride samples contain different isotopes of either hydrogen and/or lithium. Isotopes may have different masses but have similar chemical properties. **91.** tantalum(V) oxide; the formula would have the same subscripts, Ta_2S_5; 40 protons **93.** Ge^{4+}; ${}^{99}Tc$

Chapter 3

19. From the relative abundances, there would be 9889 atoms of ${}^{12}C$ and 111 atoms of ${}^{13}C$ in the 10,000-atom sample. The average mass of carbon is independent of the sample size; it will always be 12.01 amu. The total mass would be 1.201×10^5 amu. For one mol of carbon (6.022×10^{23} atoms C), the average mass would still be 12.01 amu. There would be 5.955×10^{23} atoms of ${}^{12}C$ and 6.68×10^{21} atoms of ${}^{13}C$. The total mass would be 7.232×10^{24} amu. The total mass in grams is 12.01 g/mol. **21.** Each person would have 100 trillion dollars. **23.** The mass percent of a compound is a constant no matter what amount of substance is present. Compounds always have constant composition. **25.** The information needed is mostly the coefficients in the balanced equation and the molar masses of the reactants and products. For percent yield, we would need the actual yield of the reaction and the amounts of reactants used.

a. mass of CB produced = 1.00×10^4 molecules

$$A_2B_2 \times \frac{1\ \text{mol}\ A_2B_2}{6.022 \times 10^{23}\ \text{molecules}\ A_2B_2} \times \frac{2\ \text{mol CB}}{1\ \text{mol}\ A_2B_2} \times \frac{\text{molar mass of CB}}{\text{mol CB}}$$

b. atoms of A produced = $1.00 \times 10^4\ \text{molecules}\ A_2B_2 \times \dfrac{2\ \text{atoms A}}{1\ \text{molecule}\ A_2B_2}$

c. mol of C reacted = 1.00×10^4 molecules

$$A_2B_2 \times \frac{1\ \text{mol}\ A_2B_2}{6.022 \times 10^{23}\ \text{molecules}\ A_2B_2} \times \frac{2\ \text{mol C}}{1\ \text{mol}\ A_2B_2}$$

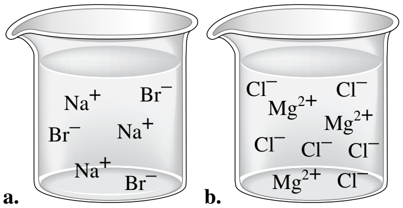
d. $\%\text{yield} = \dfrac{\text{actual mass}}{\text{theoretical mass}} \times 100$; The theoretical mass of CB produced was calculated in part a. If the actual mass of CB produced is given, then the percent yield can be determined for the reaction using the percent yield equation. **27.** 207.2 amu, Pb **29.** 185 amu **31.** There are three peaks in the mass spectrum, each 2 mass units apart. This is consistent with two isotopes, differing in mass by two mass units. **33.** 4.64×10^{-20} g Fe **35.** 1.00×10^{22} atoms C **37.** Al_2O_3, 101.96 g/mol; Na_3AlF_6, 209.95 g/mol **39. a.** 17.03 g/mol; **b.** 32.05 g/mol; **c.** 252.08 g/mol **41. a.** 0.0587 mol NH_3; **b.** 0.0312 mol N_2H_4; **c.** 3.97×10^{-3} mol $(NH_4)_2Cr_2O_7$ **43. a.** 85.2 g NH_3; **b.** 160. g N_2H_4; **c.** 1260 g $(NH_4)_2Cr_2O_7$ **45. a.** 70.1 g N; **b.** 140. g N; **c.** 140. g N **47. a.** 3.54×10^{22} molecules NH_3; **b.** 1.88×10^{22} molecules N_2H_4; **c.** 2.39×10^{21} formula units $(NH_4)_2Cr_2O_7$ **49. a.** 3.54×10^{22} atoms N; **b.** 3.76×10^{22} atoms N; **c.** 4.78×10^{21} atoms N **51.** 176.12 g/mol; 2.839×10^{-3} mol; 1.710×10^{21} molecules **53. a.** 0.9393 mol; **b.** 2.17×10^{-4} mol; **c.** 2.5×10^{-8} mol **55. a.** 4.01×10^{22} atoms N; **b.** 5.97×10^{22} atoms N; **c.** 3.67×10^{22} atoms N; **d.** 6.54×10^{22} atoms N **57. a.** 294.30 g/mol; **b.** 3.40×10^{-2} mol; **c.** 459 g; **d.** 1.0×10^{19} molecules; **e.** 4.9×10^{21} atoms; **f.** 4.9×10^{-13} g; **g.** 4.887×10^{-22} g **59. a.** 50.00% C, 5.595% H, 44.41% O; **b.** 55.80% C, 7.025% H, 37.18% O; **c.** 67.90% C, 5.699% H, 26.40% N **61.** $NO_2 = N_2O_4 < NO < N_2O$ **63.** 1360 g/mol **65. a.** 39.99% C, 6.713% H, 53.30% O; **b.** 40.00% C, 6.714% H, 53.29% O; **c.** 40.00% C, 6.714% H, 53.29% O (all the same except for rounding differences) **67. a.** NO_2; **b.** CH_2; **c.** P_2O_5; **d.** CH_2O **69.** $C_8H_{11}O_3N$ **71.** compound I: HgO; compound II: Hg_2O **73.** SN; S_4N_4 **75.** $C_3H_5O_2$; $C_6H_{10}O_4$ **77.** C_3H_8 **79.** C_3H_4, C_9H_{12} **81. 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.** $CS_2(l) + 2NH_3(g) \rightarrow H_2S(g) + NH_4SCN(s)$ **83. a.** $3Ca(OH)_2(aq) + 2H_3PO_4(aq) \rightarrow 6H_2O(l) + Ca_3(PO_4)_2(s)$; **b.** $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$; **c.** $2AgNO_3(aq) + H_2SO_4(aq) \rightarrow Ag_2SO_4(s) + 2HNO_3(aq)$ **85. a.** $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$; **b.** $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$; **c.** $C_{12}H_{22}O_{11}(s) +$

$12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(g)$; **d.** $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$; **e.** $4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$ **87. a.** $SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$; **b.** $SiCl_4(l) + 2Mg(s) \rightarrow Si(s) + 2MgCl_2(s)$; **c.** $Na_2SiF_6(s) + 4Na(s) \rightarrow Si(s) + 6NaF(s)$ **89.** 7.26 g Al; 21.5 g Fe_2O_3; 13.7 g Al_2O_3 **91.** 4.355 kg **93.** 32 kg **95. a.** 73.9 g; **b.** 1.30×10^2 g **97.** $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; NO is limiting. **99.** 0.301 g H_2O_2; 3.6×10^{-2} g HCl in excess **101.** 2.81×10^6 g HCN; 5.63×10^6 g H_2O **103.** 1.96 g (theoretical yield); 76.5% **105.** 1.20×10^3 kg = 1.20 metric tons **107.** 6 **109. a.** stoichiometric mixture; **b.** O_2; **c.** H_2; **d.** H_2; **e.** H_2; **f.** stoichiometric mixture; **g.** H_2 **111.** 9.25×10^{22} H atoms **113.** 4.30×10^{-2} mol; 2.50 g **115.** 5 **117.** 42.8% **119.** 81.1 g **121.** 86.2% **123.** $C_{20}H_{30}O$ **125.** $C_7H_5N_3O_6$ **127.** 38.7% **129.** 40.08% **131.** N_4H_6 **133.** 1.8×10^6 g $Cu(NH_3)_4Cl_2$; 5.9×10^5 g NH_3 **135.** 207 amu, Pb **137.** Al_2Se_3 **139.** 0.48 mol **141. a.** 113 Fe atoms; **b.** mass = 9.071×10^{-20} g; **c.** 540 Ru atoms **143.** M = Y, X = Cl, yttrium(III) chloride; 1.84 g

Chapter 4

9. a. Polarity is a term applied to covalent compounds. Polar covalent compounds have an unequal sharing of electrons in bonds that results in an unequal charge distribution in the overall molecule. Polar molecules have a partial negative end and a partial positive end. These are not full charges like in ionic compounds, but are charges much less 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 while the hydrogens of water (the partial positive end of the polar water molecule) align with the partial negative end of the solute. These opposite charged 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. **11.** Bromides: NaBr, KBr, and HgBr (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. **13.** The Brønsted-Lowry definitions are best for our purposes. An acid is a proton donor and a base is a proton acceptor. A proton is an H^+ ion. Neutral hydrogen has 1 electron and 1 proton, so an H^+ ion is just a proton. An acid–base reaction is the transfer of an H^+ ion (a proton) from an acid to a base. **15. a.** The species reduced is the element that gains electrons. The reducing agent causes reduction to occur by itself being oxidized. The reducing agent is generally listed as the entire formula of the compound/ion that contains the element oxidized. **b.** The species oxidized is the element that loses electrons. The oxidizing agent causes oxidation to occur by itself being reduced. The oxidizing agent is generally listed as the entire formula of the compound/ion that contains the element reduced. **c.** For simple binary ionic compounds, the actual charge on the ions are the oxidation states. For covalent compounds, nonzero oxidation states are pretend charges the elements would have if they were held together by ionic bonds (assuming the bond is between two different nonmetals). Nonzero oxidation states for elements in covalent compounds are not actual charges. Oxidation states for covalent compounds are a bookkeeping method to keep track of electrons in a reaction.

17.



c. For answers c–i, we will describe what should be in each solution. For c, the drawing should have three times as many NO_3^- anions as Al^{3+} cations. **d.** The drawing should have twice as many NH_4^+ cations as SO_4^{2-} anions. **e.** The drawing should have equal numbers of Na^+ cations and OH^- anions. **f.** The drawing should have equal numbers of Fe^{2+} cations and SO_4^{2-} anions. **g.** The drawing should have equal numbers of K^+ cations and MnO_4^- anions. **h.** The drawing should have equal numbers of H^+ cations and ClO_4^- anions. **i.** The drawing should have equal numbers of NH_4^+ cations and $C_2H_3O_2^-$ anions. **19.** $CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$ **21. a.** 0.2677 *M*; **b.** 1.255×10^{-3} *M*; **c.** 8.065×10^{-3} *M* **23. a.** $M_{Ca^{2+}} = 1.00\ M$, $M_{NO_3^-} = 2.00\ M$; **b.** $M_{Na^+} = 4.0\ M$, $M_{SO_4^{2-}} = 2.0\ M$; **c.** $M_{NH_4^+} = M_{Cl^-} = 0.187\ M$; **d.** $M_{K^+} = 0.0564\ M$, $M_{PO_4^{3-}} = 0.0188\ M$ **25.** 100.0 mL of 0.30 *M* $AlCl_3$ **27.** 4.00 g **29. a.** Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH and fill to the mark. **b.** Add 500. mL of the 1.00 *M* NaOH stock solution to a 2-L volumetric flask; fill to the mark with water. **c.** As in a, instead using 38.8 g K_2CrO_4. **d.** As in b, instead using 114 mL of 1.75 *M* K_2CrO_4 stock solution. **31.** $M_{NH_4^+} = 0.272\ M$, $M_{SO_4^{2-}} = 0.136\ M$ **33.** 5.94×10^{-8} *M* steroid **35.** Aluminum nitrate, magnesium chloride, and rubidium sulfate are soluble. **37. a.** no precipitate forms; **b.** $Al(OH)_3(s)$; **c.** $CaSO_4(s)$; **d.** $NiS(s)$ **39. a.** No reaction occurs because all possible products are soluble salts. **b.** $2Al(NO_3)_3(aq) + 3Ba(OH)_2(aq) \rightarrow 2Al(OH)_3(s) + 3Ba(NO_3)_2(aq)$; $2Al^{3+}(aq) + 6NO_3^-(aq) + 3Ba^{2+}(aq) + 6OH^-(aq) \rightarrow 2Al(OH)_3(s) + 3Ba^{2+}(aq) + 6NO_3^-(aq)$; $Al^{3+}(aq) + 3OH^-(aq) \rightarrow Al(OH)_3(s)$; **c.** $CaCl_2(aq) + Na_2SO_4(aq) \rightarrow CaSO_4(s) + 2NaCl(aq)$; $Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) + 2Na^+(aq) + 2Cl^-(aq)$; $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$; **d.** $K_2S(aq) + Ni(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + NiS(s)$; $2K^+(aq) + S^{2-}(aq) + Ni^{2+}(aq) + 2NO_3^-(aq) \rightarrow 2K^+(aq) + 2NO_3^-(aq) + NiS(s)$; $Ni^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s)$ **41. a.** $CuSO_4(aq) + Na_2S(aq) \rightarrow CuS(s) + Na_2SO_4(aq)$; $Cu^{2+}(aq) + S^{2-}(aq) \rightarrow CuS(s)$; the grey spheres are the Na^+ spectator ions and the blue-green spheres are the SO_4^{2-} spectator ions; **b.** $CoCl_2(aq) + 2NaOH(aq) \rightarrow Co(OH)_2(s) + 2NaCl(aq)$; $Co^{2+}(aq) + 2\ OH^-(aq) \rightarrow Co(OH)_2(s)$; the grey spheres are the Na^+ spectator ions and the green spheres are the Cl^- spectator ions; **c.** $AgNO_3(aq) + KI(aq) \rightarrow AgI(s) + KNO_3(aq)$; $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$; the red spheres are the K^+ spectator ions and the blue spheres are the NO_3^- spectator ions **43. a.** $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$; **b.** $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$; **c.** No reaction; **d.** No reaction; **e.** $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$ **45.** Ca^{2+}, Sr^{2+}, or Ba^{2+} could all be present. **47.** 0.607 g **49.** 0.520 g $Al(OH)_3$ **51.** 2.9 g AgCl; 0 *M* Ag^+; 0.10 *M* NO_3^-; 0.075 *M* Ca^{2+}; 0.050 *M* Cl^- **53.** 23 amu; Na **55. a.** $2HClO_4(aq) + Mg(OH)_2(s) \rightarrow Mg(ClO_4)_2(aq) + 2H_2O(l)$; $2H^+(aq) + 2ClO_4^-(aq) + Mg(OH)_2(s) \rightarrow Mg^{2+}(aq) + 2ClO_4^-(aq) + 2H_2O(l)$; $2H^+(aq) + Mg(OH)_2(s) \rightarrow Mg^{2+}(aq) + 2H_2O(l)$; **b.** $HCN(aq) + NaOH(aq) \rightarrow NaCN(aq) + H_2O(l)$; $HCN(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + CN^-(aq) + H_2O(l)$; $HCN(aq) + OH^-(aq) \rightarrow H_2O(l) + CN^-(aq)$; **c.** $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$; $H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$; $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ **57. a.** $KOH(aq) + HNO_3(aq) \rightarrow H_2O(l) + KNO_3(aq)$; $K^+(aq) + OH^-(aq) + H^+(aq) + NO_3^-(aq) \rightarrow H_2O(l) + K^+(aq) + NO_3^-(aq)$; $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$; **b.** $Ba(OH)_2(aq) + 2HCl(aq) \rightarrow 2H_2O(l) + BaCl_2(aq)$; $Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + 2Cl^-(aq) \rightarrow Ba^{2+}(aq) + 2Cl^-(aq) + 2H_2O(l)$; $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$; **c.** $3HClO_4(aq) + Fe(OH)_3(s) \rightarrow 3H_2O(l) + Fe(ClO_4)_3(aq)$; $3H^+(aq) + 3ClO_4^-(aq) + Fe(OH)_3(s) \rightarrow 3H_2O(l) + Fe^{3+}(aq) + 3ClO_4^-(aq)$; $3H^+(aq) + Fe(OH)_3(s) \rightarrow 3H_2O(l) + Fe^{3+}(aq)$ **59. a.** 100. mL; **b.** 66.7 mL; **c.** 50.0 mL **61.** 2.0×10^{-2} *M* excess OH^- **63.** 0.102 *M* **65.** 0.4178 g **67. a.** K, +1; O, −2; Mn, +7; **b.** Ni, +4; O, −2; **c.** Na, +1; Fe, +2; O,

−2; H, +1 **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 **69. a.** −3; **b.** −3; **c.** −2; **d.** +2; **e.** +1; **f.** +4; **g.** +3; **h.** +5; **i.** 0

71. Redox?	Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. Yes	Ag^+	Cu	Cu	Ag^+
b. No	—	—	—	—
c. No	—	—	—	—
d. Yes	$SiCl_4$	Mg	Mg	$SiCl_4$ (Si)
e. No	—	—	—	—

In b, c, and e, no oxidation numbers change from reactants to products.

73. a. $Zn + 2HCl \rightarrow Zn^{2+} + H_2 + 2Cl^-$; **b.** $2H^+ + 3I^- + ClO^- \rightarrow I_3^- + Cl^- + H_2O$; **c.** $7H_2O + 4H^+ + 3As_2O_3 + 4NO_3^- \rightarrow 4NO + 6H_3AsO_4$; **d.** $16H^+ + 2MnO_4^- + 10Br^- \rightarrow 5Br_2 + 2Mn^{2+} + 8H_2O$; **e.** $8H^+ + 3CH_3OH + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 3CH_2O + 7H_2O$ **75. a.** $2H_2O + Al + MnO_4^- \rightarrow Al(OH)_4^- + MnO_2$; **b.** $2OH^- + Cl_2 \rightarrow Cl^- + ClO^- + H_2O$; **c.** $OH^- + H_2O + NO_2^- + 2Al \rightarrow NH_3 + 2AlO_2^-$ **77.** $4NaCl + 2H_2SO_4 + MnO_2 \rightarrow 2Na_2SO_4 + MnCl_2 + Cl_2 + 2H_2O$ **79.** Only statement b is true. **a.** A nonelectrolyte solute can make a concentrated solution. **c.** Weak acids like acetic acid, $HC_2H_3O_2$, are weak electrolytes. **d.** Some ionic compounds do not dissolve in water (are insoluble). These compounds are not strong electrolytes (nor any type of electrolyte). The electrolyte designation refers to solutes that are soluble in water. **81. a.** $AgNO_3$, $Pb(NO_3)_2$, and $Hg_2(NO_3)_2$ would form precipitates with the Cl^- ion; $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$; $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$; $Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$; **b.** Na_2SO_4, Na_2CO_3, and Na_3PO_4 would form precipitates with the Ca^{2+} ion; $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$; $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$; $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$; **c.** NaOH, Na_2S, and Na_2CO_3 would form precipitates with the Fe^{3+} ion; $Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$; $2Fe^{3+}(aq) + 3S^{2-}(aq) \rightarrow Fe_2S_3(s)$; $2Fe^{3+}(aq) + 3CO_3^{2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$; **d.** $BaCl_2$, $Pb(NO_3)_2$, and $Ca(NO_3)_2$ would form precipitates with the SO_4^{2-} ion; $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$; $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$; $Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$; **e.** Na_2SO_4, NaCl, and NaI would form precipitates with the Hg_2^{2+} ion; $Hg_2^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Hg_2SO_4(s)$; $Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$; $Hg_2^{2+}(aq) + 2I^-(aq) \rightarrow Hg_2I_2(s)$; **f.** NaBr, Na_2CrO_4, and Na_3PO_4 would form precipitates with the Ag^+ ion; $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$; $2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$; $3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$ **83.** Ba **85.** 39.49 mg/tablet; 67.00% **87.** 2.00 *M* **89. a.** 0.8393 *M*; **b.** 5.010% **91.** $C_6H_8O_6$ **93.** $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$ are possibilities for the base. **95.** $2H^+(aq) + Mn(s) + 2HNO_3(aq) \rightarrow Mn^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$; $3H_2O(l) + 2Mn^{2+}(aq) + 5IO_4^-(aq) \rightarrow 2MnO_4^-(aq) + 5IO_3^-(aq) + 6H^+(aq)$ **97. a.** 24.8% Co, 29.7% Cl, 5.09% H, 40.4% O; **b.** $CoCl_2 \cdot 6H_2O$; **c.** $CoCl_2 \cdot 6H_2O(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Co(NO_3)_2(aq) + 6H_2O(l)$, $CoCl_2 \cdot 6H_2O(aq) + 2NaOH(aq) \rightarrow Co(OH)_2(s) + 2NaCl(aq) + 6H_2O(l)$, $4Co(OH)_2(s) + O_2(g) \rightarrow 2Co_2O_3(s) + 4H_2O(l)$ **99. a.** 7.000 *M* K^+; **b.** 0.750 *M* CrO_4^{2-} **101.** 0.123 g SO_4^{2-}, 60.0% SO_4^{2-}; 61% K_2SO_4 and 39% Na_2SO_4 **103.** 4.90 *M* **105.** Y, 2.06 mL/min; Z, 4.20 mL/min **107.** 57.6 mL **109. a.** $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$, $Mg(OH)_2(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + 2H_2O(l)$, $Al(OH)_3(s) + 3HCl(aq) \rightarrow AlCl_3(aq) + 3H_2O(l)$; **b.** MgO **111.** Citric acid has three acidic hydrogens per citric acid molecule. **113.** 0.07849 ± 0.00016 *M* or 0.0785 ± 0.0002 *M* **115.** $3(NH_4)_2CrO_4(aq) + 2Cr(NO_2)_3(aq) \rightarrow 6NH_4NO_2(aq) + Cr_2(CrO_4)_3(s)$; 7.34 g **117.** X = Se; H_2Se is hydroselenic acid; 0.252 g

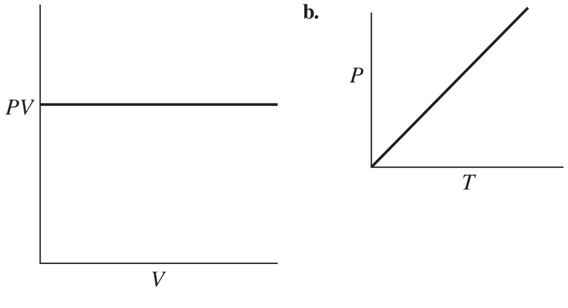
Chapter 5

17. higher than; 13.6 times taller; When the pressure of the column of liquid standing on the surface of the liquid is equal to the pressure exerted by air on the rest of the surface of the liquid, then the height of the column of liquid is a measure of atmospheric pressure. Because water is 13.6 times less dense than mercury, the column of water must be 13.6 times longer than that of mercury to match the force exerted by the columns of liquid standing on the surface. **19.** The *P* versus 1/*V* plot is incorrect. The plot should be linear with positive slope and a *y*-intercept of zero. $PV = k$ so $P = k\,(1/V)$, which is in the form of the straight-line equation $y = mx + b$. **21.** $d =$ (molar mass) P/RT; Because *d* is directly proportional to the molar mass of the gas. Helium, which has the smallest molar mass of all the noble gases, will have the smallest density. **23.** No; At any nonzero Kelvin temperature, there is a distribution of kinetic energies. Similarily, there is a distribution of velocities at any nonzero Kelvin temperature. **25.** $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$; At constant *P* and *T*, volume is directly proportional to the moles of gas present. In the reaction, the moles of gas doubles as reactants are converted to products, so the volume of the container should double. At constant *V* and *T*, *P* is directly proportional to the moles of gas present. As the moles of gas doubles, the pressure will double. The partial pressure of N_2 will be 1/2 the initial pressure of NH_3 and the partial pressure of H_2 will be 3/2 the initial pressure of NH_3. The partial pressure of H_2 will be three times the partial pressure of N_2. **27 a.** 3.6×10^3 mm Hg; **b.** 3.6×10^3 torr; **c.** 4.9×10^5 Pa; **d.** 71 psi **29.** 65 torr, 8.7×10^3 Pa, 8.6×10^{-2} atm **31. a.** 642 torr, 0.845 atm; 8.56×10^4 Pa; **b.** 975 torr; 1.28 atm; 1.30×10^5 Pa; **c.** 517 torr; 850. torr **33.** The balloon will burst. **35.** 0.89 mol **37. a.** 14.0 L; **b.** 4.72×10^{-2} mol; **c.** 678 K; **d.** 133 atm **39.** 4.44×10^3 g He; 2.24×10^3 g H_2 **41. a.** 69.6 K; **b.** 32.3 atm **43.** 1.27 mol **45.** $P_B = 2P_A$ **47.** 5.1×10^4 torr **49.** The volume of the balloon increases from 1.00 L to 2.82 L, so the change in volume is 1.82 L. **51.** 3.21 g Al **53.** 135 g NaN_3 **55.** 1.5×10^7 g Fe, 2.6×10^7 g 98% H_2SO_4 **57.** 2.47 mol H_2O **59. a.** $2CH_4(g) + 2NH_3(g) + 3O_2(g) \rightarrow 2HCN(g) + 6H_2O(g)$; **b.** 13.3 L **61.** Cl_2 **63.** 12.6 g/L **65.** 1.1 atm, $P_{CO_2} = 1.1$ atm, $P_{TOTAL} = 2.1$ atm **67.** $P_{H_2} = 317$ torr, $P_{N_2} = 50.7$ torr, $P_{TOTAL} = 368$ torr **69. 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 **71.** 0.990 atm; 0.625 g **73.** 18.0% **75.** $P_{tot} = 6.0$ atm; $P_{N_2} = 1.5$ atm; $P_{H_2} = 4.5$ atm **77.** Both $CH_4(g)$ and $N_2(g)$ have the same average kinetic energy at the various temperatures. 273 K, 5.65×10^{-21} J/molecule; 546 K, 1.13×10^{-20} J/molecule **79.** CH_4: 652 m/s (273 K); 921 m/s (546 K); N_2: 493 m/s (273 K); 697 m/s (546 K)

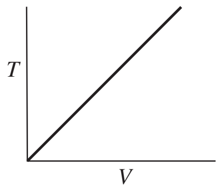
81. Average KE	**Average Velocity**	**Wall-Collision Frequency**
a. Increase	Increase	Increase
b. Decrease	Decrease	Decrease
c. Same	Same	Increase
d. Same	Same	Increase

83. a. All the same; **b.** Flask C **85.** CF_2Cl_2 **87.** The relative rates of effusion of $^{12}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$ are 1.04, 1.02, and 1.00. Advantage: CO_2 isn't as toxic as CO. Disadvantages: Can get a mixture of oxygen isotopes in CO_2, so some species would effuse at about the same rate. **89. a.** 12.24 atm; **b.** 12.13 atm; **c.** The ideal gas law is high by 0.91%. **91.** 5.2×10^{-6} atm; 1.3×10^{14} atoms He/cm³ **93.** $2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$; $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

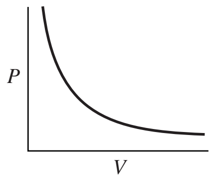
95. a.



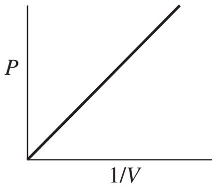
c.



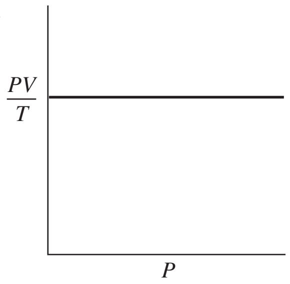
d.



e.



f.



97. 0.772 atm · L; In Sample Exercise 5.3, 1.0 mol of gas was present at 0°C. The moles of gas and/or the temperature must have been different for Boyle's data. **99.** $MnCl_4$ **101.** 1490 **103.** 24 torr **105.** 4.1×10^6 L air; 7.42×10^5 L H_2 **107.** 490 atm **109.** 13.3% N **111.** $C_{12}H_{21}NO$; $C_{24}H_{42}N_2O_2$ **113.** C_3H_8 should have the largest *b* constant. Since CO_2 has the largest *a* constant, CO_2 will have the strongest intermolecular attractions. **115.** 13.4% CaO, 86.6% BaO **117.** C_2H_6 **119. a.** 8.7×10^3 L air/min; **b.** $\chi_{CO} = 0.0017$, $\chi_{CO_2} = 0.032$, $\chi_{O_2} = 0.13$, $\chi_{N_2} = 0.77$, $\chi_{H_2O} = 0.067$ **121. a.** 1.01×10^4 g; **b.** 6.65×10^4 g; **c.** 8.7×10^3 g **123. a.** Due to air's larger average molar mass, a given volume of air at a given set of conditions has a higher density than helium. 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 **125. a.** 0.19 torr; **b.** 6.6×10^{15} molecules CO/cm^3 **127.** 0.023 mol **129.** 4.8 g/L; UF_3 will effuse 1.02 times faster.

Chapter 6

9. 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 only depend 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.
11. Both *q* and *w* are negative.

13.

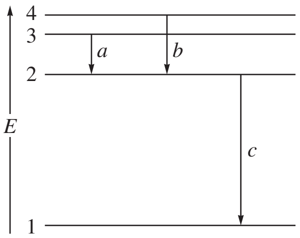
$$\begin{array}{ll} H_2O(l) + \frac{1}{2}CO_2(g) \rightarrow \frac{1}{2}CH_4(g) + O_2(g) & \Delta H_1 = -\frac{1}{2}(-891\text{ kJ}) \\ \frac{1}{2}CH_4(g) + O_2(g) \rightarrow \frac{1}{2}CO_2(g) + H_2O(g) & \Delta H_2 = \frac{1}{2}(-803\text{ kJ}) \\ \hline H_2O(l) \rightarrow H_2O(g) & \Delta H = \Delta H_1 + \Delta H_2 = 44\text{ kJ} \end{array}$$

15. Fossil fuels contain carbon; the incomplete combustion of fossil fuels produces $CO(g)$ instead of $CO_2(g)$. This occurs when the amount of oxygen reacting is not sufficient to convert all of the carbon in fossil fuels to CO_2. Carbon monoxide is a poisonous gas to humans. **17.** 150 J **19.** 1.0 kg object with velocity of 2.0 m/s. **21. a.** 41 kJ; **b.** 35 kJ; **c.** 47 kJ; **d.** part a only **23.** 375 J heat transferred to the system **25.** −13.2 kJ **27.** 11.0 L **29.** $q = 30.9$ kJ, $w = -12.4$ kJ, $\Delta E = 18.5$ kJ **31.** This is an endothermic reaction, so heat must be absorbed to convert reactants into products. The high-temperature environment of internal combustion engines provides the heat. **33. a.** endothermic; **b.** exothermic; **c.** exothermic; **d.** endothermic **35. a.** −1650 kJ; **b.** −826 kJ; **c.** −7.39 kJ; **d.** −34.4 kJ **37.** 4400 g C_3H_8 **39.** When a liquid is converted into a gas, there is an increase in volume. The 2.5 kJ/mol quantity can be considered as the work done by the vaporization process in pushing back the atmosphere. **41.** $H_2O(l)$; 2.30×10^3 J; $Hg(l)$; 140°C **43.** $Al(s)$ **45.** 311 K **47.** 23.7°C **49.** 0.25 J/g · °C **51.** −66 kJ/mol **53.** 39.2°C **55. a.** 31.5 kJ/°C; **b.** -1.10×10^3 kJ/mol **57.** −220.8 kJ **59.** 1268 kJ; No, because this reaction is very endothermic, it would not be a practical way of making ammonia due to the high energy costs. **61.** −233 kJ **63.** −713 kJ **65.** The enthalpy change for the formation of one mole of a compound from its elements, with all substances in their standard states. $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$; $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $6C_{\text{graphite}}(s) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$; $Pb(s) + S(s) + 2O_2(g) \rightarrow PbSO_4(s)$ **67. a.** −940. kJ; **b.** −265 kJ; **c.** −176 kJ **69. a.** −908 kJ, −112 kJ, −140. kJ; **b.** $12NH_3(g) + 21O_2(g) \rightarrow 8HNO_3(aq) + 4NO(g) + 14H_2O(g)$, exothermic **71.** −2677 kJ **73.** −169 kJ/mol **75.** −29.67 kJ/g **77.** For $C_3H_8(g)$, −50.37 kJ/g vs. −47.7 kJ/g for octane. Because of the low boiling point of propane, there are extra safety hazards associated with using the necessary high-pressure compressed gas tanks. **79.** 1.05×10^5 L **81. a.** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; $w > 0$; **b.** $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$; $w < 0$; **c.** $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $w = 0$; Compare the sum of the coefficients of all the product gases in the balanced equation to the sum of the coefficients of all the reactant gases. When a balanced reaction has more mol of product gases than mol of reactant gases, then the reaction will expand in volume (ΔV is positive) and the system does work on the surroundings ($w < 0$). When a balanced reaction has a decrease in the mol of gas from reactants to products, then the reaction will contract in volume (ΔV is negative) and the surroundings does compression work on the system ($w > 0$). When there is no change in the mol of gas from reactants to products, then $\Delta V = 0$ and $w = 0$. **83.** 25 J **85.** −4.2 kJ heat released **87.** The calculated ΔH value will be less positive (smaller) than it should be. **89.** 25.91°C **91. a.** 632 kJ; **b.** $C_2H_2(g)$ **93. a.** −361 kJ; **b.** −199 kJ; **c.** −227 kJ; **d.** −112 kJ **95. a.** $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$; **b.** −5630 kJ; **c.** −5630 kJ **97.** 37 m^2 **99.** 1×10^4 steps **101.** 56.9 kJ **103.** 1.74 kJ **105.** 3.3 cm

Chapter 7

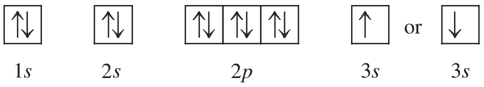
15. The equations relating the terms are $\nu\lambda = c$, $E = h\nu$, and $E = hc/\lambda$. From the equations, wavelength and frequency are inversely related, photon energy and frequency are directly related, and photon energy and wavelength are inversely related. The unit of 1 Joule (J) = 1 kg m^2/s^2. This is why you must change mass units to kg when using the deBroglie equation. **17.** Sample Exercise 7.3 calculates the deBroglie wavelength of a ball and of an electron. The ball has a wavelength on the order of 10^{-34} m. This is incredibly short and, as far as the wave-particle duality is concerned, the wave properties of large objects are insignificant. The electron, with its tiny mass, also has a short wavelength; on the order of 10^{-10} m. However, this wavelength is significant as it is on the same order as the spacing between atoms in a typical crystal. For very tiny objects like electrons, the wave properties are important. The wave properties must be considered, along with the particle properties, when hypothesizing about the electron motion in an atom. **19.** For the radial probability distribution, the space around the hydrogen nucleus is cut up into a series of thin spherical shells. When the total probability of finding the electron in each spherical shell is plotted versus the distance from the nucleus, we get the radial probability distribution graph. The plot shows a steady increase with distance from the nucleus, maximizes at a certain distance from the nucleus, then shows a steady decrease. Even though it is likely to find an electron near the nucleus, the volume of the spherical shell close to the nucleus is tiny, resulting in a low radial probability. The maximum radial probability distribution occurs at a distance of 5.29×10^{-2} nm from the nucleus; the electron is most likely to be found in the volume of the shell centered at this distance from the nucleus. The 5.29×10^{-2} nm distance is the exact radius of innermost ($n = 1$) orbit in the Bohr model. **21.** If one more electron is added to a half-filled subshell, electron–electron repulsions will increase because two electrons must now occupy the same atomic orbital. This may slightly decrease the stability of the atom. Hence, half-filled subshells minimize electron–electron repulsions. **23.** The valence electrons are strongly attracted to the nucleus for elements with large ionization energies. One would expect these species to readily accept another electron and have very exothermic electron affinities. The noble gases are an exception; they have a large ionization energy but an endothermic electron affinity. Noble gases have a stable arrangement of electrons. Adding an electron disrupts this stable arrangement, resulting in unfavorable electron affinities. **25.** For hydrogen, all orbitals with the same value of n have the same energy. For polyatomic atoms/ions, the energy of the orbitals also depends on ℓ. Because there are more nondegenerate energy levels for polyatomic atoms/ions as compared with hydrogen, there are many more possible electronic transitions resulting in more complicated line spectra. **27.** Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron–electron repulsions. **29.** Ionization energy applies to the removal of the electron from the atom in the gas phase. The work function applies to the removal of an electron from the solid. **31.** $4.5 \times 10^{14}\ \text{s}^{-1}$ **33.** $3.0 \times 10^{10}\ \text{s}^{-1}$, 2.0×10^{-23} J/photon, 12 J/mol **35.** Wave a has the longer wavelength (4.0×10^{-4} m). Wave b has the higher frequency ($1.5 \times 10^{12}\ \text{s}^{-1}$) and larger photon energy (9.9×10^{-22} J). Since both of these waves represent electromagnetic radiation, they both should travel at the same speed, *c*, the speed of light. Both waves represent infrared radiation. **37.** 1.50×10^{23} atoms **39.** 427.7 nm **41. a.** 2.4×10^{-11} m; **b.** 3.4×10^{-34} m **43.** 1.6×10^{-27} kg **45. a.** 656.7 nm (visible); **b.** 486.4 nm (visible); **c.** 121.6 nm (ultraviolet)

47.

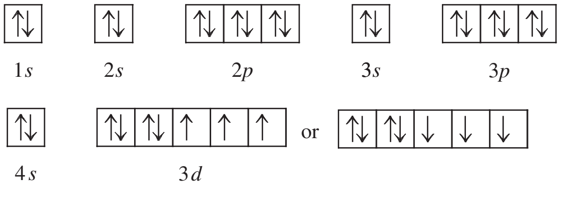


49. $n = 1 \rightarrow n = 5$, $\lambda = 95.00$ nm; $n = 2 \rightarrow n = 6$, $\lambda = 410.4$ nm; visible light has sufficient energy for the $n = 2 \rightarrow n = 6$ transition but does not have sufficient energy for the $n = 1 \rightarrow n = 5$ transition. **51.** $n = 1$, 91.20 nm; $n = 2$, 364.8 nm **53.** $n = 2$ **55. a.** 5.79×10^{-4} m; **b.** 3.64×10^{-33} m; **c.** The diameter of an H atom is roughly 1.0×10^{-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. **57.** $n = 1, 2, 3, \ldots$; $\ell = 0, 1, 2, \ldots (n - 1)$; $m_\ell = -\ell, \ldots, -2, -1, 0, 1, 2, \ldots, +\ell$. **59. b.** For $\ell = 3$, m_ℓ can range from -3 to $+3$; thus $+4$ is not allowed. **c.** n cannot equal zero. **d.** ℓ cannot be a negative number. **61.** ψ^2 gives the probability of finding the electron at that point. **63.** 3; 1; 5; 25; 16 **65. a.** 32; **b.** 8; **c.** 25; **d.** 10; **e.** 6

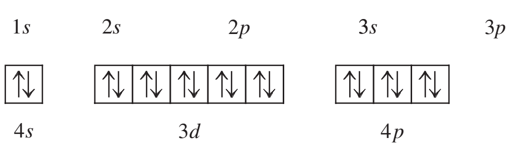
67. a.



b.



c.



69. Si: $1s^22s^22p^63s^23p^2$ or $[\text{Ne}]3s^23p^2$; Ga: $1s^22s^22p^63s^23p^64s^23d^{10}4p^1$ or $[\text{Ar}]4s^23d^{10}4p^1$; As: $[\text{Ar}]4s^23d^{10}4p^3$; Ge: $[\text{Ar}]4s^23d^{10}4p^2$; Al: $[\text{Ne}]3s^23p^1$; Cd: $[\text{Kr}]5s^24d^{10}$; S: $[\text{Ne}]3s^23p^4$; Se: $[\text{Ar}]4s^23d^{10}4p^4$ **71.** 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: $[\text{Xe}]6s^24f^7$); Pt: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^8$ (Actual: $[\text{Xe}]6s^14f^{14}5d^9$); Xe: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$; Br: $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$; **73. a.** I: $[\text{Kr}]5s^24d^{10}5p^5$; **b.** element 120: $[\text{Rn}]7s^25f^{14}6d^{10}7p^68s^2$; **c.** Rn: $[\text{Xe}]6s^24f^{14}5d^{10}6p^6$; **d.** Cr: $[\text{Ar}]4s^13d^5$ **75. a.** 18; **b.** 30; **c.** 10; **d.** 40

77. B: $1s^22s^22p^1$

	n	ℓ	m_ℓ	m_s
$1s$	1	0	0	$+\frac{1}{2}$
$1s$	1	0	0	$-\frac{1}{2}$
$2s$	2	0	0	$+\frac{1}{2}$
$2s$	2	0	0	$-\frac{1}{2}$
$2p$	2	1	-1	$+\frac{1}{2}$

N: $1s^22s^22p^3$

	n	ℓ	m_ℓ	m_s
$1s$	1	0	0	$+\frac{1}{2}$
$1s$	1	0	0	$-\frac{1}{2}$
$2s$	2	0	0	$+\frac{1}{2}$
$2s$	2	0	0	$-\frac{1}{2}$
$2p$	2	1	-1	$+\frac{1}{2}$
$2p$	2	1	0	$+\frac{1}{2}$
$2p$	2	1	$+1$	$+\frac{1}{2}$

For boron, there are six possibilities for the $2p$ electron. For nitrogen, all the $2p$ electrons could have $m_s = -\frac{1}{2}$. **79.** none; an excited state; energy released **81.** C, O, Si, S, Ti, Ni, Ge, Se **83.** Li (1 unpaired electron), N (3 unpaired electrons), Ni (2 unpaired electrons), and Te (2 unpaired electrons) are all expected to be paramagnetic because they have unpaired electrons. **85. a.** S < Se < Te; **b.** Br < Ni; < K; **c.** F < Si < Ba **87. a.** Te < Se < S; **b.** K < Ni < Br; **c.** Ba < Si < F **89. a.** He; **b.** Cl; **c.** element 117; **d.** Si; **e.** Na^+ **91. a.** $[\text{Rn}]7s^25f^{14}6d^4$; **b.** W; **c.** SgO_3 and $\text{SgO}_4{}^{2-}$ probably would form (similar to Cr). **93.** Se is an exception to the general ionization trend. There are extra electron–electron repulsions in Se because two electrons are in the same $4p$ orbital, resulting in a lower ionization energy than expected. **95. a.** C, Br; **b.** N, Ar; **c.** C, Br **97.** Al (-44), Si (-120), P (-74), S (-200.4), Cl (-348.7); Based on the increasing nuclear charge, we would expect the electron affinity (EA) values to become more exothermic as we go from left to right in the period. Phosphorus is out of line. The reaction for the EA of P is

$$\text{P}(g) + \text{e}^- \rightarrow \text{P}^-(g)$$

$$[\text{Ne}]3s^23p^3 \qquad [\text{Ne}]3s^23p^4$$

The additional electron in P^- will have to go into an orbital that already has one electron. There will be greater repulsions between the paired electrons in P^-, causing the EA of P to be less favorable than predicted based solely on attractions to the nucleus. **99. a.** I < Br < F < Cl; **b.** N < O < F **101. a.** $\text{Se}^{3+}(g) \rightarrow \text{Se}^{4+}(g) + \text{e}^-$; **b.** $\text{S}^-(g) + \text{e}^- \rightarrow \text{S}^{2-}(g)$; **c.** $\text{Fe}^{3+}(g) + \text{e}^- \rightarrow \text{Fe}^{2+}(g)$; **d.** $\text{Mg}(g) \rightarrow \text{Mg}^+(g) + \text{e}^-$ **103.** potassium peroxide, K_2O_2; K^{2+} unstable **105.** $6.582 \times 10^{14}\ \text{s}^{-1}$; 4.361×10^{-19} J **107.** Yes; the ionization energy general trend decreases down a group and the atomic radius trend increases down a group. The data in Table 7.8 confirm both of these general trends. **109. a.** $6\text{Li}(s) + \text{N}_2(g) \rightarrow 2\text{Li}_3\text{N}(s)$; **b.** $2\text{Rb}(s) + \text{S}(s) \rightarrow \text{Rb}_2\text{S}(s)$ **111.** 386 nm **113.** 200 s **115.** $\lambda = 4.104 \times 10^{-5}$ cm so violet light is emitted. **117. a.** true for H only; **b.** true for all atoms; **c.** true for all atoms **119.** 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. **121.** The element with the smallest first ionization energy (I_1) is Al (the green plot), the next highest I_1 belongs to Mg (the blue plot), and Si has the largest I_1 (the red plot). Mg is the element with the huge jump between I_2 and I_3; it has two valence electrons so the third electron removed is an inner-core electron. Inner-core electrons are always much more difficult to remove as compared to valence electrons because they are closer to the nucleus, on average, as compared to the valence electrons. **123.** Valence electrons are easier to remove than inner-core electrons. The large difference in energy between I_2 and I_3 indicates that this element has two valence electrons. The element is most likely an alkaline earth metal because alkaline earth metals have two valence electrons. **125. a.** 146 kJ; **b.** 407 kJ; **c.** 1117 kJ; **d.** 1524 kJ **127. a.** line A, $n = 6$ to $n = 3$; line B, $n = 5$ to $n = 3$; **b.** 121.6 nm **129.** For $r = a_0$ and $\theta = 0°$, $\psi^2 = 2.46 \times 10^{28}$. For $r = a_0$ and $\theta = 90°$, $\psi^2 = 0$. As expected, the xy plane is a node for the $2p_z$, atomic orbital.

131. a.

1							2
3							4
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

b. 2, 4, 12, and 20; **c.** There are many possibilities. One example of each formula is $XY = 1 + 11$, $XY_2 = 6 + 11$, $X_2Y = 1 + 10$, $XY_3 = 7 + 11$, and $X_2Y_3 = 7 + 10$; **d.** 6; **e.** 0; **f.** 18 **133.** The ratios for Mg, Si, P, Cl, and Ar are about the same. However, the ratios for Na, Al, and S are higher. For Na, the second IE is extremely high because the electron is taken from $n = 2$ (the first electron is taken from $n = 3$). For Al, the first electron requires a bit less energy than expected by the trend due to the fact it is a $3p$ electron. For S, the first electron requires a bit less energy than expected by the trend due to electrons being paired in one of the p orbitals. **135. a.** As we remove succeeding electrons, the electron being removed is closer to the nucleus and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus and it takes more energy to remove these electrons. **b.** For I_4, we begin removing an electron with $n = 2$. For I_3, we removed an electron with $n = 3$. In going from $n = 3$ to $n = 2$ there is a big jump in ionization energy because the $n = 2$ electrons (inner core) are much closer to the nucleus on the average than the $n = 3$ electrons (valence electrons). Since the $n = 2$ electrons are closer to the nucleus, they are held more tightly and require a much larger amount of energy to remove them. **c.** Al^{4+}; the electron affinity for Al^{4+} is ΔH for the reaction

$$Al^{4+}(g) + e^- \longrightarrow Al^{3+}(g) \qquad \Delta H = -I_4 = -11{,}600 \text{ kJ/mol}$$

d. The greater the number of electrons, the greater the size. So

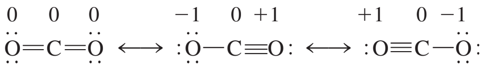
$$Al^{4+} < Al^{3+} < Al^{2+} < Al^+ < Al$$

137. Solving for the molar mass of the element gives 40.2 g/mol; this is calcium. **139. a.** $Fr = [Rn]7s^1$, $Fr^+ = [Rn]$; **b.** 7.7×10^{22} Fr atoms; **c.** 2.27790×10^{-22} g

Chapter 8

13. $(NH_4)_2SO_4$ and $Ca_3(PO_4)_2$ are compounds with both ionic and covalent bonds. **15.** Electronegativity increases left to right across the periodic table and decreases from top to bottom. Hydrogen has an electronegativity value between B and C in the second row, and identical to P in the third row. Going further down the periodic table, H has an electronegativity value between As and Se (row 4) and identical to Te (row 5). It is important to know where hydrogen fits into the electronegativity trend, especially for rows 2 and 3. If you know where H fits into the trend, then you can predict bond dipole directions for nonmetals bonded to hydrogen. **17.** For ions, concentrate on the number of protons and the number of electrons present. The species whose nucleus holds the electrons most tightly will be smallest. For example, compare the size of an anion to the neutral atom. The anion has more electrons held by the same number of protons in the nucleus. These electrons will not be held as tightly, resulting in a bigger size for the anion as compared to the neutral atom. For isoelectronic ions, the same number of electrons are held by different numbers of protons in the various ions. The ion with the most protons holds the electrons tightest and has smallest size. **19.** Fossil fuels contain a lot of carbon and hydrogen atoms. Combustion of fossil fuels (reaction with O_2) produces CO_2 and H_2O. Both these compounds have very strong bonds. Because strong bonds are formed, combustion reactions are very exothermic.

21.



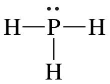
The formal charges are shown above the atoms in the three Lewis structures. The best Lewis structure for CO_2, from a formal charge standpoint, is the first structure with each oxygen double bonded to carbon. This structure has a formal charge of zero on all atoms (which is preferred). The other two resonance structures have nonzero formal charges on the oxygens, making them less reasonable. For CO_2, we usually ignore the last two resonance structures and think of the first structure as the true Lewis structure for CO_2. **23. a.** C < N < O; **b.** Se < S < Cl; **c.** Sn < Ge < Si; **d.** Tl < Ge < S **25. a.** Ge—F; **b.** P—Cl; **c.** S—F; **d.** Ti—Cl **27.** Order of electronegativity from Fig. 8.3: **a.** C(2.5) < N (3.0) < O (3.5), same; **b.** Se (2.4) < S (2.5) < Cl (3.0), same; **c.** Si = Ge = Sn (1.8), different; **d.** Tl (1.8) = Ge (1.8) < S (2.5), different. Most polar bonds using actual electronegativity values: **a.** Si—F and Ge—F equal polarity (Ge—F predicted); **b.** P—Cl (same as predicted); **c.** S—F (same as predicted); **d.** Ti—Cl (same as predicted) **29.** Incorrect: b, d, e; **b.** ${}^{\delta-}Cl—I^{\delta+}$; **d.** nonpolar bond so no dipole moment; **e.** ${}^{\delta-}O—P^{\delta+}$ **31.** F—H > O—H > N—H > C—H > P—H **33.** Fr^+: $[Xe]6s^24f^{14}5d^{10}6p^6$; Be^{2+}: $1s^2$; P^{3-} and Cl^-: $[Ne]3s^23p^6$; Se^{2-}: $[Ar]4s^23d^{10}4p^6$ **35. a.** Sc^{3+}; **b.** Te^{2-}; **c.** Ce^{4+}, Ti^{4+}; **d.** Ba^{2+} **37.** Sb^{3-}, Te^{2-}, I^-, Cs^+, Ba^{2+}, and La^{3+} are some possibilities. $La^{3+} < Ba^{2+} < Cs^+ < I^- < Te^{2-} < Sb^{3-}$ **39. 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.** $Te^{2-} > I^- > Cs^+ > Ba^{2+} > La^{3+}$ **41. a.** Al_2S_3, aluminum sulfide; **b.** K_3N_1, Potassium nitride; **c.** $MgCl_2$, Magnesium chloride; **d.** CsBr, Cesium bromide **43. a.** NaCl, Na^+ smaller than K^+; **b.** LiF, F^- smaller than Cl^-; **c.** MgO, O^{2-} greater charge than OH^-; **d.** $Fe(OH)_3$, Fe^{3+} greater charge than Fe^{2+}; **e.** Na_2O, O^{2-} greater charge than Cl^-; **f.** MgO, Mg^{2+} smaller than Ba^{2+}, and O^{2-} smaller than S^{2-}. **45.** −437 kJ/mol **47.** The lattice energy for $Mg^{2+}O^{2-}$ will be much more exothermic than for Mg^+O^-. **49.** 181 kJ/mol **51.** Ca^{2+} has greater charge than Na^+, and Se^{2-} is smaller than Te^{2-}. Charge differences affect lattice energy values more than size differences, and we expect the trend from most exothermic to least exothermic to be:

CaSe	>	CaTe	>	Na_2Se	>	Na_2Te
(−2862)		(−2721)		(−2130)		(−2095)

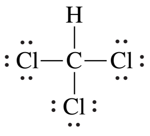
53. a. −183 kJ; **b.** −109 kJ **55.** −42 kJ **57.** −1276 kJ **59.** −295 kJ **61.** 485 kJ/mol **63. a.** Using standard enthalpies of formation, $\Delta H° = -184$ kJ vs. −183 kJ from bond energies; **b.** Using standard enthalpies of formation, $\Delta H = -92$ kJ vs. −109 kJ from bond energies. Bond energies give a reasonably good estimate for ΔH, especially when all reactants and products are gases. **65. a.** Using SF_4 data: $D_{SF} = 342.5$ kJ/mol. Using SF_6 data: $D_{SF} = 327.0$ kJ/mol. **b.** The S—F bond energy in the table is 327 kJ/mol. The value in the table was based on the S—F bond in SF_6. **c.** $S(g)$ and $F(g)$ are not the most stable forms of the elements at 25°C. The most stable forms are $S_8(s)$ and $F_2(g)$; $\Delta H_f° = 0$ for these two species.

67. a. H—C≡N :

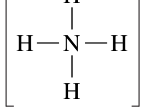
b.



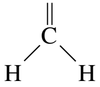
c.



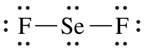
d.



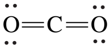
e.



f.



g.



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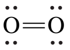
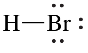
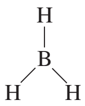


i.

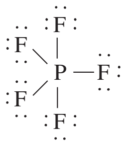


69. H—Be—H

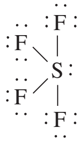


71.

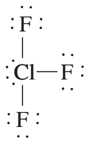
PF_5



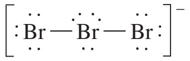
SF_4



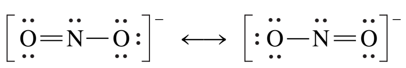
ClF_3



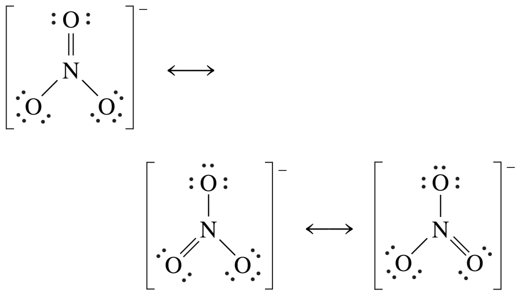
Br_3^-



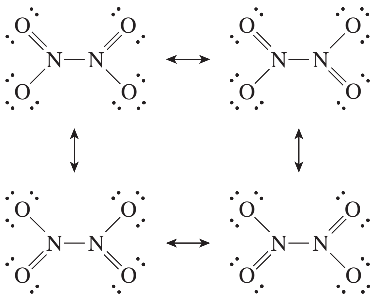
73. a. NO_2^-



NO_3^-

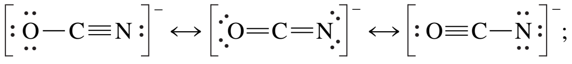


N_2O_4

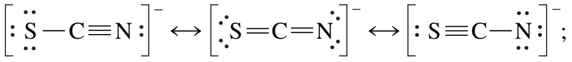


b.

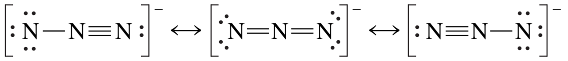
OCN^-



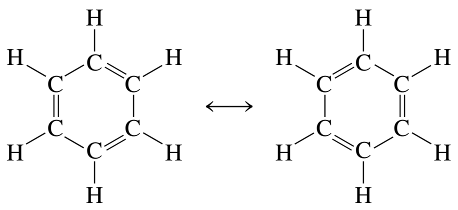
SCN^-



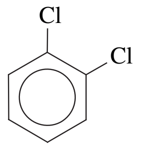
N_3^-

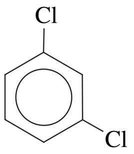


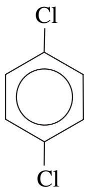
75.



77. With resonance all carbon–carbon bonds are equivalent (we indicate this with a circle in the ring), giving three different structures:



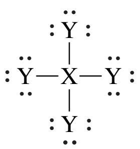




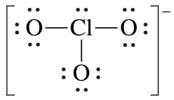
Localized double bonds give four unique structures.

79. N_2 (triple bond) $<$ N_2F_2 (double bond) $<$ N_2F_4 (single bond)

81. a.–f. and **h.** all have similar Lewis structures:

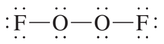


g. ClO_3^-



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

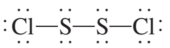
83.



	F	O	O	F
Formal charge:	0	0	0	0
Oxidation number:	−1	+1	+1	−1

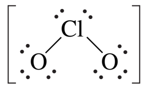
Oxidation numbers are more useful. We are forced to assign +1 as the oxidation number for oxygen. Oxygen is very electronegative and +1 is not a stable oxidation state for this element.

85.



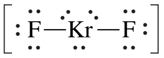
87. [67] **a.** linear, 180°; **b.** trigonal pyramid, <109.5°; **c.** tetrahedral, 109.5°; **d.** tetrahedral, 109.5°; **e.** trigonal planar, 120°; **f.** V-shaped, <109.5°; **g.** linear, 180°; **h.** and **i.** linear, no bond angle in diatomic molecules; [73] **a.** NO_2^-: V-shaped, ~120°; NO_3^-: trigonal planar, 120°; N_2O_4: trigonal planar about both N atoms, 120°; **b.** all are linear, 180° **89.** Br_3^-: linear; ClF_3; T-shaped; SF_4: see-saw **91. a.** trigonal planar; 120°; **b.** V-shaped; ~120° **93. a.** linear; 180°; **b.** T-shaped; ~90°; **c.** see-saw; ~90° and ~120°; **d.** trigonal bipyramid; 90° and 120° **95.** SeO_2 (bond dipoles do not cancel each other out in SeO_2) **97.** ICl_3 and TeF_4 (bond dipoles do not cancel each other out in ICl_3 and TeF_4)

99. a. OCl_2



V-shaped, polar

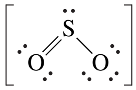
KrF_2



Linear, nonpolar

BeH_2 H—Be—H Linear, nonpolar

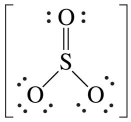
SO_2



V-shaped, polar

(one other resonance structure possible)

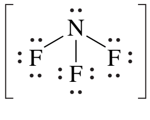
b. SO_3



Trigonal planar, nonpolar

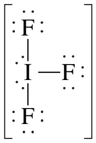
(Two other resonance structures possible)

NF_3



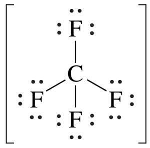
Trigonal pyramid, polar

IF_3



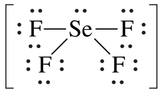
T-shaped, polar

c. CF_4



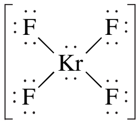
Tetrahedral, nonpolar

SeF_4



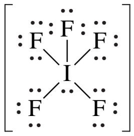
See-saw, polar

KrF_4



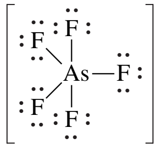
Square planar, nonpolar

d. IF_5



Square pyramid, polar

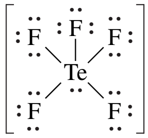
AsF_5



Trigonal bipyramid, nonpolar

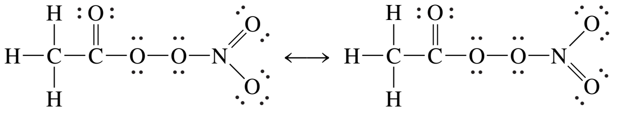
101. Element E is a halogen (F, Cl, Br, or I); trigonal pyramid; <109.5° **103.** The polar bonds are symmetrically arranged about the central atoms, and all the individual bond dipoles cancel to give no net dipole moment for each molecule, i.e., the molecules are nonpolar. **105. a.** radius: $N^+ < N < N^-$; I.E. $N^- < N < N^+$; **b.** radius: $Cl^+ < Cl < Se < Se^-$; I.E. $Se^- < Se < Cl < Cl^+$; **c.** radius: $Sr^{2+} < Rb^+ < Br^-$; I.E. $Br^- < Rb^+ < Sr^{2+}$; **107. a.** 1549 kJ; **b.** 1390. kJ **c.** 1312 kJ; **d.** 1599 kJ **109. 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 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 row 2 elements). **111. a.** Both have one or more 180° bond angles; both are made up entirely of Xe and Cl; both have the individual bond dipoles arranged so they cancel each other (both are nonpolar); both have lone pairs on the central Xe atom; both have a central Xe atom that has more than 8 electrons around it. **b.** All have lone pairs on the central atom; all have a net dipole moment (all are polar). **113.** Yes, each structure has the same number of effective pairs around the central atom. (We count a multiple bond as a single group of electrons.)

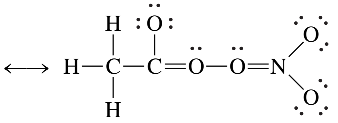
115.



The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs. The stronger repulsion pushes the four square planner F atoms away from the lone pair, reducing the bond angles between the axial F atom and the square planar F atoms. **117.** 17 kJ/mol **119.** See Fig. 8.11 to see the data supporting MgO as an ionic compound. Note that the lattice energy is large enough to overcome all of the other processes (removing 2 electrons from Mg, and so on). The bond energy for O_2 (247 kJ/mol) and electron affinity (737 kJ/mol) are the same when making CO. However, the energy needed to ionize carbon to form a C^{2+} ion must be too large. Figure 7.30 shows that the first ionization energy for carbon is about 400 kJ/mol greater than the first IE for magnesium. If all other numbers were equal, the overall energy change would be ~200 kJ/mol (see Fig. 8.11). It is not unreasonable to assume that the second ionization energy for carbon is more than 200 kJ/mol greater than the second ionization energy of magnesium. **121.** 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. **123.** reaction i: −2636 kJ; reaction ii: −3471 kJ; reaction iii: −3543 kJ; Reaction iii yields the most energy per kg (−8085 kJ/kg)

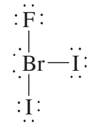
125.



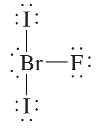


(This form is not important by formal charge arguments.)

127. a. Two possible structures exist; each has a T-shaped molecular structure:

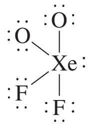


90° bond angle between I atoms

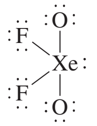


180° bond angle between I atoms

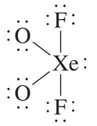
b. Three possible structures exist; each has a see-saw molecular structure.



90° bond angle between O atoms

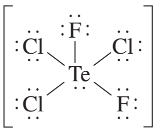


180° bond angle between O atoms

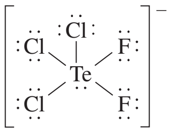


120° bond angle between O atoms

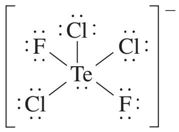
c. Three possible structures exist; each has a square pyramid molecular structure.



One F atom is 180° from lone pair.



Both F atoms are 90° from lone pair and 90° from each other.



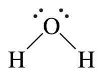
Both F atoms are 90° from lone pair and 180° from each other.

129. $\Delta H = 0$ **131.** X is iodine; square pyramid **133.** $Cr < As < P < Cl$

Chapter 9

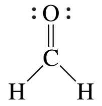
7. In hybrid orbital theory, some or all of the valence atomic orbitals of the central atom in a molecule are mixed together to form hybrid orbitals; these hybrid orbitals point to where the bonded atoms and lone pairs are oriented. The σ bonds are formed from the hybrid orbitals overlapping head to head with an appropriate orbital on the bonded atom. The π bonds in hybrid orbital theory are formed from unhybridized *p* atomic orbitals. The *p* orbitals overlap side to side to form the π bond where the π electrons occupy the space above and below a line joining the atoms π the internuclear axis). Assuming the *z*-axis is the internuclear axis, then the p_z atomic orbital will always be hybridized whether the hybridization is sp, sp^2, sp^3, dsp^2 or d^2sp^3. For *sp* hybridization, the p_x and p_y atomic orbitals are unhybridized; they are used to form two π bonds to the bonded atom(s). For sp^2 hybridization, either the p_x or p_y atomic orbital is hybridized (along with the *s* and p_z orbitals); the other *p* orbital is used to form a π bond to a bonded atom. For sp^3 hybridization, the *s* and all of the *p* orbitals are hybridized; no unhybridized *p* atomic orbitals are present, so typical π bonds do not form with sp^3 hybridization. For dsp^3 and d^2sp^3 hybridization, we just mix in one or two *d* orbitals into the hybridization process. Which specific *d* orbitals are used is not important to our discussion. **9.** We use *d* orbitals when we have to; i.e., 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 the electrons over eight. 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 sulfur, 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 while iodine would hybridize 5*d* orbitals since the valence electrons are in $n = 5$. **11.** 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 of which it is composed. Antibonding orbitals form when out-of-phase orbitals combine. The mismatched phases produce destructive interference leading to a node in the 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 of which it is composed. **13.** The localized electron model does not deal effectively with molecules containing unpaired electrons. We can draw all of the possible resonance structures for NO, but still not have a good feel for whether the bond in NO is weaker or stronger than the bond in NO^-. MO theory can handle odd electron species without any modifications. In addition, hybrid orbital theory does not predict that NO^- is paramagnetic. The MO theory correctly makes this prediction.

15. H_2O:



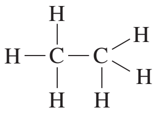
H_2O has a tetrahedral arrangement of the electron pairs about the O atom that requires sp^3 hybridization. Two of the sp^3 hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two sp^3 hybrid orbitals hold the two lone pairs on oxygen.

17. H_2CO:



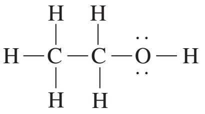
The central carbon atom has a trigonal planar arrangement of the electron pairs that requires sp^2 hybridization. Two of the sp^2 hybrid orbitals are used to form the two bonds to hydrogen. The other sp^2 hybrid orbital forms the σ bond to oxygen. The unchanged (unhybridized) *p* orbital on carbon is used to form the π bond between carbon and oxygen.

19. Ethane:

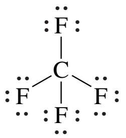


The carbon atoms are sp^3 hybridized. The six C—H bonds are formed from the sp^3 hybrid orbitals on C with the 1*s* atomic orbitals from the hydrogen atoms. The carbon–carbon bond is formed from an sp^3 hybrid orbital on each C atom.

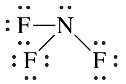
Ethanol:



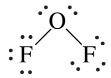
The two C atoms and the O atom are all sp^3 hybridized. All bonds are formed from these sp^3 hybrid orbitals. The C—H and O—H bonds form from sp^3 hybrid orbitals and the 1*s* atomic orbitals from the hydrogen atom. The C—C and C—O bonds are formed from sp^3 hybrid orbitals on each atom. **21.** [67] **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 [73] **a.** NO_2^-, sp^2; NO_3^-, sp^2; N_2O_4: both N atoms are sp^2 hybridized; **b.** All are *sp* hybridized. **23.** All exhibit dsp^3 hybridization. **25.** The molecules in Exercise 91 all exhibit sp^2 hybridization about the central atom; the molecules in Exercise 92 all exhibit sp^3 hybridization about the central atom. **27.** **a.** tetrahedral, 109.5°, sp^3, nonpolar



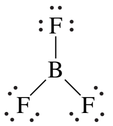
b. trigonal pyramid, <109.5°, sp^3, polar



c. V-shaped, <109.5°, sp^3, polar



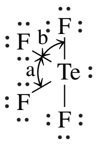
d. trigonal planar, 120°, sp^2, nonpolar



e. linear, 180°, *sp*, nonpolar

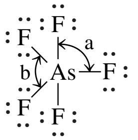
H—Be—H

f.



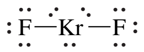
a ≈ 120°, see-saw, dsp^3, polar
b ≈ 90°

g.



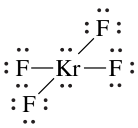
a = 90°, trigonal bipyramid, dsp^3, nonpolar
b = 120°

h.



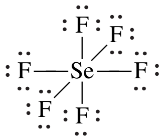
linear, 180°, dsp^3, nonpolar

i.



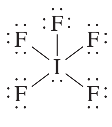
square planar, 90°, d^2sp^3, nonpolar

j.

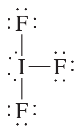


octahedral, 90°, d^2sp^3, nonpolar

k.



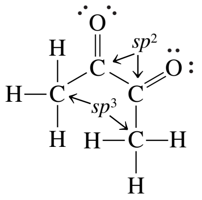
l.



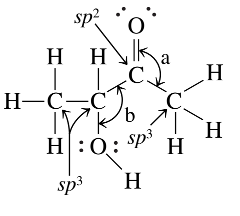
square pyramid, ≈90°; d^2sp^3, polar

T-shaped, ≈90°; dsp^3, polar

29. The π bond forces all six atoms into the same plane. **31.** Biacetyl

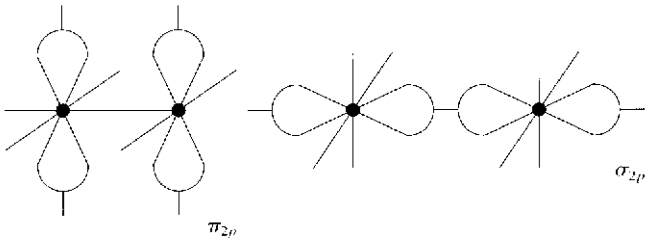


All CCO angles are 120°. The six atoms are not in the same plane. 11σ and 2π
Acetoin

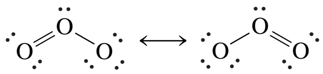


angle a = 120°, angle b = 109.5°, 13 σ and 1 π bond **33.** To complete the Lewis structure, add lone pairs to complete octets for each atom. **a.** 6; **b.** 4; **c.** The center N in —N═N═N group; **d.** 33 σ; **e.** 5 π; **f.** 180°; **g.** <109.5°; **h.** sp^3 **35. a.** H_2^+, H_2, H_2^-; **b.** He_2^{2+} and He_2^+ **37. a.** $(\sigma_{2s})^2$; B.O. = 1; diamagnetic (0 unpaired electrons); **b.** $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$; B.O. = 2; diamagnetic (0 unpaired electrons); **c.** $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$; B.O. = 2; paramagnetic (2 unpaired electrons) **39.** When O_2 loses an electron, it comes from a pi antibonding orbital, which strengthens the bond from a bond order of 2 to a bond order of 2.5. When N_2 loses an electron, it comes a pi bonding orbital, which changes the bond order from 3 to 2.5 (the bond weakens). **41.** N_2^- and N_2^+ **43. a.** $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; B.O. = 3; diamagnetic; **b.** $(\sigma_{2s})^2(\sigma_{2s}^*)^2$ $(\pi_{2p})^4(\sigma_{2p})^1$; B.O. = 2.5; paramagnetic; **c.** $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$; B.O. = 2; diamagnetic; bond length: CO < CO^+ < CO^{2+}; bond energy: CO^{2+} < CO^+ < CO **45.** H_2; B_2; C_2^{2-}

47.

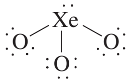


49. a. The electrons would be closer to F on the average. The F atom is more electronegative than the H atom, and the 2p orbital of F is lower in energy than the 1s orbital of H; **b.** The bonding MO would have more fluorine 2p character because it is closer in energy to the fluorine 2p orbital; **c.** 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. **51.** O_3 and NO_2^- have identical Lewis structures, so we need to discuss only one of them. The Lewis structure for O_3 is

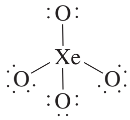


Localized electron model: The central oxygen atom is sp^2 hybridized, which is used to form the two σ bonds and hold the lone pair of electrons. An unchanged (unhybridized) p atomic orbital forms the π bond with the neighboring oxygen atoms. The π bond resonates between the two positions. Molecular orbital model: There are two localized σ bonds and a π bond that is delocalized over the entire surface of the molecule. The delocalized π bond results from overlap of a p atomic oribtal on each oxygen atom in O_3.

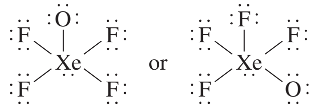
53. a. Trigonal pyramid; sp^3



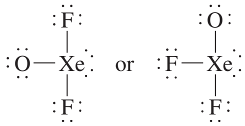
b. Tetrahedral; sp^3



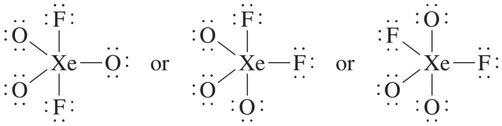
c. Square pyramid; d^2sp^3



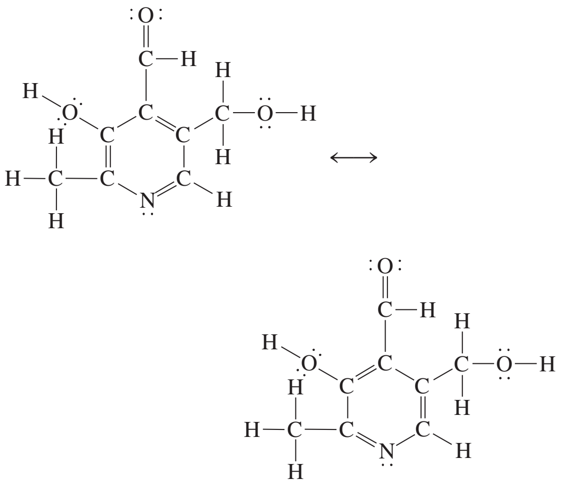
d. T-shaped; dsp^3



e. Trigonal bipyramid; dsp^3

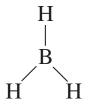


55.



a. 21 σ bonds; 4 π bonds (The electrons in the 3 π bonds in the ring are delocalized.) **b.** angles *a*, *c*, and *g*: ≈109.5°; angles *b*, *d*, *e*, and *f*: ≈120°; **c.** 6 sp^2 carbons; **d.** 4 sp^3 atoms; **e.** Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp^2 hybridized. This leaves a *p* orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these *p* orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Fig. 9.48 of the text). **57.** 267 kJ/mol; this amount of energy must be supplied to break the π bond.

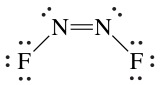
59. a.



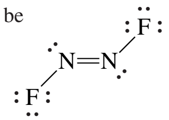
Trigonal planar, nonpolar, 120°, sp^2

b. N_2F_2

can also be



Polar

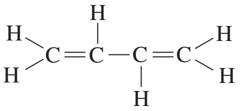


Nonpolar

V-shaped about both N atoms, ≈120°, sp^2

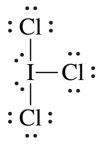
These are distinctly different molecules.

c.



Trigonal planar about all C atoms, nonpolar, 120°, sp^2

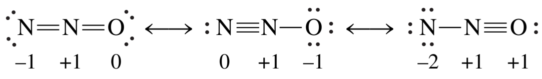
d. ICl_3



T-shaped, polar, ≈90°, dsp^3

61. 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.

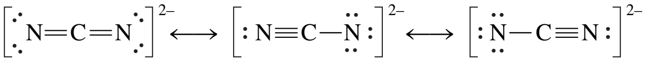
b.



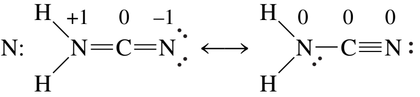
Formal charges

The central N is *sp* hybridized. We can probably ignore the third resonance structure on the basis of formal charge. **c.** *sp* hybrid orbitals on the center N overlap with atomic orbitals (or hybrid orbitals) on the other two atoms to form two σ bonds. The remaining *p* orbitals on the center N overlap with *p* orbitals on the other N to form two π bonds. **63.** N_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ in ground state, B.O. = 3, diamagnetic; 1st excited state: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}^*)^1$, B.O. = 2, paramagnetic (two unpaired electrons) **65.** F_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$; F_2 should have a lower ionization energy than F. The electron removed from F_2 is in a π_{2p}^* antibonding molecular orbital, which is higher in energy than the 2*p* atomic orbitals from which the electron in atomic fluorine is removed. Since the electron removed from F_2 is higher in energy than the electron removed from F, then it should be easier to remove an electron from F_2 than from F. **67.** π molecular orbital **69.** 6 sp^2; 6 sp^3; 0 *sp*; 25 σ; 4π **71. a.** No, some atoms are attached differently; **b.** Structure 1: All N = sp^3, all C = sp^2; structure 2: All C and N = sp^2; **c.** The first structure with the carbon–oxygen double bonds is slightly more stable.

73. a. NCN^{2-}:

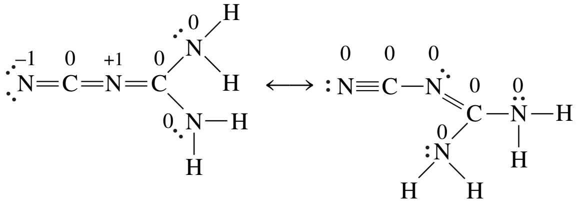


H_2NCN:



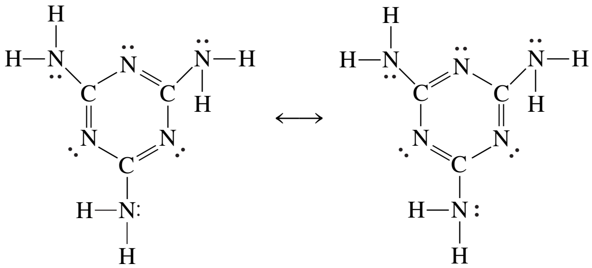
Favored by formal charge

Dicyandiamide:

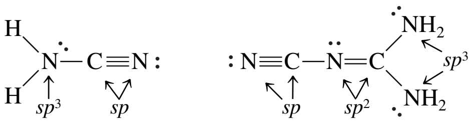


Favored by formal charge

Melamine:

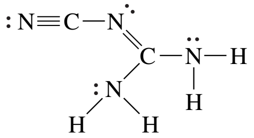


b. NCN^{2-}: C is *sp* hybridized. Each resonance structure predicts a different hybridization for the N atoms. For the remaining compounds, we will predict hybrids for the favored resonance structures only.



Melamine: N in NH_2 groups are all sp^3 hybridized. Atoms in ring are all sp^2 hybridized; **c.** NCN^{2-}: 2 σ and 2 π bonds; H_2NCN: 4 σ and 2 π bonds; dicyandiamide: 9 σ and 3 π bonds; melamine: 15 σ and 3 π bonds; **d.** The π system forces the ring to be planar just as the benzene ring is planar.

e. The structure

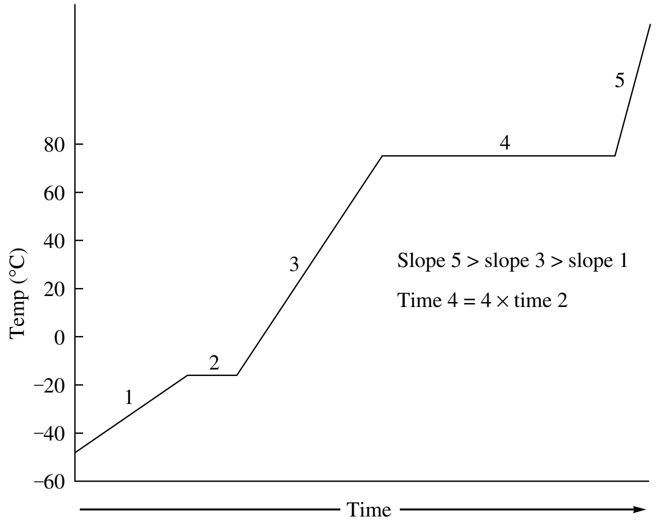


is the most important because it has three different CN bonds. This structure is also favored on the basis of formal charge. **75. a.** 25-nm light has sufficient energy to ionize N and N_2 and to break the triple bond in N_2. Thus, N_2, N_2^+, N, and N^+ will all be present, assuming excess N_2. **b.** $85.33 \text{ nm} < \lambda \leq 127$ nm; **c.** The ionization energy of a substance is the energy it takes to completely remove an electron. N_2: $(\sigma_{2s})^2(\sigma_{2s}{}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; the electron removed from N_2 is in the σ_{2p} molecular orbital, which is lower in energy than the $2p$ 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 removed in N, then the ionization energy of N_2 is greater than the ionization energy of N. **77.** Both reactions apparently involve only the breaking of the N—Cl bond. However, in the reaction $ONCl \rightarrow NO + Cl$ some energy is released in forming the stronger NO bond, lowering the value of ΔH. Therefore, the apparent N—Cl bond energy is artificially low for this reaction. The first reaction involves only the breaking of the N—Cl bond. **79. 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 to bond to the oxygen end of CO on the basis of electronegativity. **b.** The formal charge on C is -1, and the formal charge on O is $+1$. From formal charge, we would expect metal cations to bond to the carbon (with the negative formal charge.) **c.** In molecular orbital 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 molecular orbitals of CO that have proper symmetry to overlap with *d* orbitals are the $\pi_{2p}{}^*$ orbitals, whose shape is similar to that of the *d* orbitals (see Fig. 9.34). Since the antibonding molecular orbitals have more carbon character, one would expect the bond to form through carbon. **81.** The species with the smallest ionization energy has the highest energy electron. O_2, N_2^{2-}, N_2^-, and O_2^+ all have at least one electron in the high-energy $\pi_{2p}{}^*$ orbitals. Because N_2^{2-} has the highest ratio of electrons to protons, the $\pi_{2p}{}^*$ electrons are least attracted to the nuclei and easiest to remove, translating into the smallest ionization energy. **83. a.** Li_2 bond order = 1; B_2 bond order = 1; **b.** 4 electrons must be removed; **c.** 4.5×10^5 kJ **85.** T-shaped and dsp^3 hybridized

Chapter 10

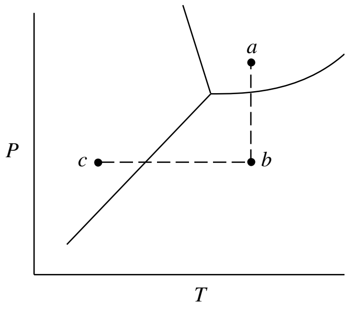
13. Atoms have an approximately spherical shape. It is impossible to pack spheres together without some empty space between the spheres. **15.** Evaporation takes place when some molecules at the surface of a liquid have enough energy to break the intermolecular forces holding them in the liquid phase. When a liquid evaporates, the molecules that escape have high kinetic energies. The average kinetic energy of the remaining molecules is lower; thus the temperature of the liquid is lower. **17.** An alloy is a substance that contains a mixture of elements and has metallic properties. In a substitutional alloy, some of the host metal atoms are replaced by other metal atoms of similar size (e.g., in brass, pewter, plumber's solder). An interstitial alloy is formed when some of the interstices (holes) in the closest packed metal structure are occupied by smaller atoms (e.g., in carbon steels). **19. a.** As intermolecular forces increase, the rate of evaporation decreases. **b.** increase *T*: increase rate; **c.** increase surface area: increase rate **21.** Sublimation will occur, allowing water to escape as $H_2O(g)$. **23.** The strength of intermolecular forces determines relative boiling points. The types of intermolecular forces for covalent compounds are London dispersion forces, dipole forces, and hydrogen bonding. Because the three compounds are assumed to have similar molar mass and shape, the strength of the London dispersion forces will be about equal between the three compounds. One of the compounds will be nonpolar so it only has London dispersion forces. The other two compounds will be polar so they have additional dipole forces and will boil at a higher temperature than the nonpolar compound. One of the polar compounds will have an H covalently bonded to either N, O, or F. This gives rise to the strongest type of covalent intermolecular force, hydrogen bonding. This compound exhibiting hydrogen bonding will have the highest boiling point while the polar compound with no hydrogen bonding will boil at an intermediate temperature. **25. a.** Both CO_2 and H_2O are molecular solids. Both have an ordered array of the individual molecules, with the molecular units occupying the lattice points. A difference within each solid lattice is the strength of the intermolecular forces. CO_2 is nonpolar and only exhibits London dispersion forces. H_2O exhibits the relatively strong hydrogen bonding interactions. The difference in strength is evidenced by the solid phase change that occurs at 1 atm. CO_2 sublimes at a relatively low temperature of $-78°C$. In sublimation, all of the intermolecular forces are broken. However, H_2O doesn't have a solid phase change until 0°C, and in this phase change from ice to water, only a fraction of the intermolecular forces are broken. The higher temperature and the fact that only a portion of the intermolecular forces are broken are attributed to the strength of the intermolecular forces in H_2O as compared to CO_2. Related to the intermolecular forces is the relative densities of the solid and liquid phases for these two compounds. $CO_2(s)$ is denser than $CO_2(l)$ while $H_2O(s)$ is less dense than $H_2O(l)$. For $CO_2(s)$ and for most solids, the molecules pack together as close as possible, which is why solids are usually more dense than the liquid phase. For H_2O, each molecule has two lone pairs and two bonded hydrogen atoms. Because of the equal number of lone pairs and O—H bonds, each H_2O molecule can form two hydrogen bonding interactions to other H_2O molecules. To keep this symmetric arrangement (which maximizes the hydrogen bonding interactions), the $H_2O(s)$ molecules occupy positions that create empty space in the lattice. This translates into smaller density for $H_2O(s)$ (less mass per unit volume). **b.** Both NaCl and CsCl are ionic compounds with the anions at the lattice points of the unit cell and the cations occupying the empty spaces created by the anions (called holes). In NaCl, the Cl^- anions occupy the lattice points of a face-centered unit cell with the Na^+ cations occupying the octahedral holes. Octahedral holes are the empty spaces created by six Cl^- ions. CsCl has the Cl^- ions at the lattice points of a simple cubic unit cell with the Cs^+ cations occupying the middle of the cube. **27.** In the $\ln P_{\text{vap}}$ versus $1/T$ plot, the slope of the straight line is equal to $-\Delta H_{\text{vap}}/R$. Because ΔH_{vap} is always positive, the slope of the line will always be negative. **29. a.** LD (London dispersion); **b.** dipole, LD; **c.** hydrogen bonding, LD; **d.** ionic; **e.** LD; **f.** dipole, LD; **g.** ionic **31. a.** OCS; **b.** SeO_2; **c.** $H_2NCH_2CH_2NH_2$; **d.** H_2CO; **e.** CH_3OH **33. a.** Neopentane is more compact than *n*-pentane. There is less surface area contact among neopentane molecules. This leads to weaker London dispersion 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 London dispersion forces. Ionic forces are much stronger than the forces for molecular solids. **d.** *n*-Hexane is a larger molecule, so it has stronger London dispersion forces. **35. a.** HBr has dipole forces in addition to LD forces; **b.** NaCl, stronger ionic forces; **c.** I_2, larger molecule so stronger LD forces; **d.** N_2, smallest nonpolar compound present, has weakest LD forces; **e.** CH_4, smallest nonpolar compound present, has weakest LD forces; **f.** HF, can form relatively strong hydrogen bonding interactions, unlike the other compounds; **g.** $CH_3CH_2CH_2OH$, unlike others, has relatively strong hydrogen bonding. **37.** H_2O is attracted to glass while Hg is not. **39.** The structure of H_2O_2 produces greater hydrogen bonding than water. Long chains of hydrogen bonded H_2O_2 molecules then get tangled together. **41.** 313 pm **43.** 0.704 Å **45.** 1.54 g/cm^3 **47.** 174 pm; 11.6 g/cm^3 **49.** edge, 328 pm; radius, 142 pm **51.** face-centered cubic unit cell **53.** For a cubic closest packed structure, 74.06% of the volume of each unit cell is occupied by atoms; in a simple cubic unit cell structure, 52.36% is occupied. The cubic (and hexagonal) closest packed structures provide the most efficient means for packing atoms. **55.** Doping silicon with phosphorus produces an n-type semiconductor. The phosphorus adds electrons at energies near the conduction band of silicon. Electrons do not need as much energy to move from filled to unfilled energy levels so conduction increases. Doping silicon with gallium produces a p-type semiconductor. Because gallium has fewer valence electrons than silicon, holes (unfilled energy levels) at energies in the previously filled molecular orbitals are created, which induces greater electron movement (greater conductivity). **57.** p-type **59.** 5.0×10^2 nm **61.** NaCl: $4Na^+$, $4Cl^-$; CsCl: $1Cs^+$, $1Cl^-$; ZnS: $4Zn^{2+}$, $4S^{2-}$; TiO_2: $2Ti^{4+}$, $4O^{2-}$ **63.** CoF_2 **65.** $ZnAl_2S_4$ **67.** MF_2 **69.** $r_{O^{2-}} = 1.49 \times 10^{-8}$ cm; $r_{Mg^{2+}} = 6.15 \times 10^{-9}$ cm **71. a.** CO_2: molecular; **b.** SiO_2: covalent network; **c.** Si: atomic, covalent network; **d.** CH_4: molecular; **e.** Ru: atomic, metallic; **f.** I_2: molecular; **g.** KBr: ionic; **h.** H_2O: molecular; **i.** NaOH: ionic; **j.** U: atomic, metallic; **k.** $CaCO_3$: ionic; **l.** PH_3: molecular **73. a.** The unit cell consists of Ni at the cube corners and Ti at the body center or Ti at the cube corners and Ni at the body center. **b.** NiTi; **c.** Both have a coordination number of 8. **75.** $CaTiO_3$; six oxygens around each Ti **77. a.** $YBa_2Cu_3O_9$; **b.** The structure of this superconductor material is based on the second perovskite structure. The $YBa_2Cu_3O_9$ structure is three of these cubic perovskite unit cells stacked on top of each other. The oxygens are in the same places, Cu takes the place of Ti, two Ca are replaced by two Ba, and one Ca is replaced by Y. **c.** $YBa_2Cu_3O_7$ **79.** Li, 158 kJ/mol; Mg, 139 kJ/mol. Bonding is stronger in Li. **81.** 89°C **83.** 77°C

85.



87. 1680 kJ **89.** 1490 g **91.** 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. **93. 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. **95.** 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. **97.** Chalk is composed of the ionic compound calcium carbonate ($CaCO_3$). The electrostatic forces in ionic compounds are much stronger than the intermolecular forces in covalent compounds. Therefore, $CaCO_3$ should have a much higher boiling point than the covalent compounds found in motor oil and in H_2O. Motor oil is composed of nonpolar C—C and C—H bonds. The intermolecular forces in motor oil are therefore London dispersion forces. We generally consider these forces to be weak. However, with compounds that have large molar masses, these London dispersion forces add up significantly and can overtake the relatively strong hydrogen-bonding interactions in water. **99.** A: CH_4; B: SiH_4 C: NH_3 **101.** If TiO_2 conducts electricity as a liquid, then it would be ionic. **103.** B_2H_6, molecular; SiO_2, network; CsI, ionic; W, metallic **105.** 4.65 kg/h **107.** $\Delta E = 27.86$ kJ/mol; $\Delta H = 30.79$ kJ/mol **109.** 46.7 kJ/mol; 90% **111.** The solids with high melting points (NaCl, $MgCl_2$, NaF, MgF_2, AlF_3) are all ionic solids. $SiCl_4$, SiF_4, Cl_2, F_2, PF_5, and SF_6 are nonpolar covalent molecules with LD forces. PCl_3 and SCl_2 are polar molecules with LD and dipole forces. In these 8 molecular substances the intermolecular forces are weak and the melting points low. $AlCl_3$ is intermediate. The melting point indicates there are stronger forces present than in the nonmetal halides, but not as strong as for an ionic solid. $AlCl_3$ illustrates a gradual transition from ionic to covalent bonding; from an ionic solid to discrete molecules. **113.** $TiO_{1.182}$ or $Ti_{0.8462}O$; 63.7% Ti^{2+}, 36.3% Ti^{3+} **115.** 6.58 g/cm^3

117.



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.

119. The volume of the hole is $\frac{4}{3}\pi\left[\left(\frac{2\sqrt{3}-2}{2}\right)r\right]^3$ **121.** CdS; n-type

123. 2.53 torr; 6.38×10^{22} atoms

Chapter 11

9. 9.74 *M* **11.** 4.5 *M* **13.** 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 will escape to the vapor phase, and the solubility of the gas will decrease. **15.** The levels of the liquids in each beaker will become constant when the concentration of solute is the same in both beakers. Because the solute is less volatile, the beaker on the right will have a larger volume when the concentrations become equal. Water will initially condense in this beaker in a larger amount than solute is evaporating, while the net change occurring initially in the other beaker is for water to evaporate in a larger amount than solute is condensing. Eventually the rate that solute and H_2O leave and return to each beaker will become equal when the concentrations become equal. **17.** No. For an ideal solution, $\Delta H_{soln} = 0$ **19.** Normality is the number of equivalents per liter of solution. For an acid or a base, an equivalent is the mass of acid or base that can furnish 1 mol of protons (if an acid) or accept 1 mol of protons (if a base). A proton is an H^+ ion. Molarity is defined as the moles of solute per liter of solution. When the number of equivalents equals the number of moles of solute, then normality = molarity. This is true for acids which only have one acidic proton in them and for bases that accept only one proton per formula unit. Examples of acids where equivalents = moles solute are HCl, HNO_3, HF, and $HC_2H_3O_2$. Examples of bases where equivalents = moles solute are NaOH, KOH, and NH_3. When equivalents ≠ moles solute, then normality ≠ molarity. This is true for acids that donate more than one proton (H_2SO_4, H_3PO_4, H_2CO_3, etc.) and for bases that react with more than one proton per formula unit [$Ca(OH)_2$, $Ba(OH)_2$, $Sr(OH)_2$, etc.]. **21.** Only statement b is true. A substance freezes when the vapor pressure of the liquid and solid phases are the same. When a solute is added to water, the vapor pressure of the solution at 0°C is less than the vapor pressure of the solid; the net result is for any ice present to convert to liquid in order to try to equalize the vapor pressures (which never can occur at 0°C). A lower temperature is needed to equalize the vapor pressure of water and ice, hence the freezing point is depressed. For statement a, the vapor pressure of a solution is directly related to the mole fraction of solvent (not solute) by Raoult's law. For statement c, colligative properties depend on the number of solute particles present and not on the identity of the solute. For statement d, the boiling point of water is increased because the sugar solute decreases the vapor pressure of the water; a higher temperature is required for the vapor pressure of the solution to equal the external pressure so boiling can occur. **23.** Isotonic solutions are those which have identical osmotic pressures. Crenation and hemolysis refer to a phenomena that occurs when red blood cells are bathed in solutions having a mismatch in osmotic pressure between the inside and the outside of the cell. When red blood cells are in a solution having a higher osmotic pressure than that of the cells, the cells shrivel as there is a net transfer of water out of the cells. This is called crenation. Hemolysis occurs when the red blood cells are bathed in a solution having lower osmotic pressure than that inside the cell. Here, the cells rupture as there is a net transfer of water to inside the red blood cells. **25.** 1.06 g/mL; 0.0180 mole fraction H_3PO_4, 0.9820 mole fraction H_2O; 0.981 mol/L; 1.02 mol/kg **27.** HCl: 12 M, 17 m, 0.23; HNO_3: 16 M, 37 m, 0.39; H_2SO_4: 18 M, 200 m, 0.76; $HC_2H_3O_2$: 17 M, 2000 m, 0.96; NH_3: 15 M, 23 m, 0.29 **29.** 35%; 0.39; 7.3 m; 3.1 M **31.** 23.9%; 1.6 m, 0.028, 4.11 N **33.** $NaI(s) \rightarrow Na^+(aq) + I^-(aq)$ $\Delta H_{soln} = -8$ kJ/mol **35.** The attraction of water molecules for Al^{3+} and OH^- cannot overcome the larger lattice energy of $Al(OH)_3$. **37. a.** CCl_4; **b.** H_2O; **c.** H_2O; **d.** CCl_4; **e.** H_2O; **f.** H_2O; **g.** CCl_4; **39.** Ability to form hydrogen bonding interactions, ability to break up into ions, and polarity are some factors affecting solute solubility. **a.** CH_3CH_2OH; **b.** $CHCl_3$; **c.** CH_3CH_2OH **41.** As the length of the hydrocarbon chain increases, the solubility decreases because the nonpolar hydrocarbon chain interacts poorly with the polar water molecules. **43.** 1.04×10^{-3} mol/L · atm; 1.14×10^{-3} mol/L **45.** 50.0 torr **47.** 3.0×10^2 g/mol **49. a.** 290 torr; **b.** 0.69 **51.** $\chi_{methanol} = \chi_{propanol} = 0.500$ **53.** solution c **55.** $P_{ideal} = 188.6$ torr; $\chi_{acetone} = 0.512$, $\chi_{methanol} = 0.488$; the actual vapor pressure of the solution is smaller than the ideal vapor pressure, so this solution exhibits a negative deviation from Raoult's law. This occurs when solute–solvent attractions are stronger than for the pure substances. **57.** 101.5°C **59.** 14.8 g $C_3H_8O_3$ **61.** $T_f = -29.9°C$, $T_b = 108.2°C$ **63.** 776 g/mol **65. a.** $\Delta T = 2.0 \times 10^{-5}°C$, $\pi = 0.20$ torr; **b.** Osmotic pressure is better for determining the molar mass of large molecules. A temperature change of $10^{-5}°C$ is very difficult to measure. A change in height of a column of mercury by 0.2 mm is not as hard to measure precisely. **67.** 0.327 M **69. a.** 0.010 m Na_3PO_4 and 0.020 m KCl; **b.** 0.020 m HF; **c.** 0.020 m $CaBr_2$ **71. a.** $T_f = -0.28°C$; $T_b = 100.077°C$; **b.** $T_f = -0.37°C$; $T_b = 100.10°C$ **73.** 2.63 (0.0225 m), 2.60 (0.0910 m), 2.57 (0.278 m); $i_{average} = 2.60$ **75. a.** yes; **b.** no **77. a.** 26.6 kJ/mol; **b.** −657 kJ/mol **79. a.** Water boils when the vapor pressure equals the pressure above the water. In an open pan, $P_{atm} \approx 1.0$ atm. In a pressure cooker, $P_{inside} > 1.0$ atm and water boils at a higher temperature. The higher the cooking temperature, the faster the cooking time. **b.** Salt dissolves in water, forming a solution with a melting point lower than that of pure water ($\Delta T_f = K_f m$). This happens in water on the surface of ice. If it is not too cold, the ice melts. This process won't occur if the ambient temperature is lower than the depressed freezing point of the salt solution. **c.** When water freezes from a solution, if freezes as pure water, leaving behind a more concentrated salt solution. **d.** On the CO_2 phase diagram, the triple point is above 1 atm and $CO_2(g)$ is the stable phase at 1 atm and room temperature. $CO_2(l)$ can't exist at normal atmospheric pressures, which explains why dry ice sublimes rather than boils. In a fire extinguisher, $P > 1$ atm and $CO_2(l)$ can exist. When CO_2 is released from the fire extinguisher, $CO_2(g)$ forms as predicted from the phase diagram. **e.** Adding a solute to a solvent increases the boiling point and decreases the freezing point of the solvent. Thus, the solvent is a liquid over a wider range of temperatures when a solute is dissolved. **81.** 0.600 **83.** $C_2H_4O_3$; 151 g/mol (exp.); 152.10 g/mol (calc.); $C_4H_8O_6$ **85.** 1.97% NaCl **87. a.** 100.77°C; **b.** 23.1 mm Hg; **c.** Assume an ideal solution; assume no ions form (i = 1).

89. 30.% A: $\chi_A = \dfrac{0.30y}{0.70x - 0.30y}$, $\chi_B = 1 - \chi_A$;

50.% A: $\chi_A = \dfrac{y}{x - y}$, $\chi_B = 1 - \dfrac{y}{x - y}$;

80.% A: $\chi_A = \dfrac{0.80y}{0.20x - 0.80y}$, $\chi_B = 1 - \chi_A$;

30.% A: ${\chi_A}^V = \dfrac{0.30x}{0.30x + 0.70y}$, ${\chi_B}^V = 1 - \dfrac{0.30x}{0.30x + 0.70y}$;

50.% A: ${\chi_A}^V = \dfrac{x}{x + y}$, ${\chi_B}^V = 1 - {\chi_A}^V$;

80.% A: ${\chi_A}^V = \dfrac{0.80x}{0.80x + 0.20y}$, ${\chi_B}^V = 1 - {\chi_A}^V$

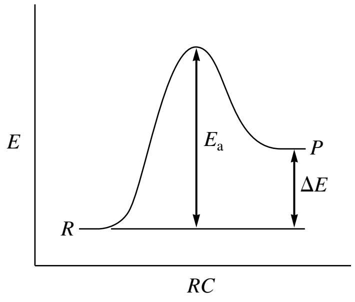
91. 72.7% sucrose and 27.3% NaCl by mass; 0.2 **93.** 0.050 **95.** 44% naphthalene, 56% anthracene **97.** −0.20°C, 100.056°C **99. a.** 46 L; **b.** No; A reverse osmosis system that applies 8.0 atm can purify only water with solute concentrations less than 0.32 mol/L. Salt water has a solute concentration of 2(0.60 M) = 1.2 M ions. The solute concentration of salt water is much too high for this reverse osmosis unit to work. **101.** i = 3.00; $CdCl_2$

Chapter 12

9. 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 orientation is very small, making termolecular steps very unlikely. **11.** All of these choices would affect the rate of the reaction, but only b and c affect the rate by affecting the value of the rate constant k. The value of the rate constant is dependent on temperature. It also depends on the activation energy. A catalyst will change the value of k because the activation energy changes. Increasing the concentration (partial pressure) of either H_2 or NO does not affect the value of k, but it does increase the rate of the reaction because both concentrations appear in the rate law. **13.** The average rate decreases with time because the reverse reaction occurs more frequently as the concentration of products increase. Initially, with no products present, the rate of the forward reaction is at its fastest; but as time goes on, the rate gets slower and slower since products are converting back into reactants. The instantaneous rate will also decrease with time. The only rate that is constant is the initial rate. This is the instantaneous rate taken at $t \approx 0$. At this time, the amount of products is insignificant and the rate of the reaction only depends on the rate of the forward reaction. **15.** When the rate doubles as the concentration quadruples, the order is 1/2. For a reactant that has an order of −1, the rate will decrease by a factor of 1/2 when the concentrations are doubled. **17.** Two reasons are: **a.** the collision must involve enough energy to produce the reaction; i.e., the collision energy must equal or exceed the activation energy. **b.** the relative orientation of the reactants must allow formation of any new bonds necessary to produce products. **19.** P_4: 6.0×10^{-4} mol/L · s; H_2: 3.6×10^{-3} mol/L · s **21. a.** average rate of decomposition of $H_2O_2 = 2.31 \times 10^{-5}$ mol/L · s, rate of production of $O_2 = 1.16 \times 10^{-5}$ mol/L · s; **b.** average rate of decomposition of $H_2O_2 = 1.16 \times 10^{-5}$ mol/L · s, rate of production of $O_2 = 5.80 \times 10^{-6}$ mol/L · s **23. a.** mol/L · s; **b.** mol/L · s; **c.** s^{-1}; **d.** L/mol · s; **e.** L^2/mol^2 · s **25. a.** rate = $k[NO]^2[Cl_2]$; **b.** 1.8×10^2 L^2/mol^2 · min **27. a.** rate = $k[NOCl]^2$; **b.** 6.6×10^{-29} cm^3/molecules · s; **c.** 4.0×10^{-8} L/mol · s **29. a.** first order in Hb and first order in CO; **b.** rate = $k[Hb][CO]$; **c.** 0.280 L/μmol · s; **d.** 2.26 μmol/L · s **31.** rate = $k[H_2O_2]$; $\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$; $k = 8.3 \times 10^{-4}$ s^{-1}; 0.037 M **33.** rate = $k[NO_2]^2$; $\dfrac{1}{[NO_2]} = kt + \dfrac{1}{[NO_2]_0}$; $k = 2.08 \times 10^{-4}$ L/mol · s; 0.131 M **35. a.** rate = k; $[C_2H_5OH] = -kt + [C_2H_5OH]_0$; because slope = $-k$, then $k = 4.00 \times 10^{-5}$ mol/L · s; **b.** 156 s; **c.** 313 s **37.** rate = $k[C_4H_6]^2$; $\dfrac{1}{[C_4H_6]} = kt +$

$\frac{1}{[C_4H_6]_0}$; $k = 1.4 \times 10^{-2}$ L/mol · s **39.** second order; 0.1 M **41.** **a.** $[A] = -kt + [A]_0$; **b.** 1.0×10^{-2} s; **c.** 2.5×10^{-4} M **43.** **a.** 160. s = $t_{1/2}$ for both the first and second half-life; **b.** 532 s **45.** 12.5 s **47.** **a.** 1.1×10^{-2} M; **b.** 0.025 M **49.** **a.** rate = $k[CH_3NC]$; **b.** rate = $k[O_3][NO]$; **c.** rate = $k[O_3]$; **d.** rate = $k[O_3][O]$ **51.** Rate = $k[C_4H_9Br]$; $C_4H_9Br + 2H_2O \rightarrow C_4H_9OH + Br^- + H_3O^+$; the intermediates are $C_4H_9^+$ and $C_4H_9OH_2^+$.

53.



55. 341 kJ/mol **57.** The graph of ln$k$ versus $1/T$ is linear with slope = $-E_a/R = -1.2 \times 10^4$ K; $E_a = 1.0 \times 10^2$ kJ/mol **59.** 9.5×10^{-5} L/mol · s **61.** 51°C **63.** $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$ should have the faster rate. H_3O^+ and OH^- will be electrostatically attracted to each other; Ce^{4+} and Hg_2^{2+} will repel each other (so E_a is much larger). **65.** **a.** NO; **b.** NO_2; **c.** 2.3 **67.** $CH_2D—CH_2D$ should be the product. If the mechanism is possible, then the reaction must be $C_2H_4 + D_2 \rightarrow CH_2DCH_2D$. If we got this product, then we could conclude that this is a possible mechanism. If we got some other product, e.g., CH_3CHD_2, then we would conclude that the mechanism is wrong. Even though this mechanism correctly predicts the products of the reaction, we cannot say conclusively that this is the correct mechanism; we might be able to conceive of other mechanisms that would give the same product as our proposed one. **69.** 215°C **71.** 5.68×10^{18} molecules/cm^3 · s **73.** 1.0×10^2 kJ/mol **75.** 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. **77.** **a.** 115 L^3/mol^3 · s; **b.** 87.0 s; **c.** $[A] = 1.27 \times 10^{-5}$ M, $[B] = 1.00$ M **79.** rate = $\frac{k[I^-][OCl^-]}{[OH^-]}$; $k = 6.0 \times 10^1$ s^{-1} **81.** **a.** first order with respect to both reactants; **b.** rate = $k[NO][O_3]$; **c.** $k' = 1.8$ s^{-1}; $k'' = 3.6$ s^{-1}; **d.** $k = 1.8 \times 10^{-14}$ cm^3/molecules · s **83.** **a.** 25 kJ/mol; **b.** 12 s; **c.**

T	Interval	54 − 2(Intervals)
21.0°C	16.3 s	21°C
27.8°C	13.0 s	28°C
30.0°C	12 s	30.°C

This rule of thumb gives excellent agreement to two significant figures. **85.** **a.** [B] ⩾ [A] so that [B] can be considered constant over the experiments. (This gives us a pseudo-order rate law equation.) **b.** Rate = $k[A]^2[B]$, $k = 0.050$ L^2/mol^2 · s **87.** Rate = $k[A][B]^2$, $k = 1.4 \times 10^{-2}$ L^2/mol^2 · s **89.** 2.20×10^{-5} s^{-1}; 5.99×10^{21} molecules **91.** 1.3×10^{-5} s^{-1}; 112 torr

Chapter 13

9. No, equilibrium is a dynamic process. Both the forward and reverse reactions are occurring at equilibrium, just at equal rates. Thus the forward and reverse reactions will distribute ^{14}C atoms between CO and CO_2. **11.** 4 molecules H_2O, 2 molecules CO, 4 molecules H_2, and 4 molecules CO_2 are present at equilibrium. **13.** K and K_p are equilibrium constants as determined by the law of mass action. For K, the units used for concentrations are mol/L, 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. Q is of use 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 determine what has to be the net charge for the system to get to equilibrium. **15.** We always try to make good assumptions that simplify the math. In some problems, we can set up the problem so that the net change, x, that must occur to reach equilibrium is a small number. This comes in handy when you have expressions like $0.12 - x$ or $0.727 + 2x$. Since x is small, we assume that it makes little difference when subtracted from or added to some relatively big number. When this is true, $0.12 - x \approx 0.12$ and $0.727 + 2x \approx 0.727$. If the assumption holds by the 5% rule, then the assumption is assumed valid. The 5% rule refers to x (or $2x$ or $3x$, etc.) that was assumed small compared to some number. If x (or $2x$ or $3x$, etc.) is less than 5% of the number the assumption was made against, then the assumption will be assumed valid. If the 5% rule fails to work, one can generally use a math procedure called the method of successive approximations to solve the quadratic or cubic equation.

17. **a.** $K = \frac{[NO]^2}{[N_2][O_2]}$; **b.** $K = \frac{[NO_2]^2}{[N_2O_4]}$; **c.** $K = \frac{[SiCl_4][H_2]^2}{[SiH_4][Cl_2]^2}$; **d.** $K = \frac{[PCl_3]^2[Br_2]^3}{[PBr_3]^2[Cl_2]^3}$ **19.** **a.** 0.11; **b.** 77; **c.** 8.8; **d.** 4.6×10^{-4} **21.** 4.0×10^6 **23.** 1.7×10^{-5} **25.** 6.3×10^{-13} **27.** 1.1×10^3 **29.** **a.** $K = \frac{[H_2O]}{[NH_3]^2[CO_2]}$, $K_p = \frac{P_{H_2O}}{P_{NH_3}^2 \times P_{CO_2}}$; **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.** $K = \frac{[H_2O]}{[H_2]}$, $K_p = \frac{P_{H_2O}}{P_{H_2}}$ **31.** 8.0×10^9 **33.** **a.** $Q > K$, so reaction shifts left to reach equilibrium. **b.** $Q = K$, so reaction is at equilibrium. **c.** $Q < K$, so reaction shifts right to reach equilibrium. **35.** **a.** decrease; **b.** no change; **c.** no change; **d.** increase **37.** 8.0×10^{-2} M **39.** 3.4 **41.** 0.056 **43.** $[N_2]_0 = 10.0$ M, $[H_2]_0 = 11.0$ M **45.** $[SO_3] = [NO] = 1.06$ M; $[SO_2] = [NO_2] = 0.54$ M **47.** 7.8×10^{-2} atm **49.** $P_{SO_2} = 0.38$ atm; $P_{O_2} = 0.44$ atm; $P_{SO_3} = 0.12$ atm **51.** **a.** $[NO] = 0.032$ M, $[Cl_2] = 0.016$ M, $[NOCl] = 1.0$ M; **b.** $[NO] = [NOCl] = 1.0$ M, $[Cl_2] = 1.6 \times 10^{-5}$ M; **c.** $[NO] = 8.0 \times 10^{-3}$ M, $[Cl_2] = 1.0$ M, $[NOCl] = 2.0$ M **53.** $[CO_2] = 0.39$ M, $[CO] = 8.6 \times 10^{-3}$ M, $[O_2] = 4.3 \times 10^{-3}$ M **55.** 0.27 atm **57.** **a.** no effect; **b.** shifts left; **c.** shifts right **59.** **a.** right **b.** right; **c.** no effect; **d.** left; **e.** no effect **61.** **a.** left; **b.** right; **c.** left; **d.** no effect; **e.** no effect; **f.** right **63.** increase **65.** 2.6×10^{81} **67.** **a.** 0.379 atm; **b.** 0.786 **69.** **a.** 1.16 atm; **b.** 0.10 atm; **c.** 2.22 atm; **d.** 91.4% **71.** $[H_2] = [F_2] = 0.0251$ M; $[HF] = 0.450$ M **73.** Added OH^- reacts with H^+ to produce H_2O. As H^+ is removed, the reaction shifts right to produce more H^+ and CrO_4^{2-}. Because more CrO_4^{2-} is produced, the solution turns yellow. **75.** 9.0×10^{-3} M **77.** $P_{PCl_3} = P_{Cl_2} = 0.2230$ atm, $P_{PCl_5} = 0.0259$ atm; $K_p = 1.92$ **79.** $[NOCl] = 2.0$ M, $[NO] = 0.050$ M, $[Cl_2] = 0.025$ M **81.** 2.1×10^{-3} atm **83.** $P_{NO_2} = 0.704$ atm, $P_{N_2O_4} = 0.12$ atm **85.** 0.63 **87.** 0.240 atm **89.** 9.17×10^{-3} **91.** 192 g; 0.25 atm **93.** $C_{10}H_8$; 0.0919%

Chapter 14

17. 10.78 (4 significant figures); 6.78 (3 significant figures); 0.78 (2 significant figures); A pH value is a logarithm. The numbers to the left of the decimal place identify the power of 10 to which $[H^+]$ is expressed in scientific notation—for example, 10^{-11}, 10^{-7}, 10^{-1}. The number of decimal places in a pH value identifies the number of significant figures in $[H^+]$. In all three pH values, the $[H^+]$ should be expressed only to two significant figures since these pH values have only two decimal places. **19.** **a.** These would be 0.10 M solutions of strong acids like HCl, HBr, HI, HNO_3, H_2SO_4 or $HClO_4$. **b.** These are salts of the conjugate acids of the bases in Table 14.3. These conjugate acids are all weak acids. Three examples would be 0.10 M solutions of NH_4Cl, $CH_3NH_3NO_3$, and $C_2H_5NH_3Br$. Note that the anions used to form these salts are conjugate bases of strong acids; this is because they have no acidic or basic properties in water (with the exception of HSO_4^-, which has weak acid properties). **c.** These would be 0.10 M solutions of strong bases like 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 14.2. The conjugate bases of weak acids are weak bases themselves. Three examples would be 0.10 *M* solutions of $NaClO_2$, $KC_2H_3O_2$, 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 in the list of the strong bases listed in part c that 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 the strong bases. These ions have no acidic/basic properties in water so salts of these ions are neutral. Three examples would be 0.10 *M* solutions of 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.

21. a. $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ or

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K = K_w = [H^+][OH^-]$$

b. $HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$ or

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K = K_a = \frac{[H^+][F^-]}{[HF]}$$

c. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$

$$K = K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

23. a. This expression holds true for solutions of strong acids having a concentration greater than 1.0×10^{-6} *M*. For example, 0.10 *M* HCl, 7.8 *M* HNO_3, and 3.6×10^{-4} *M* $HClO_4$ are solutions where this expression holds true. **b.** This expression holds true for solutions of weak acids where the two normal assumptions hold. The two assumptions are that the contribution of H^+ from water is negligible and that the acid is less than 5% dissociated in water (from the assumption that x is small compared to some number). This expression will generally hold true for solutions of weak acids having a K_a value less than 1×10^{-4}, as long as there is a significant amount of weak acid present. Three example solutions are 1.5 *M* $HC_2H_3O_2$, 0.10 *M* HOCl, and 0.72 *M* NH_4NO_3. **c.** This expression holds true for strong bases that donate 2 OH^- ions per formula unit. As long as the concentration of the base is above 5×10^{-7} *M*, this expression will hold true. Three examples are 5.0×10^{-3} *M* $Ca(OH)_2$, 2.1×10^{-4} *M* $Sr(OH)_2$, and 9.1×10^{-5} *M* $Ba(OH)_2$. **d.** This expression holds true for solutions of weak bases where the two normal assumptions hold. The assumptions are that the OH^- contribution from water is negligible and that the base is less than 5% ionized in water. For the 5% rule to hold, you generally need bases with $K_b < 1 \times 10^{-4}$ and concentrations of weak base greater than 0.10 *M*. Three examples are 0.10 *M* NH_3, 0.54 *M* $C_6H_5NH_2$, and 1.1 *M* C_5H_5N. **25.** One reason HF is a weak acid is that the H—F bond is unusually strong and thus, is difficult to break. This contributes to the reluctance of the HF molecules to dissociate in water. **27. a.** $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$ or $HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-(aq)$; water is commonly omitted from K_a reactions. **b.** $CH_3CH_2CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CH_2CO_2^-(aq)$; **c.** $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$ **29. a.** H_2O, base; H_2CO_3, acid; H_3O^+, conjugate acid; HCO_3^-, conjugate base; **b.** $C_5H_5NH^+$, acid; H_2O, base; C_5H_5N, conjugate base; H_3O^+, conjugate acid; **c.** HCO_3^-, base; $C_5H_5NH^+$, acid; H_2CO_3, conjugate acid; C_5H_5N, conjugate base **31. a.** $HClO_4$, strong acid; **b.** HOCl, weak acid; **c.** H_2SO_4, strong acid; **d.** H_2SO_3, weak acid **33.** $HClO_4 > HClO_2 > NH_4^+ > H_2O$ **35. a.** HCl; **b.** HNO_2; **c.** HCN since it has a larger K_a value. **37. a.** 1.0×10^{-7} *M*, neutral; **b.** 12 *M*, basic; **c.** 8.3×10^{-16} *M*, acidic; **d.** 1.9×10^{-10} *M*, acidic **39. a.** endothermic; **b.** $[H^+] = [OH^-] = 2.34 \times 10^{-7}$ *M* **41.** [37] **a.** pH = pOH = 7.00; **b.** pH = 15.08, pOH = −1.08; **c.** pH = −1.08, pOH = 15.08; **d.** pH = 4.27, pOH = 9.73 [38] **a.** pH = 14.18, pOH = −0.18; **b.** pH = −0.44, pOH = 14.44; **c.** pH = pOH = 7.00; **d.** pH = 10.85, pOH = 3.14 **43. a.** pH = 6.88, pOH = 7.12, $[H^+] = 1.3 \times 10^{-7}$ *M*, $[OH^-] = 7.6 \times 10^{-8}$ *M*, acidic; **b.** pH = 0.92, pOH = 13.08, $[H^+] = 0.12$ *M*, $[OH^-] = 8.4 \times 10^{-14}$ *M*, acidic; **c.** pH = 10.89, pOH = 3.11, $[H^+] = 1.3 \times 10^{-11}$ *M*, $[OH^-] = 7.8 \times 10^{-4}$ *M*, basic; **d.** pH = pOH = 7.00, $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ *M*, neutral **45.** pOH = 11.9, $[H^+] = 8 \times 10^{-3}$ *M*, $[OH^-] = 1 \times 10^{-12}$ *M*, acidic **47. a.** H^+, ClO_4^-, H_2O; 0.602; **b.** H^+, NO_3^-, H_2O; 0.602 **49.** $[H^+] = 0.088$ *M*, $[OH^-] = 1.1 \times 10^{-13}$ *M*, $[Cl^-] = 0.013$ *M*, $[NO_3^-] = 0.075$ *M* **51.** Add 4.2 mL of 12 *M* HCl to water with mixing; add enough water to bring the solution volume to 1600 mL. **53. a.** HNO_2 and H_2O, 2.00; **b.** $HC_2H_3O_2$ and H_2O, 2.68 **55.** $[H^+] = [CH_3COO^-] = 5.8 \times 10^{-4}$ *M*, $[CH_3COOH] = 0.0181$ *M*, pH = 3.24 **57.** $[H^+] = [F^-] = 3.5 \times 10^{-3}$ *M*, $[OH^-] = 2.9 \times 10^{-12}$ *M*, $[HF] = 0.017$ *M*, 2.46 **59.** 1.96 **61. a.** 1.00; **b.** 1.30 **63. a.** 0.60%; **b.** 1.9%; **c.** 5.8%; **d.** Dilution shifts equilibrium to the side with the greater number of particles (% dissociation increases). **e.** $[H^+]$ also depends on initial concentration of weak acid. **65.** 1.4×10^{-4} **67.** 3.5×10^{-4} **69.** 0.024 *M*

71. a. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]};$$

b. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

73. $NH_3 > C_5H_5N > H_2O > NO_3^-$ **75. a.** $C_6H_5NH_2$; **b.** $C_6H_5NH_2$; **c.** OH^-; **d.** CH_3NH_2 **77. a.** 13.00; **b.** 7.00; **c.** 14.30 **79. a.** K^+, OH^-, and H_2O, 0.015 *M*, 12.18; **b.** Ba^{2+}, OH^-, and H_2O, 0.030 *M*, 12.48 **81.** 0.16 g **83.** NH_3 and H_2O, 1.6×10^{-3} *M*, 11.20 **85. a.** $[OH^-] = 8.9 \times 10^{-3}$ *M*, $[H^+] = 1.1 \times 10^{-12}$ *M*, 11.96; **b.** $[OH^-] = 4.7 \times 10^{-5}$ *M*, $[H^+] = 2.1 \times 10^{-10}$ *M*, 9.68 **87.** 12.00 **89. a.** 1.3%; **b.** 4.2% **91.** 9.2×10^{-7}

93. $H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq) \qquad K_{a_1}$ reaction

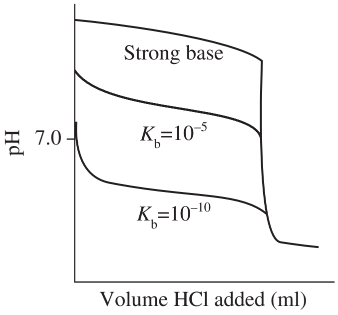
$HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H^+(aq) \qquad K_{a_2}$ reaction

95. a. 1.62; **b.** 3.68 **97.** −0.30 **99.** $HCl > NH_4Cl > KCl > KCN > KOH$ **101.** OCl^- **103.** $[HN_3] = [OH^-] = 2.3 \times 10^{-6}$ *M*, $[Na^+] = 0.010$ *M*, $[N_3^-] = 0.010$ *M*, $[H^+] = 4.3 \times 10^{-9}$ *M* **105. a.** 5.82; **b.** 10.95 **107.** NaF **109.** 3.08 **111. a.** neutral; **b.** basic; $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$; **c.** acidic; $C_5H_5NH^+ \rightleftharpoons C_5H_5N + H^+$; **d.** acidic because NH_4^+ is a stronger acid than NO_2^- is a base; $NH_4^+ \rightleftharpoons NH_3 + H^+$; $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$; **e.** basic; $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$; **f.** basic because OCl^- is a stronger base than NH_4^+ is an acid; $OCl^- + H_2O \rightleftharpoons HOCl + OH^-$, $NH_4^+ \rightleftharpoons NH_3 + H^+$ **113. a.** $HIO_3 < HBrO_3$; as the electronegativity of the central atom increases, acid strength increases. **b.** $HNO_2 < HNO_3$; as the number of oxygen atoms attached to the central atom increases, acid strength increases. **c.** HOI < HOCl; same reasoning as in part a. **d.** $H_3PO_3 < H_3PO_4$; same reasoning as in part b. **115. a.** $H_2O < H_2S < H_2Se$; acid strength increases as bond energy decreases. **b.** $CH_3CO_2H < FCH_2CO_2H < F_2CHCO_2H < F_3CCO_2H$; as the electronegativity of the neighboring atoms increases, acid strength increases. **c.** $NH_4^+ < HONH_3^+$; same reasoning as in part b. **d.** $NH_4^+ < PH_4^+$; same reasoning as in part a. **117. a.** basic; $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$; **b.** acidic; $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$; **c.** acidic; $Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$ **119. a.** $B(OH)_3$, acid; H_2O, base; **b.** Ag^+, acid; NH_3, base; **c.** BF_3, acid; F^-, base **121.** $Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l)$; $Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ **123.** Fe^{3+}; because it is smaller with a greater positive charge, Fe^{3+} will be more strongly attracted to a lone pair of electrons from a Lewis base. **125.** 990 mL H_2O **127. a.** 2.80; **b.** 1.1×10^{-3} *M* **129.** NH_4Cl **131.** 4.2×10^{-2} *M* **133.** 3.00 **135. a.** 2.62; **b.** 2.4%; **c.** 8.48 **137. a.** 1.66; **b.** Fe^{2+} ions will produce a less acidic solution (higher pH) due to the lower charge on Fe^{2+} as compared with Fe^{3+}. As the charge on a metal ion increases, acid strength of the hydrated ion increases. **139.** acidic; $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$; 1.54 **141. a.** $Hb(O_2)_4$ in lungs, HbH_4^{4+} in cells; **b.** Decreasing $[CO_2]$ will decrease $[H^+]$, favoring $Hb(O_2)_4$ formation. Breathing into a bag raises $[CO_2]$. **c.** $NaHCO_3$ lowers the acidity from accumulated CO_2.

143. a. H_2SO_3; **b.** $HClO_3$; **c.** H_3PO_3; NaOH and KOH are ionic compounds composed of either Na^+ or K^+ cations and OH^- anions. When soluble ionic compounds dissolve in water, they form the ions from which they are formed. The acids in this problem are all covalent compounds. When these acids dissolve in water, the covalent bond between oxygen and hydrogen breaks to form H^+ ions. **145.** 7.20. **147.** 4540 mL **149.** 4.17 **151.** 0.022 *M* **153.** 2.5×10^{-3} **155.** PO_4^{3-}, $K_b = 0.021$; HPO_4^{2-}, $K_b = 1.6 \times 10^{-7}$; $H_2PO_4^-$, $K_b = 1.3 \times 10^{-12}$; from the K_b values, PO_4^{3-} is the strongest base. **157. a.** basic; **b.** acidic; **c.** basic; **d.** acidic; **e.** acidic **159.** 1.0×10^{-3} **161.** 5.4×10^{-4} **163.** 3.36

Chapter 15

13. When an acid dissociates or when a salt dissolves, ions are produced. A common ion is when one of the product ions in a particular equilibrium is added from an outside source. For a weak acid dissociating to its conjugate base and H^+, the common ion would be the conjugate base; this would be added by dissolving a soluble salt of the conjugate base into the acid solution. The presence of the conjugate base from an outside source shifts the equilibrium to the left so less acid dissociates. For the K_{sp} reaction of a salt dissolving into its respective ions, the common ion would be if one of the ions in the salt was added from an outside source. When a common ion is present, the K_{sp} equilibrium shifts to the left resulting in less of the salt dissolving into its ions. **15.** The more weak acid and conjugate base present, the more H^+ and/or OH^- that can be absorbed by the buffer without significant pH change. When the concentrations of weak acid and conjugate base are equal (so that $pH = pK_a$), the buffer system is equally efficient at absorbing either H^+ or OH^-. If the buffer is overloaded with weak acid or with conjugate base, then the buffer is not equally efficient at absorbing either H^+ or OH^-. **17.** The three key points to emphasize in your sketch are the initial pH, pH at the halfway point to equivalence, and the pH at the equivalence point. For the two weak bases titrated, $pH = pK_a$ at the halfway point to equivalence (50.0 mL HCl added) because [weak base] = [conjugate acid] at this point. For the initial pH, the strong base has the highest pH (most basic), while the weakest base has the lowest pH (least basic). At the equivalence point, the strong base titration has pH = 7.0. The weak bases titrated have acidic pHs at the equivalence point because the conjugate acids of the weak bases titrated are the major species present. The weakest base has the strongest conjugate acid so its pH will be lowest (most acidic) at the equivalence point.



19. i. This is the result when you have a salt that breaks up into two ions. Examples of these salts (but not all) would be AgCl, $SrSO_4$, $BaCrO_4$, and $ZnCO_3$ **ii.** This is the result when you have a salt that breaks up into three ions, either two cations and one anion or one cation and two anions. Some examples are SrF_2, Hg_2I_2, and Ag_2SO_4. **iii.** This is the result when you have a salt that breaks up into four ions, either three cations and one anion (Ag_3PO_4) or one cation and three anions (ignoring the hydroxides, there are no examples of this type of salt in Table 15.4). **iv.** This is the result when you have a salt that breaks up into five ions, either three cations and two anions [$Sr_3(PO_4)_2$] or two cations and three anions (no examples of this type of salt are in Table 15.4). **21.** When strong acid or strong base is added to a sodium bicarbonate/sodium carbonate buffer mixture, the strong acid/base is neutralized. The reaction goes to completion resulting in the strong acid/base being replaced with a weak acid/base. This results in a new buffer solution. The reactions are $H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$; $OH^-(aq) + HCO_3^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$ **23. a.** 2.96; **b.** 8.94; **c.** 7.00; **d.** 4.89 **25.** 1.1% vs. 1.3×10^{-2}% dissociated; the presence of $C_3H_5O_2^-$ in solution 23d greatly inhibits the dissociation of $HC_3H_5O_2$. This is called the *common ion effect.* **27. a.** 1.70; **b.** 5.49; **c.** 1.70; **d.** 4.71 **29. a.** 4.29; **b.** 12.30; **c.** 12.30; **d.** 5.07 **31.** solution d; solution d is a buffer solution that resists pH changes. **33.** 3.40 **35.** 3.48; 3.22 **37.** 4.36 **39. a.** 7.97; **b.** 8.73; both solutions have an initial pH = 8.77. The two solutions differ in their buffer capacity. Solution b with the larger concentrations has the greater capacity to resist pH change. **41.** 15 g **43. a.** 0.19; **b.** 0.59; **c.** 1.0; **d.** 1.9 **45.** HOCl; there are many possibilities. One possibility is a solution with [HOCl] = 1.0 *M* and [NaOCl] = 0.35 *M*. **47.** solution d **49. a.** 1.0 mol; **b.** 0.30 mol; **c.** 1.3 mol **51. a.** ~22 mL base added; **b.** buffer region is from ~1 mL to ~21 mL base added. The maximum buffering region would be from ~5 mL to ~17 mL of base added with the halfway point to equivalence (~11 mL) as the best buffer point. **c.** ~11 mL base added; **d.** 0 mL base added; **e.** ~22 mL base added (the stoichiometric point); **f.** any point after the stoichiometric point (volume base added > ~22 mL) **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.** 2.1×10^{-6} **65. a.** yellow; **b.** 8.0; **c.** blue **67.** phenolphthalein **69.** Phenol red is one possible indicator for the titration in Exercise 53. Phenolphthalein is one possible indicator for the titration in Exercise 55. **71.** Phenolphthalein is one possible indicator for Exercise 57. Bromcresol green is one possible indicator for Exercise 59. **73.** The pH is between 5 and 8. **75. a.** $AgC_2H_3O_2(s) \rightleftharpoons Ag^+(aq) + C_2H_3O_2^-(aq)$; $K_{sp} = [Ag^+][C_2H_3O_2^-]$; **b.** $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$; $K_{sp} = [Al^{3+}][OH^-]^3$; **c.** $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$; $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ **77. a.** 2.3×10^{-9}; **b.** 8.20×10^{-19} **79.** 3.92×10^{-5} **81. a.** 1.6×10^{-5} mol/L; **b.** 9.3×10^{-5} mol/L; **c.** 6.5×10^{-7} mol/L **83.** 3.30×10^{-43} **85.** 2.5×10^{-22} mol/L **87. a.** CaF_2; **b.** $FePO_4$ **89. a.** 4×10^{-17} mol/L; **b.** 4×10^{-11} mol/L; **c.** 4×10^{-29} mol/L **91.** 2.3×10^{-11} mol/L **93.** 1.5×10^{-19} g **95.** 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 because Cl^- and I^- are terrible bases (the conjugate bases of strong acids).

$$Ag_3PO_4(s) + H^+(aq) \longrightarrow 3Ag^+(aq) + HPO_4^{2-}(aq) \xrightarrow{\text{excess } H^+} 3Ag^+(aq) + H_3PO_4(aq)$$

$$CaCO_3(s) + H^+(aq) \longrightarrow Ca^{2+}(aq) + HCO_3^-(aq) \xrightarrow{\text{excess } H^+} Ca^{2+}(aq) + H_2CO_3(aq)\,[H_2O(l) + CO_2(g)]$$

$$CdCO_3(s) + H^+(aq) \longrightarrow Cd^{2+}(aq) + HCO_3^-(aq) \xrightarrow{\text{excess } H^+} Cd^{2+}(aq) + H_2CO_3(aq)\,[H_2O(l) + CO_2(g)]$$

$$Sr_3(PO_4)_2(s) + 2H^+(aq) \longrightarrow 3Sr^{2+}(aq) + 2HPO_4^{2-}(aq) \xrightarrow{\text{excess } H^+} 3Sr^{2+}(aq) + 2H_3PO_4(aq)$$

97. yes; $Q = 1.9 \times 10^{-4} > K_{sp}$ **99.** $[K^+] = 0.160\ M$, $[C_2O_4^{2-}] = 3.3 \times 10^{-7}\ M$, $[Ba^{2+}] = 0.0700\ M$, $[Br^-] = 0.300\ M$ **101.** $[Ag^+] > 5.6 \times 10^{-5}\ M$

103. a.

$$\begin{array}{lcll}
Ni^{2+} + CN^- & \rightleftharpoons & NiCN^+ & K_1 \\
NiCN^+ + CN^- & \rightleftharpoons & Ni(CN)_2 & K_2 \\
Ni(CN)_2 + CN^- & \rightleftharpoons & Ni(CN)_3^- & K_3 \\
Ni(CN)_3^- + CN^- & \rightleftharpoons & Ni(CN)_4^{2-} & K_4 \\
\hline
Ni^{2+} + 4CN^- & \rightleftharpoons & Ni(CN)_4^{2-} &
\end{array}$$

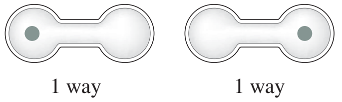
b.

$$\begin{array}{lcll}
V^{3+} + C_2O_4^{2-} & \rightleftharpoons & VC_2O_4^+ & K_1 \\
VC_2O_4^+ + C_2O_4^{2-} & \rightleftharpoons & V(C_2O_4)_2^- & K_2 \\
V(C_2O_4)_2^- + C_2O_4^{2-} & \rightleftharpoons & V(C_2O_3)^{3-} & K_2 \\
\hline
V^{3+} + 3\,C_2O_4^{2-} & \rightleftharpoons & V(C_2O_4)_3^{3-} &
\end{array}$$

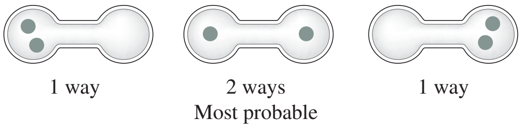
105. 6.2×10^5 **107.** $Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$ (orange precipitate); $HgI_2(s) + 2I^-(aq) \rightarrow HgI_4^{2-}(aq)$ (soluble complex ion) **109.** $3.3 \times 10^{-32}\ M$ **111. a.** 1.2×10^{-8} mol/L; **b.** 1.5×10^{-4} mol/L; **c.** The presence of NH_3 increases the solubility of AgI. Added NH_3 removes Ag^+ from solution by forming the complex ion $Ag(NH_3)_2^+$. As Ag^+ is removed, more AgI will dissolve to replenish the Ag^+ concentration. **113.** 4.7×10^{-2} mol/L **115.** Test tube 1: added Cl^- reacts with Ag^+ to form the 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 the soluble complex ion $Ag(NH_3)_2^+$. As this complex ion forms, Ag^+ is removed from solution, which causes $AgCl(s)$ to dissolve. When enough NH_3 is added, then 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, Ag^+ ions are released to solution, which can then react with Cl^- to reform $AgCl(s)$. The equations are $Ag(NH_3)_2^+(aq) + 2H^+(aq) \rightarrow Ag^+(aq) + 2NH_4^+(aq)$ and $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. **117.** $pOH = pK_b + \log\frac{[\text{acid}]}{[\text{base}]}$ **119. a.** 10.44; **b.** 10.74 **121. a.** potassium fluoride + HCl; **b.** benzoic acid + NaOH; **c.** acetic acid + sodium acetate; **d.** HOCl + NaOH; **e.** ammonium chloride + NaOH **123. a.** 1.8×10^9; **b.** 5.6×10^4; **c.** 1.0×10^{14} **125.** 4.4 L **127.** 180. g/mol; 3.3×10^{-4}; assume acetylsalicylic acid is a weak monoprotic acid. **129.** 65 mL **131.** 0.210 M **133. a.** 1.6×10^{-6}; **b.** 0.056 mol/L **135.** 2.7×10^{-5} mol/L; the solubility of hydroxyapatite will increase as a solution gets more acidic, since both phosphate and hydroxide can react with H^+. 6×10^{-8} mol/L; the hydroxyapatite in the tooth enamel is converted to the less soluble fluorapatite by fluoride-treated water. The less soluble fluorapatite will then be more difficult to dissolve, making teeth less susceptible to decay. See Chemical Impact on "The Chemistry of Teeth." **137. a.** 6.7×10^{-6} mol/L; **b.** 1.2×10^{-13} mol/L; **c.** $Pb(OH)_2(s)$ will not form since $Q < K_{sp}$ **139.** 49 mL **141.** 3.9 L **143. a.** 200.0 mL; **b.** i. H_2A, H_2O; ii. H_2A, HA^-, H_2O, Na^+; iii. HA^-, H_2O, Na^+; iv. HA^-, A^{2-}, H_2O, Na^+; v. A^{2-}, H_2O, Na^+; vi. A^{2-}, H_2O, Na^+, OH^-; **c.** $K_{a_1} = 1 \times 10^{-4}$; $K_{a_2} = 1 \times 10^{-8}$ **145.** $pH \approx 5.0$; $K_a \approx 1 \times 10^{-10}$ **147.** 3 M **149. a.** 5.8×10^{-4} mol/L; **b.** Greater; F^- is a weak base ($K_b = 1.4 \times 10^{-11}$), so some of the F^- is removed by reaction with water. As F^- is removed, more SrF_2 will dissolve; **c.** 3.5×10^{-3} mol/L **151.** 3.00 **153.** 2.78

Chapter 16

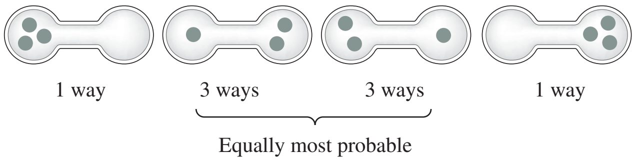
7. Living organisms need an external energy source to produce the necessary "ordering." **9.** ΔS_{univ} **11.** As any process occurs, ΔS_{univ} will increase; ΔS_{univ} cannot decrease. Time also goes in one direction, just as ΔS_{univ} goes in one direction. **13.** Possible arrangements for one molecule:



Both are equally probable.
Possible arrangements for two molecules:



Possible arrangement for three molecules:



15. 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 when these ions are placed in water. The hydrating water molecules must be in a highly ordered state when surrounding these anions. **17.** One can determine $\Delta S°$ and $\Delta H°$ for the reaction using the standard entropies and standard enthalpies of formation in Appendix 4, then use the equation $\Delta G° = \Delta H° - T\Delta S°$. One can also use the standard free energies of formation in Appendix 4. And finally, one can use Hess's law to calculate $\Delta G°$. Here, reactions having known $\Delta G°$ values are manipulated to determine $\Delta G°$ for a different reaction. For temperatures other than 25(C, $\Delta G°$ is estimated using the $\Delta G° = \Delta H° - T\Delta S$ equation. The assumptions made are that the $\Delta H°$ and $\Delta S°$ values determined from Appendix 4 data are temperature independent. We use the same $\Delta H°$ and $\Delta S°$ values as determined when $T = 25°C$, then plug in the new temperature in Kelvin into the equation to estimate $\Delta G°$ at the new temperature. **19.** a, b, c **21.** We draw all of the possible arrangements of the two particles in the three levels.

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. **23. a.** H_2 at 100°C and 0.5 atm; **b.** N_2 at STP; **c.** $H_2O(l)$ **25. a.** negative; **b.** positive **27.** $\Delta G < 0$ for b, c, d **29.** 89.3 J/K · mol **31. a.** yes ($\Delta G < 0$); **b.** 196 K **33. a.** negative; **b.** positive; **c.** negative; **d.** positive **35. a.** $C_{graphite}(s)$; **b.** $C_2H_5OH(g)$; **c.** $CO_2(g)$ **37. a.** negative, −186 J/K; **b.** positive, 187 J/K; **c.** hard to predict since $\Delta n = 0$.; 138 J/K **39.** 262 J/K · mol **41. a.** ΔH and ΔS are both positive; **b.** $S_{rhombic}$ **43. a.** ΔH and ΔS are both negative; **b.** low temperatures **45.** **a.** $\Delta H° = -803$ kJ, $\Delta S° = -4$ J/K, $\Delta G° = -802$ kJ; **b.** $\Delta H° = 2802$ kJ, $\Delta S° = -262$ J/K, $\Delta G° = 2880.$ kJ; **c.** $\Delta H° = -416$ kJ, $\Delta S° = -209$ J/K, $\Delta G° = -354$ kJ; **d.** $\Delta H° = -176$ kJ, $\Delta S° = -284$ J/K, $\Delta G° = -91$ kJ **47.** -5.40 kJ; 328.6 K; $\Delta G°$ is negative below 328.6 K. **49.** $CH_4(g) + CO_2(g) \rightarrow CH_3CO_2H(l)$, $\Delta H° = -16$ 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. It should be run at temperatures below 622 K. **51.** -817 kJ **53.** -731 kJ/mol **55.** yes **57.** -188 kJ **59.** **a.** shifts right; **b.** no shift since the reaction is at equilibrium; **c.** shifts left **61.** 8.72; 0.0789 **63.** 140 kJ **65.** -71 kJ/mol **67.** $\Delta H° = 1.1 \times 10^5$ J/mol; $\Delta S° = 330$ J/K · mol; The major difference in the plot is the slope of the line. An endothermic process has a negative slope for the $\ln(K)$ versus $1/T$ plot, whereas an exothermic process has a positive slope. **69.** -447 J/K · mol **71.** decreases; ΔS will be negative since 2 mol of gaseous reactants form 1 mol of gaseous product. For ΔG to be negative, ΔH must be negative (exothermic). For exothermic reactions, K decreases as T increases, so the ratio of the partial pressure of PCl_5 to the partial pressure of PCl_3 will decrease. **73.** 43.7 K **75.** 60 **77.** **a.** 1.8×10^4 J/mol; shifts left; **b.** 0; no shift since at equilibrium; **c.** -1.1×10^4 J/mol; shifts right; **d.** 0; no shift since at equilibrium; **e.** 2×10^3 J/mol; shifts left **79.** **a.** 2.22×10^5; **b.** 94.3; **c.** 0.29 mol ATP **81.** ΔS is more favorable for reaction 2 than for reaction 1, resulting in $K_2 > K_1$. In reaction 1, seven particles in solution form one particle. In reaction 2, four particles form one, which results in a smaller decrease in disorder than for reaction 1. **83.** 725 K **85.** $\Delta H° = 286$ 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 9.5×10^{17} L of air. Equilibrium is probably not maintained under the conditions because the concentration of ozone is not large enough to maintain equilibrium **87.** **a.** Because $k_f = A\exp\left(\frac{-E_a}{RT}\right)$ and $k_r = A\exp\left(\frac{-(E_a - \Delta G°)}{RT}\right)$, Because $\frac{k_f}{k_r} = \exp\left(\frac{-E_a}{RT} + \frac{(E_a - \Delta G°)}{RT}\right) = \exp\left(\frac{-\Delta G°}{RT}\right)$. Because $K = \exp\left(\frac{-\Delta G°}{RT}\right)$, then $K = \frac{k_f}{k_r}$. **b.** A catalyst increases the value of the rate constant (increases rate) by lowering the activation energy. For the equilibrium constant K to remain constant, both k_f and k_r must increase by the same factor. Therefore, a catalyst must increase the rate of both the forward and the reverse reactions. **89.** **a.** 0.333; **b.** $P_A = 1.50$ atm; $P_B = 0.50$ atm; **c.** $\Delta G = \Delta G° + RT\ln(P_B/P_A) = 2722\text{ J} - 2722\text{ J} = 0$ **91.** at least 7.5 torr **93.** 16 g **95.** 61 kJ **97.** -4.1 kJ/mol

Chapter 17

13. Oxidation: increase in oxidation number, loss of electrons; reduction: decrease in oxidation number, gain of electrons **15.** Reactions a, b, and c are oxidation–reduction reactions.

Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. H_2O	CH_4	CH_4(C)	H_2O(H)
b. $AgNO_3$	Cu	Cu	$AgNO_3$(Ag)
c. HCl	Zn	Zn	HCl(H)

17. Magnesium is an alkaline earth metal; Mg will oxidize to Mg^{2+}. The oxidation state of hydrogen in HCl is +1. To be reduced, the oxidation state of H must decrease. The obvious choice for the hydrogen product is $H_2(g)$ where hydrogen has a zero oxidation state. The balanced reaction is: $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$. Mg goes from the 0 to the +2 oxidation state by losing two electrons. Each H atom goes from the 0 to the −1 oxidation state by gaining one electron. Since there are two H atoms in the balanced equation, then a total of two electrons are gained by the H atoms. Hence, two electrons are transferred in the balanced reaction. When the electrons are transferred directly from Mg to H^+, no work is obtained. In order to harness this reaction to do useful work, we must control the flow of electrons through a wire. This is accomplished by making a galvanic cell which separates the reduction reaction from the oxidation reaction in order to control the flow of electrons through a wire to produce a voltage. **19.** An extensive property is one that depends on the amount of substance. The free energy change for a reaction depends on whether 1 mol of product is produced or 2 mol of product is produced or 1 million mol of product is produced. This is not the case for cell potentials which do not depend on the amount of substance. The equation that relates ΔG to E is $\Delta G = -nFE$. It is the n term that converts the intensive property E into the extensive property ΔG. The n is the number of mol of electrons transferred in the balanced reaction that ΔG is associated with. **21.** A potential hazard when jump-starting a car is that the electrolysis of $H_2O(l)$ can occur. When $H_2O(l)$ is electrolyzed, the products are the explosive gas mixture of $H_2(g)$ and $O_2(g)$. A spark produced during jump starting a car could ignite any $H_2(g)$ and $O_2(g)$ produced. Grounding the jumper cable far from the battery minimizes the risk of a spark nearby the battery where $H_2(g)$ and $O_2(g)$ could be collecting. **23.** You need to know the identity of the metal so you know which molar mass to use. You need to know the oxidation state of metal ion in the salt so the mol of electrons transferred can be determined. And finally, you need to know the amount of current and the time the current was passed through the electrolytic cell. If you know these four quantities, then the mass of metal plated out can be calculated. **25.** See Figure 17.3 of the text 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. For each of the following answers, all solutes are 1.0 M and all gases are at 1.0 atm. **a.** $7H_2O(l) + 2Cr^{3+}(aq) + 3Cl_2(g) \rightarrow Cr_2O_7^{2-}(aq) + 6Cl^-(aq) + 14H^+(aq)$; 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.** $Cu^{2+}(aq) + Mg(s) \rightarrow Cu(s) + Mg^{2+}(aq)$; cathode: Cu electrode; Cu^{2+} in solution; anode: Mg electrode; Mg^{2+} in solution **27.** **a.** 0.03 V; **b.** 2.71 V **29.** See Exercise 25 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. In the salt bridge, cations flow to the cathode and anions flow to the anode. **a.** $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$, $\mathscr{E}° = 0.27$ V; cathode: Pt electrode; $Cl_2(g)$ bubbled in, Cl^- in solution; anode: Pt electrode; Br_2 and Br^- in solution; **b.** $3H_2O(l) + 5IO_4^-(aq) + 2Mn^{2+}(aq) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$, $\mathscr{E}° = 0.09$ 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 **31.** 25a. $Pt|Cr^{3+}$ (1.0 M), H^+ (1.0 M), $Cr_2O_7^{2-}$ (1.0 M) $\|$ Cl_2 (1.0 atm)$|Cl^-$ (1.0 M) $|$ Pt; 25b. Mg $|$ Mg^{2+} (1.0 M) $\|$ Cu^{2+} (1.0 M) $|$ Cu; 29a. Pt $|$ Br^- (1.0 M), Br_2 (1.0 M) $\|$ Cl_2 (1.0 atm) $|$ Cl^- (1.0 M) $|$ Pt; 29b. Pt $|$ Mn^{2+} (1.0 M), MnO_4^- (1.0 M), H^+ (1.0 M) $\|$ IO_4^- (1.0 M), H^+(1.0 M) IO_3^- (1.0 M), $|$ Pt **33.** **a.** $Au^{3+}(aq) + 3Cu^+(aq) \rightarrow 3Cu^{2+}(aq) + Au(s)$, $\mathscr{E}° = 1.34$ V; **b.** $2VO_2^+(aq) + 4H^+(aq) + Cd(s) \rightarrow Cd^{2+}(aq) + 2VO^{2+}(aq) + 2H_2O(l)$, $\mathscr{E}° = 1.40$ V **35.** **a.** $16H^+ + 2MnO_4^- + 10I^- \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$, $\mathscr{E}°_{cell} = 0.97$ V, spontaneous; **b.** $16H^+ + 2MnO_4^- + 10F^- \rightarrow 5F_2 + 2Mn^{2+} + 8H_2O$, $\mathscr{E}°_{cell} = -1.36$ V,not spontaneous **37.** $\mathscr{E}° = 0.41$ V, $\Delta G° = -79$ kJ **39.** 33a. -388 kJ; 33b. $-270.$ kJ **41.** 1.21 V **43.** $K^+ < H_2O < Cd^{2+} < I_2 < AuCl_4^- < IO_3^-$ **45.** **a.** no; **b.** yes; **c.** yes; **d.** no **47.** **a.** $Cr_2O_7^{2-}$, O_2, MnO_2, IO_3^-; **b.** $PbSO_4$, Cd^{2+}, Fe^{2+}, Cr^{3+}, Zn^{2+}, H_2O **49.** $ClO^-(aq) + 2NH_3(aq) \rightarrow Cl^-(aq) + N_2H_4(aq) + H_2O(l)$, $\mathscr{E}°_{cell} = 1.00$ V; Because $\mathscr{E}°_{cell}$ is positive for this reaction, at standard conditions ClO^- can spontaneously oxidize NH_3 to the somewhat toxic N_2H_4. **51.** **a.** larger; **b.** smaller **53.** 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; **b.** 0.018 V; compartment with $[Ag^+] = 2.0$ M is cathode; **c.** 0.059 V; compartment with $[Ag^+] = 1.0$ M is cathode; **d.** 0.26 V; compartment with $[Ag^+] = 1.0$ M is cathode; **e.** 0 **55.** 2.12 V **57.** 1.09 V **59.** **a.** 0.23 V; **b.** 1.2×10^{-5} M **61.** 0.16 V, copper is oxidized. **63.** 1.7×10^{-30} **65.** [25] **a.** $\Delta G° = -20$ kJ; 1×10^3; **b.** $\Delta G° = -523$ kJ; 5.12×10^{91}; [29] **a.** $\Delta G° = -52$ kJ; 1.4×10^9; **b.** $\Delta G° = -90$ kJ; 2×10^{15} **67.** 2.5×10^{26} **69.** **a.** no reaction; **b.** $Cl_2(g) + 2I^-(aq) \rightarrow I_2(s) + 2Cl^-(aq)$, $\mathscr{E}°_{cell} = 0.82$ V; $\Delta G° = -160$ kJ; $K = 5.6 \times 10^{27}$; **c.** no reaction; **d.** $4Fe^{2+}(aq) + 4H^+(aq) + O_2(g) \rightarrow$

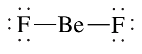
$4Fe^{3+}(aq) + 2H_2O(l)$, $\mathscr{E}°_{cell} = 0.46$ V; $\Delta G° = -180$ kJ; $K = 1.3 \times 10^{31}$; **71. a.** $Au^{3+}(aq) + 3Tl(s) \rightarrow Au(s) + 3Tl^{+}(aq)$; $\mathscr{E}°_{cell} = 1.84$ V; **b.** $\Delta G° = -533$ kJ; $K = 2.52 \times 10^{93}$; **c.** 2.04 V **73.** 5.1×10^{-20} **75.** 6.19×10^{52} **77. a.** 30. hours; **b.** 33 s; **c.** 1.3 hours **79. a.** 16 g; **b.** 25 g; **c.** 71 g; **d.** 4.9 g **81.** Bi **83.** 9.12 L F_2 (anode), 29.2 g K (cathode) **85.** 7.44×10^4 A **87.** 1.14×10^{-2} *M* **89.** Au followed by Ag followed by Ni followed by Cd **91. 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: $2I^- \rightarrow I_2 + 2e^-$ **93. a.** 0.10 V, SCE is anode; **b.** 0.53 V, SCE is anode; **c.** 0.02 V, SCE is cathode; **d.** 1.90 V, SCE is cathode; **e.** 0.47 V, SCE is cathode **95. a.** decrease; **b.** increase; **c.** decrease; **d.** decrease; **e.** same **97. a.** $\Delta G° = -582$ kJ; $K = 3.45 \times 10^{102}$; $\mathscr{E}° = 1.01$ V; **b.** -0.65 V; **99.** Aluminum has the ability to form a durable oxide coating over its surface. Once the HCl dissolves this oxide coating, Al is exposed to H^+ and is easily oxidized to Al^{3+}. Thus, the Al foil disappears after the oxide coating is dissolved. **101.** The claim is impossible. The strongest oxidizing agent and reducing agent when combined give $\mathscr{E}°$ of only about 6 V. **103.** $w_{max} = -13{,}200$ kJ; the work done can be no larger than the free energy change. If the process were reversible all of the free energy released would go into work, but this does not occur in any real process. Fuel cells are more efficient in converting chemical energy to electrical energy; they are also less massive. Major disadvantage: They are expensive. **105.** 0.98 V **107.** 0.250 mol **109.** +3 **111.** $\mathscr{E}° = \dfrac{T\Delta S°}{nF} - \dfrac{\Delta H°}{nF}$; if we graph $\mathscr{E}°$ versus T, we should get a straight line ($y = mx + b$). The slope of the line is equal to $\Delta S°/nF$ and the y-intercept is equal to $-\Delta H°/nF$. $\mathscr{E}°$ will have little temperature dependence for cell reactions with $\Delta S°$ close to zero. **113.** 9.8×10^{-6} **115.** 2.39×10^{-7} **117. a.** ± 0.02 pH units; $\pm 6 \times 10^{-6}$ *M* H^+; **b.** ± 0.001 V **119. a.** 0.16 V; **b.** 8.6 mol **121.** $[Ag^+] = 4.6 \times 10^{-18}$ *M*; $[Ni^{2+}] = 1.5$ *M* **123. a.** 0.12 V; **b.** 0.54 V **125. a.** 5.77×10^{10}; **b.** -12.2 kJ/mol **127.** Osmium(IV) nitrate; $[Ar]4s^13d^{10}$

Chapter 18

1. The characteristic frequencies of energies emitted in a nuclear reaction suggest that discrete energy levels exist in the nucleus. The extra stability of certain numbers of nucleons and the predominance of nuclei with even numbers of nucleons suggest that the nuclear structure might be described by using quantum numbers. **3.** β-particle production has the net effect of turning a neutron into a proton. Radioactive nuclei having too many neutrons typically undergo β-particle decay. Positron production has the net effect of turning a proton into a neutron. Nuclei having too many protons typically undergo positron decay. **5.** The transuranium elements are the elements having more protons than uranium. They are synthesized by bombarding heavier nuclei with neutrons and positive ions in a particle accelerator. **7.** $\Delta E = \Delta mc^2$; The key difference is the mass change when going from reactants to products. In chemical reactions, the mass change is indiscernible. In nuclear processes, the mass change is discernable. It is the conversion of this discernable mass change into energy that results in the huge energies associated with nuclear processes. **9.** Sr-90 is an alkaline earth metal having chemical properties similar to calcium. Sr-90 can collect in bones replacing some of the calcium. Once imbedded inside the human body, β particles can do significant damage. Rn-222 is a noble gas so one would expect Rn to be unreactive and pass through the body quickly; it does. The problem with Rn-222 is the rate at which it produces alpha particles. With a short half-life, the few moments that Rn-222 is in the lungs, a significant number of decay events can occur; each decay event produces an alpha particle which is very effective at causing ionization and can produce a dense trail of damage. **11. a.** ${}^{51}_{24}Cr + {}^{0}_{-1}e \rightarrow {}^{51}_{23}V$; **b.** ${}^{131}_{53}I \rightarrow {}^{0}_{-1}e + {}^{131}_{54}Xe$ **13. 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.** ${}^{129}_{51}Sb \rightarrow {}^{0}_{-1}e + {}^{129}_{52}Te$ **15.** 10 α particles; 5 β particles **17.** ${}^{53}_{26}Fe$ has too many protons. It will undergo positron production, electron capture, and/or alpha-particle production. ${}^{59}_{26}Fe$ has too many neutrons and will undergo beta-particle production. (See Table 18.2 of the text.) **19. a.** ${}^{249}_{98}Cf + {}^{18}_{8}O \rightarrow {}^{263}_{106}Sg + 4{}^{1}_{0}n$; **b.** ${}^{259}_{104}Rf$ **21.** 690 hours **23.** ${}^{81}Kr$ is most stable since it has the longest half-life. ${}^{73}Kr$ is "hottest" since it decays very rapidly due to its very short half-life. ${}^{73}Kr$, 81s; ${}^{74}Kr$, 34.5 min; ${}^{76}Kr$, 44.4 h; ${}^{81}Kr$, 6.3×10^5 yr **25.** 6.22 mg ${}^{32}P$ remains **27.** 0.230 **29.** 26 g **31.** 2.3 counts per minute per gram of C. No; for a 10.-mg C sample, it would take roughly 40 min to see a single disintegration. This is too long to wait, and the background radiation would probably be much greater than the ${}^{14}C$ activity. Thus ${}^{14}C$ dating is not practical for very small samples. **33.** 3.8×10^9 yr **35.** 4.3×10^6 kg/s **37.** ${}^{232}Pu$, -1.715×10^{14} J/mol; ${}^{231}Pa$, -1.714×10^{14} J/mol **39.** ${}^{12}C$: 1.23×10^{-12} J/nucleon; ${}^{235}U$: 1.2154×10^{-12} J/nucleon; since ${}^{56}Fe$ is the most stable known nucleus, then the binding energy per nucleon for ${}^{56}Fe$ would be larger than that of ${}^{12}C$ or ${}^{235}U$. (See Fig. 18.9 of the text.) **41.** 6.01513 amu **43.** -2.0×10^{10} J/g of hydrogen nuclei **45.** 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 off because, at high activities, radioactive particles are entering the tube faster than the tube can respond to them. **47.** All evolved $O_2(g)$ comes from water. **49.** 2 neutrons; 4 β particles **51.** Strontium. Xe is chemically unreactive and not readily incorporated into the body. Sr can be easily oxidized to Sr^{2+}. Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca^{2+}. The chemical properties determine where radioactive material may be concentrated in the body or how easily it may be excreted. **53. a.** unstable; beta production; **b.** stable; **c.** unstable; positron production or electron capture; **d.** unstable, positron production, electron capture, or alpha production. **55.** 49.7 yr **57.** 1975 **59.** 900 g ${}^{235}U$ **61.** 7×10^5 m/s; 8×10^{-16} J/nuclei; **63.** 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. **65. a.** ${}^{12}_{6}C$; **b.** ${}^{13}N$, ${}^{13}C$, ${}^{14}N$, ${}^{15}O$, and ${}^{15}N$; **c.** -5.950×10^{11} J/mol ${}^{1}H$ **67.** 4.3×10^{-29} **69.** ${}^{249}_{97}Bk + {}^{22}_{10}Ne \rightarrow {}^{267}_{107}Bh + 4{}^{1}_{0}n$; 62.7s; $[Rn]7s^25f^{14}6d^5$

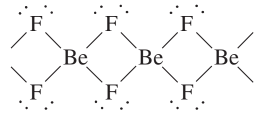
Chapter 19

1. The gravity of the earth cannot keep H_2 in the atmosphere. **3.** The acidity decreases. Solutions of Be^{2+} are acidic, while solutions of the other M^{2+} ions are neutral. **5.** The planes of carbon atoms slide easily. Graphite is not volatile so the lubricant will not be lost when used in a high vacuum environment. **7.** p-type semiconductor **9.** For groups 1A–3A, the small size of H (as compared to Li), Be (as compared to Mg), and B (as compared to Al) seems to be the reason why these elements have nonmetallic properties, while others in the groups 1A–3A are strictly metallic. The small size of H, Be, and B also causes these species to polarize the electron cloud in nonmetals, thus forcing a sharing of electrons when bonding occurs. For groups 4A–6A, a major difference between the first and second members of a group is the ability to form π bonds. The smaller elements form stable π bonds, while the larger elements do not exhibit good overlap between parallel *p* orbitals and, in turn, do not form strong π bonds. For group 7A, the small size of F as compared to Cl is used to explain the low electron affinity of F and the weakness of the F—F bond. **11.** In order to maximize hydrogen bonding interactions in the solid phase, ice is forced into an open structure. This open structure is why $H_2O(s)$ is less dense than $H_2O(l)$. **13. a.** $\Delta H° = 207$ kJ, $\Delta S° = 216$ J/K; **b.** $T > 958$ K **15. a.** lithium oxide; **b.** potassium superoxide; **c.** sodium peroxide **17. a.** $Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$; **b.** $Na_2O_2(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2O_2(aq)$; **c.** $LiH(s) + H_2O(l) \rightarrow H_2(g) + LiOH(aq)$; **d.** $2KO_2(s) + 2H_2O(l) \rightarrow 2KOH(aq) + O_2(g) + H_2O_2(aq)$ **19.** $2Li(s) + 2C_2H_2(g) \rightarrow 2LiC_2H(s) + H_2(g)$; oxidation–reduction **21. a.** magnesium carbonate; **b.** barium sulfate; **c.** strontium hydroxide **23.** $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + H_2O(l) + CO_2(g)$ **25.** In the gas phase, linear molecules would exist:



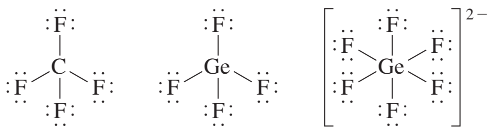
$$:\ddot{\underset{..}{F}}—Be—\ddot{\underset{..}{F}}:$$

In the solid state, BeF_2 has the following extended structure:



27. 2×10^{-2} *M* **29.** 3.84×10^{6} g Ba **31. a.** AlN; **b.** GaF_3; **c.** Ga_2S_3 **33.** $B_2H_6(g) + 3O_2(g) \rightarrow 2B(OH)_3(s)$ **35.** $In_2O_3(s) + 6H^+(aq) \rightarrow 2In^{3+}(aq) + 3H_2O(l)$; $In_2O_3(s) + OH^-(aq) \rightarrow$ no reaction; $Ga_2O_3(s) + 6H^+(aq) \rightarrow 2Ga^{3+}(aq) + 3H_2O(l)$; $Ga_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Ga(OH)_4^-(aq)$ **37.** $2Ga(s) + 3F_2(g) \rightarrow 2GaF_3(s)$; $4Ga(s) + 3O_2(g) \rightarrow 2Ga_2O_3(s)$; $16Ga(s) + 3S_8(s) \rightarrow 8Ga_2S_3(s)$; $2Ga(s) + N_2(g) \rightarrow 2GaN(s)$; $2Ga(s) + 6HCl(aq) \rightarrow 2GaCl_3(aq) + 3H_2(g)$

39.



Tetrahedral; 109.5°; sp^3 Tetrahedral; 109.5°; sp^3 Octahedral; 90°; d^2sp^3

To form CF_6^{2-}, carbon would have to expand its octet of electrons. Carbon compounds do not expand their octet because of the small atomic size of carbon and because there are no low energy *d* orbitals on carbon to accommodate the extra electrons. **41. a.** $SiO_2(s) + 2C(s) \rightarrow Si(s) + 2CO(g)$; **b.** $SiCl_4(l) + 2Mg(s) \rightarrow Si(s) + 2MgCl_2(s)$; **c.** $Na_2SiF_6(s) + 4Na(s) \rightarrow Si(s) + 6NaF(s)$ **43.** Lead is very toxic. As the temperature of the water increases, the solubility of Pb increases. Drinking hot tap water from pipes containing lead solder could result in higher Pb concentrations in the body. **45.** $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$ **47.** The π electrons are free to move in graphite, thus giving it a greater conductivity (lower resistance). The electrons have the greatest mobility within the sheets of carbon atoms. Electrons in diamond are not mobile (high resistance). The structure of diamond is uniform in all directions; thus there is no directional dependence of the resistivity. **49.** Only some of the ice will melt; 0°C **51.** 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. **53.** 60 **55.** 2.12 V **57.** 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. **59.** The inert-pair effect refers to the difficulty of removing the pair of valence *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. **61.** 3.08 **63.** If the compound contained Ga(II) it would be paramagnetic and if the compound contained Ga(I) and Ga(III), it would be diamagnetic. Paramagnetic compounds have an apparent greater mass in a magnetic field. **65.** 59 atm in the gas phase; 1.8 mol CO_2/L in the wine **67.** $Pb(NO_3)_2(aq) + H_3AsO_4(aq) \rightarrow PbHAsO_4(s) + 2HNO_3(aq)$ **69.** Ca; 12.698 **71.** 3.34, 5.6×10^{-11} *M* **73.** 2.0×10^{-37} *M* **75.** Carbon is much smaller than Si and cannot form a fifth bond in the transition state. **77.** I **79. a.** 7.1 g; **b.** 979 nm; This electromagnetic radiation is not visible to humans; it is in the infrared region of the electromagnetic radiation spectrum, **c.** n-type

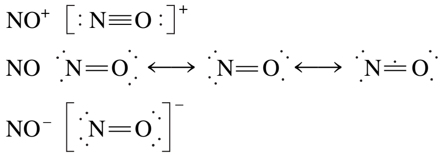
Chapter 20

1. This is due to nitrogen's ability to form strong π bonds whereas heavier group 5A elements do not form strong π bonds. Therefore, P_2, As_2, and Sb_2 do not form since two π bonds are required to form these diatomic substances. **3.** There are medical studies that have shown an inverse relationship between the incidence of cancer and the selenium levels in soil. The foods grown in these soils and eventually digested are assumed to somehow furnish protection from cancer. Selenium is also involved in the activity of vitamin E and certain enzymes in the human body. In addition, selenium deficiency has been linked to the occurrence of congestive heart failure. **5.** +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 **7. a.** $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; this reaction produces a lot of energy which can be used in a cannon apparatus to send a stopper flying across the room. To initiate this extremely slow reaction, light of specific wavelengths is needed. This is the purpose of lighting the magnesium strip. When magnesium is oxidized to MgO, an intense white light is produced. Some of the wavelengths of this light can break Cl—Cl bonds and get the reaction started. **b.** Br_2 is brown. The disappearance of the brown color indicates that all of the Br_2 has reacted with the alkene (no free Br_2 remains). **c.** $2Al(s) + 3I_2(s) \rightarrow 2AlI_3(s)$; This is a highly exothermic reaction, hence the sparks that accompany this reaction. The purple smoke is excess $I_2(s)$ being vaporized [the purple smoke is $I_2(g)$]. **9.** Nitrogen's small size does not provide room for all four oxygen atoms, making NO_4^{3-} unstable. Phosphorus is larger so PO_4^{3-} is more stable. To form NO_3^-, a pi bond must form. Phosphorus doesn't form strong pi bonds as readily as nitrogen. **11.** $NO_2 = N_2O_4 < NO < N_2O$ **13. a.** $NH_4NO_3(s) \xrightarrow{\text{Heat}} N_2O(g) + 2H_2O(g)$; **b.** $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$; **c.** $2K_3P(s) + 6H_2O(l) \rightarrow 2PH_3(g) + 6KOH(aq)$; **d.** $PBr_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HBr(aq)$; **e.** $2NH_3(aq) + NaOCl(aq) \rightarrow N_2H_4(aq) + NaCl(aq) + H_2O(l)$ **15.** $CaF_2 \cdot 3Ca_3(PO_4)_2(s) + 10H_2SO_4(aq) + 20H_2O(l) \rightarrow 6H_3PO_4(aq) + 2HF(aq) + 10CaSO_4 \cdot 2H_2O(s)$ **17.** 2.08 mol **19.** $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$; $\Delta H = -590.$ kJ **21.** $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$ $\Delta G° = \Delta G°_{f(NO)}$; NO (and some other oxides of nitrogen) have weaker bonds as compared with the triple bond of N_2 and the double bond of O_2. Because of this, NO (and some other oxides of nitrogen) has a higher (positive) standard free energy of formation as compared to the relatively stable N_2 and O_2 molecules.

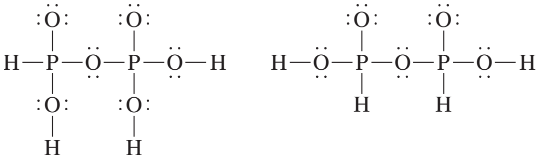
23.

		Bond order	# unpaired e^-
M.O.	NO	2.5	1
	NO^+	3	0
	NO^-	2	2

Lewis



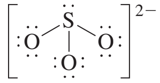
Lewis structures are not adequate for NO and NO^-. The M.O. model gives correct results for all three species. For NO, Lewis structures fail for odd-electron species. For NO^-, Lewis structures fail to predict that NO^- is paramagnetic. **25. a.** $H_3PO_4 > H_3PO_3$; **b.** $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$ **27.** The acidic protons are attached to oxygen.



$H_4P_2O_6$ $H_4P_2O_5$

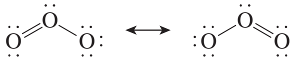
29. 821 nm **31. a.** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; **b.** $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$; **c.** $2Na_2S_2O_3(aq) + I_2(aq) \rightarrow Na_2S_4O_6(aq) + 2NaI(aq)$; **d.** $Cu(s) + 2H_2SO_4(aq) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(aq)$

33. a.



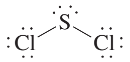
Trigonal pyramid; ≈109.5°; sp^3

b.



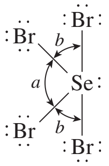
V-shaped; ≈120°; sp^2

c.



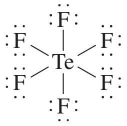
V-shaped; ≈109.5°; *sp*^{3}

d.



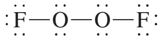
See-saw; $a \approx 120°$, $b \approx 90°$; *dsp*^{3}

e.



Octahedral; 90°; d^2sp^3

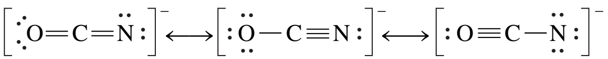
35. 0.301 g H_2O_2; 3.6 × 10^{-2} g excess HCl **37.** From the following Lewis structure, each oxygen atom has a tetrahedral arrangement of electron pairs. Therefore, bond angles ≈109.5°, and each O is *sp*^{3} hybridized.



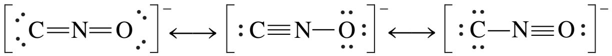
Formal charge:	0	0	0	0
Oxidation state:	−1	+1	+1	−1

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. **39. a.** $BaCl_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HCl(g)$; **b.** $BrF(s) + H_2O(l) \rightarrow HF(aq) + HOBr(aq)$; **c.** $SiO_2(s) + 4HF(aq) \rightarrow SiF_4(g) + 2H_2O(l)$ **41.** ClO^- can oxide NH_3 to the somewhat toxic N_2H_4. **43. a.** IO_4^-; **b.** IO_3^-; **c.** IF_2^-; **d.** IF_4^-; **e.** IF_6^- **45.** XeF_2 can react with oxygen and water to produce explosive xenon oxides and oxyfluorides. **47.** Release of Sr is probably more harmful. Xe is chemically unreactive. Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca. This puts the radioactive Sr in the bones, and red blood cells are produced in bone marrow. Xe would not be readily incorporated into the body. The chemical properties determine where a radioactive material may concentrate in the body or how easily it may be excreted. The length of time of exposure and the body part exposed to radiation significantly affects the health hazard. **49.** As the halogen atoms get larger, it becomes more difficult to fit three halogens around the small N.

51.



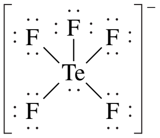
Formal charge: 0 0 −1 −1 0 0 +1 0 −2



Formal charge: −2 +1 0 −1 +1 −1 −3 +1 +1

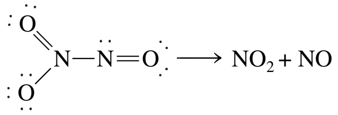
All the resonance structures for fulminate involve greater formal charges than in cyanate, making fulminate more reactive (less stable). **53.** 32 kg bacterial tissue

55.

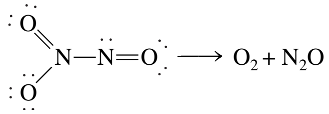


The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs, pushing the four square planar F's away from the lone pair. **57.** exothermic **59.** $MgSO_4(s) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$; $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$ **61.** F, Cl, Br, or I; trigonal pyramid; ≈109.5° **63.** XeF_2

65. For the reaction



the activation energy must in some way involve the breaking of a nitrogen–nitrogen single bond. For the reaction

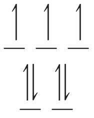


at some point nitrogen–oxygen bonds must be broken. N—N single bonds (160 kJ/mol) are weaker than N—O single bonds (201 kJ/mol). In addition, resonance structures indicate that there is more double-bond character in the N—O bonds than in the N—N bond. Thus NO_2 and NO are preferred by kinetics because of the lower activation energy. **67. a.** NO; **b.** NO_2; **c.** $k_{cat}/k_{un} = 2.3$; **d.** $ClO(g) + O(g) \rightarrow O_2(g) + Cl(g)$; $O_3(g) + O(g) \rightarrow 2O_2(g)$; **e.** The Cl-catalyzed reaction is roughly 52 times faster (more efficient) than the NO-catalyzed reaction. **69.** 5.89 **71.** 20. g **73. a.** 287 kJ/mol; **b.** $[IF_2]^+$: V-shaped; *sp*^{3}; $[BF_4]^-$: tetrahedral; *sp*^{3}

Chapter 21

5. $Fe_2O_3(s) + 6\,H_2C_2O_4(aq) \rightarrow 2\,Fe(C_2O_4)_3^{3-}(aq) + 3\,H_2O(l) + 6\,H^+(aq)$; The oxalate anion forms a soluble complex ion with iron in rust (Fe_2O_3), which allows rust stains to be removed. **7.** No; both the *trans* or the *cis* forms of $Co(NH_3)_4Cl_2^+$ have mirror images that are superimposable. For the *cis* form, the mirror image only needs a 90° rotation to produce the original structure. Hence, neither the *trans* nor *cis* forms are optically active.

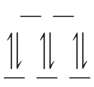
9. a.



small Δ

$CoCl_4^{2-}$ is an example of a weak-field case having three unpaired electrons.

b.

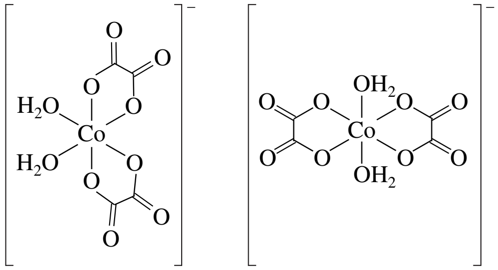


large Δ

CN^- is a strong field ligand so $Co(CN)_6^{3-}$ will be a low-spin case having zero unpaired electrons.

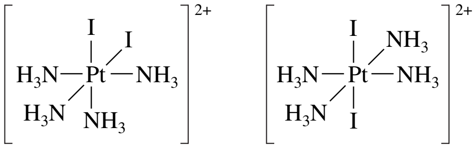
11. At high altitudes, the oxygen content of air is lower, so less oxyhemoglobin is formed which diminishes the transport of oxygen in the blood. A serious illness called high-altitude sickness can result from the decrease of O_2 in the blood. High altitude acclimatization is the phenomena that occurs in the human body in response to the lower amounts of oxyhemoglobin in the blood. This response is to produce more hemoglobin, and, hence, increase the oxyhemoglobin in the blood. High-altitude acclimatization takes several weeks to take hold for people moving from lower altitudes to higher altitudes. **13. a.** Ni: $[Ar]4s^23d^8$; **b.** Cd: $[Kr]5s^24d^{10}$; **c.** Zr: $[Kr]5s^24d^2$; **d.** Os: $[Xe]6s^24f^{14}5d^6$ **15. a.** Ti: $[Ar]4s^23d^2$; Ti^{2+}: $[Ar]3d^2$; Ti^{4+}: $[Ne]3s^23p^6$ or [Ar]; **b.** Re: $[Xe]6s^24f^{14}5d^5$; Re^{2+}: $[Xe]4f^{14}5d^5$; Re^{3+}: $[Xe]4f^{14}5d^4$; **c.** Ir: $[Xe]6s^24f^{14}5d^7$; Ir^{2+}: $[Xe]4f^{14}5d^7$; Ir^{3+}: $[Xe]4f^{14}5d^6$ **17. a.** Fe^{3+}: $[Ar]3d^5$; **b.** Ag^+: $[Kr]4d^{10}$; **c.** Ni^{2+}: $[Ar]3d^8$; **d.** Cr^{3+}: $[Ar]3d^3$ **19. a.** molybdenum(IV) sulfide, molybdenum(VI) oxide; **b.** MoS_2, +4; MoO_3, +6; $(NH_4)_2\,Mo_2O_7$, +6; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, +6 **21.** 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. This leads to a greater similarity in the chemistry of the 4*d* and 5*d* elements in a given vertical group. **23.** If rain is imminent, the large amount of water vapor in the air would cause the reaction to shift to the right. The indicator would take on the color of the pink $CoCl_2 \cdot 6H_2O$. **25.** Test tube 1: added Cl^- reacts with Ag^+ to form the 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 the 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, then 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, Ag^+ ions are released to solution, which can then react with Cl^- to reform $AgCl(s)$. The equations are $Ag(NH_3)_2^+(aq) + 2H^+(aq) \rightarrow Ag^+(aq) + 2NH_4^+(aq)$ and $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. **27.** $[Co(NH_3)_6]I_3$: 3 mol AgI; $[Pt(NH_3)_4I_2]I_2$: 2 mol AgI; $Na_2[PtI_6]$: 0 mol AgI; $[Cr(NH_3)_4I_2]I$: 1 mol AgI. **29.** **a.** pentaamminechlororuthenium(III) ion; **b.** hexacyanoferrate(II) ion; **c.** tris(ethylenediamine)manganese(II) ion; **d.** pentaamminenitrocobalt(III) ion **31.** **a.** hexaamminecobalt(II) chloride; **b.** hexaaquacobalt(III) iodide; **c.** potassiumtetrachloro-platinate(II); **d.** potassium hexachloroplatinate(II); **e.** pentaamminechlorocobalt(III) chloride; **f.** triamminetrinitrocobalt(III) **33.** **a.** $K_2[CoCl_4]$; **b.** $[Pt(H_2O)(CO)_3]Br_2$; **c.** $Na_3[Fe(CN)_2(C_2O_4)_2]$; **d.** $[Cr(NH_3)_3Cl(H_2NCH_2CH_2NH_2)]I_2$

35. **a.**



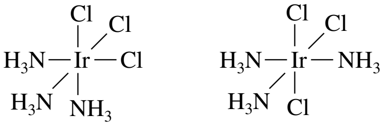
cis *trans*

b.



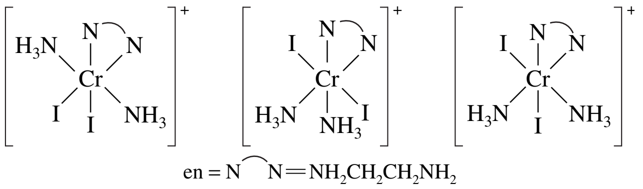
cis *trans*

c.

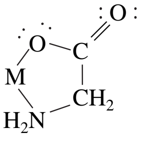


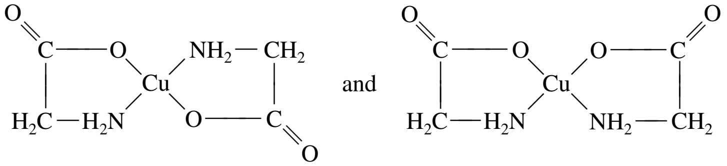
cis *trans*

d.



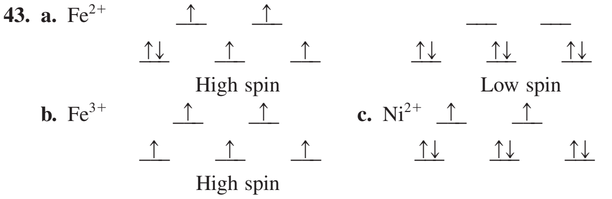
37.





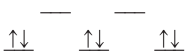
39. SCN^-, NO_2^-, and OCN^- can form linkage isomers; all are able to bond to the metal ion in two different ways. **41.** $Cr(acac)_3$ and *cis*-$Cr(acac)_2(H_2O)_2$ are optically active.

43.

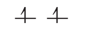


45. weak field **47.** **a.** 0; **b.** 2; **c.** 2 **49.** $[Co(CN)_6]^{3-} < [Co(en)_3]^{3+} < [Co(H_2O)_6]^{3+} < [CoI_6]^{3-}$ **51.** The violet complex ion absorbs yellow-green light ($\lambda \approx 570$ nm), the yellow complex ion absorbs blue light ($\lambda \approx 450$ nm), and the green complex ion absorbs red light ($\lambda \approx 650$ nm). The violet complex ion is $Cr(H_2O)_6^{3+}$, the yellow complex ion is $Cr(NH_3)_6^{3+}$, and the green complex ion is $Cr(H_2O)_4Cl_2^+$. **53.** $CoBr_4^{2-}$ is a tetrahedral complex ion, while $CoBr_6^{4-}$ is an octahedral complex ion. Since tetrahedral *d*-orbital splitting is less than one-half the octahedral *d*-orbital splitting, the octahedral complex ion ($CoBr_6^{4-}$) will absorb higher-energy light, which will have a shorter wavelength than 3.4×10^{-6} m ($E = hc/\lambda$). **55.** 5 **57.** **a.** -11 kJ; **b.** $\Delta H° = 172.5$ kJ; $\Delta S° = 176$ J/K; $T > 980.$ K **59.** $8CN^-(aq) + 4Ag(s) + O_2(g) + 2H_2O(l) \rightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)$ **61.** $[Cr(NH_3)_5I]I_2$; octahedral **63.** $Hg^{2+}(aq) + 2I^-(aq) \rightarrow HgI_2(s)$, orange precipitate; $HgI_2(s) + 2I^-(aq) \rightarrow HgI_4^{2-}(aq)$, soluble complex ion **65.** **a.** 2; **b.** 3; **c.** 4; **d.** 4 **67.** **a.** optical isomerism

b.



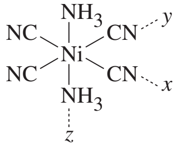
69. Octahedral Cr^{2+} complexes should be used. Cr^{2+}: $[Ar]3d^4$; High-spin (weak-field) Cr^{2+} complexes have four unpaired electrons and low-spin (strong-field) Cr^{2+} complexes have two unpaired electrons. Ni^{2+}: $[Ar]3d^8$; Octahedral Ni^{2+} complexes will always have two unpaired electrons, whether high or low spin. Therefore, Ni^{2+} complexes cannot be used to distinguish weak- from strong-field ligands by examining magnetic properties. Alternatively, the ligand field strengths can be measured using visible spectra. Either Cr^{2+} or Ni^{2+} complexes can be used for this method. **71.** $Pb(OH)_2$ will not form since Q is less than K_{sp}. **73.** 60 **75.** $Ni^{2+} = d^8$; If A and B produced very similar crystal fields, the complex *trans*-$[NiA_2B_4]^{2+}$ would give an octahedral crystal field diagram:

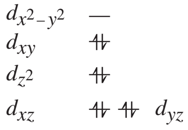


This is paramagnetic. Because the complex ion is diamagnetic, ligands A and B must produce different crystal fields resulting in a unique *d*-orbital splitting diagram. **77.** **a.** -0.26 V; **b.** From standard reduction potentials, Co^{3+} ($\mathscr{E}° = 1.82$ V) is a much stronger oxidizing agent 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. If we assume a strong-field case for each complex ion, then the *d*-orbital splitting diagram for each has the six electrons paired in the lower-energy t_{2g} orbitals. When each complex ion gains an electron, the electron enters the higher-energy e_g orbitals. Since en is a stronger-field ligand than H_2O, then 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. **79.** No, since in all three cases six bonds are formed between Ni^{2+} and nitrogen. So ΔH values should be similar. $\Delta S°$ for formation of the complex ion is most negative for $6NH_3$ molecules reacting with a metal ion (7 independent species become 1). For penten reacting with a metal ion, 2 independent species become 1, so $\Delta S°$ is the least negative. 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.

81. ___ d_{z^2}
___ ___ $d_{x^2-y^2}, d_{xy}$
___ ___ d_{xz}, d_{yz}

83. Place the *trans* NH_3 ligands on the z axis with the CN^- ligands oriented as indicated in the following diagram. Since CN^- produces a much stronger crystal field, the diagram will most resemble that of a square planar complex:

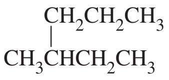




85. a. +6; $[Ar]3d^2$; **b.** 0.0496 L N_2

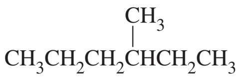
Chapter 22

1. a. 1-sec-butylpropane


$CH_3\overset{\overset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_3$

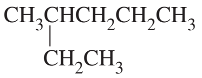
3-methylhexane is correct.

b. 4-methylhexane


$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$

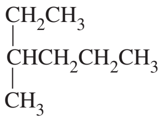
3-methylhexane is correct.

c. 2-ethylpentane


$CH_3\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_3$

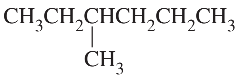
3-methylhexane is correct.

d. 1-ethyl-1-methylbutane

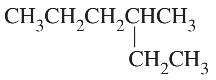

$\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}HCH_2CH_2CH_3$

3-methylhexane is correct.

e. 3-methylhexane


$CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$

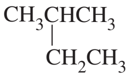
f. 4-ethylpentane


$CH_3CH_2CH_2\underset{\underset{CH_2CH_3}{|}}{C}HCH_3$

3-methylhexane is correct.

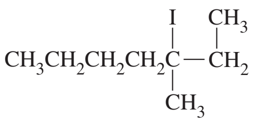
All six of these are the same compound. They only differ from each other by rotations about one or more carbon-carbon single bonds. Only one isomer of C_7H_{16} is present in all of these names, 3-methylhexane.

3. a.


$CH_3\underset{\underset{CH_2CH_3}{|}}{C}HCH_3$

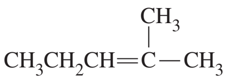
The longest chain is 4 carbons long. The correct name is 2-methylbutane.

b.


$CH_3CH_2CH_2CH_2\overset{\overset{I}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH_2}$

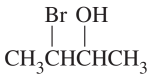
The longest chain is 7 carbons long and we would start the numbering system at the other end for lowest possible numbers. The correct name is 3-iodo-3-methylheptane.

c.


$CH_3CH_2CH{=}\overset{\overset{CH_3}{|}}{C}-CH_3$

This compound cannot exhibit *cis–trans* isomerism since 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.

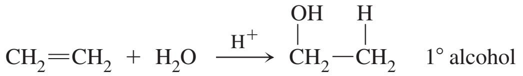

$CH_3\overset{\overset{Br}{|}}{C}H\overset{\overset{OH}{|}}{C}HCH_3$

The OH functional group gets the lowest number. 3-bromo-2-butanol is correct.

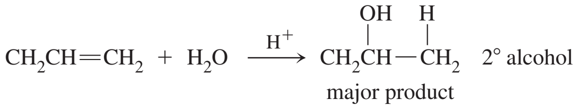
5. Hydrocarbons are nonpolar substances exhibiting only London dispersion forces. Size and shape are the two most important structural features relating to the strength of London dispersion forces. For size, the bigger the molecule (the larger the molar mass), the stronger the London dispersion forces and the higher the boiling point. For shape, the more branching present in a compound, the weaker the London dispersion forces and the lower the boiling point.

7. The correct order of strength is polyhydrocarbon < polyester < polyamide. The difference in strength is related to the types of intermolecular forces present. All of these polymers have London dispersion forces. However, polyhydrocarbons only have London dispersion forces. The polar ester group in polyesters and the polar amide group in polyamides give rise to additional dipole forces. The polyamide has the ability to form relatively strong hydrogen bonding interactions, hence why it would form the strongest fibers.

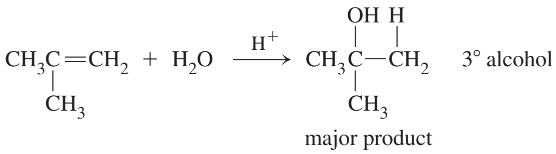
9. a.


$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} \overset{\overset{OH}{|}}{CH_2}-\overset{\overset{H}{|}}{CH_2}$ 1° alcohol

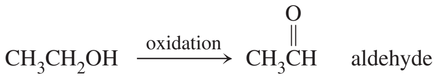
b.


$CH_2CH{=}CH_2 + H_2O \xrightarrow{H^+} \underset{\text{major product}}{CH_2\overset{\overset{OH}{|}}{C}H-\overset{\overset{H}{|}}{CH_2}}$ 2° alcohol

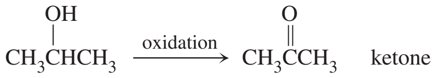
c.


$CH_3\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O \xrightarrow{H^+} \underset{\text{major product}}{CH_3\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{H}{|}}{CH_2}}$ 3° alcohol

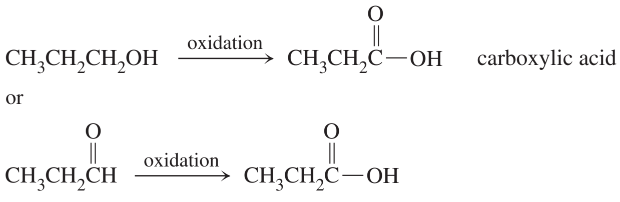
d.


$CH_3CH_2OH \xrightarrow{\text{oxidation}} CH_3\overset{\overset{O}{\|}}{C}H$ aldehyde

e.


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

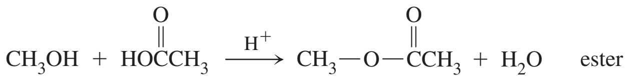
f.


$CH_3CH_2CH_2OH \xrightarrow{\text{oxidation}} CH_3CH_2\overset{\overset{O}{\|}}{C}-OH$ carboxylic acid

or

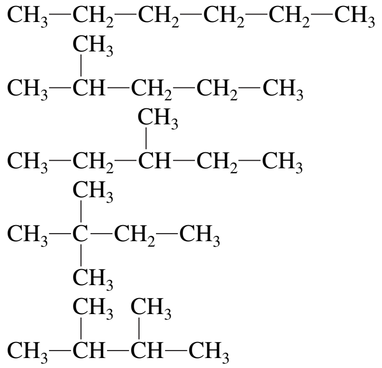
$CH_3CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow{\text{oxidation}} CH_3CH_2\overset{\overset{O}{\|}}{C}-OH$

g.


$CH_3OH + HO\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{H^+} CH_3-O-\overset{\overset{O}{\|}}{C}CH_3 + H_2O$ ester

11. 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 an 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 all present, or to have a carbon-carbon double bond, an amine functional group, and a carboxylic acid functional group present.

13.



$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

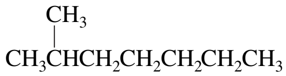
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3$

$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_3$

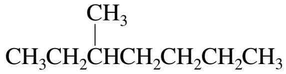
$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$

15. a.



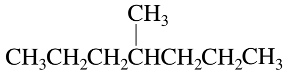
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_2CH_3$

2-methylheptane



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

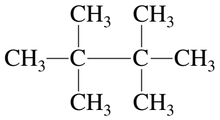
3-methylheptane



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

4-methylheptane

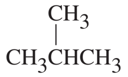
b.



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

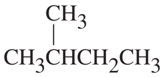
2,2,3,3-tetramethylbutane

17. a.



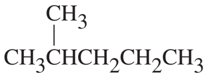
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_3$

b.



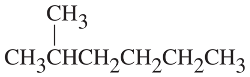
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

c.



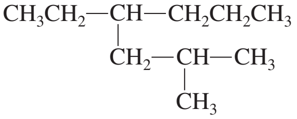
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

d.



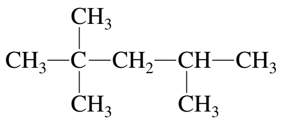
$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$

19. a.



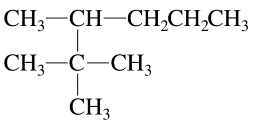
$CH_3CH_2-\underset{CH_2-\underset{CH_3}{CH}-CH_3}{\underset{|}{CH}}-CH_2CH_2CH_3$

b.



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

c.

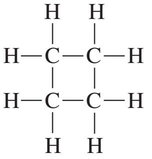


$CH_3-\underset{CH_3-\underset{CH_3}{C}-CH_3}{\underset{|}{CH}}-CH_2CH_2CH_3$

d. 4-ethyl-2-methylheptane; 2,2,3-trimethylhexane

21. a. 2,2,4-trimethylhexane: **b.** 5-methylnonane; **c,** 2,2,4,4-tetramethylpentane; **d.** 3-ethyl-3-methyloctane

23. $CH_3-CH_2-CH_2-CH_3$;

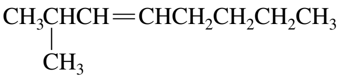


Each carbon is bonded to four other atoms.

25. a. 1-butene; **b.** 4-methyl-2-hexene; **c.** 2,5-dimethyl-3-heptene

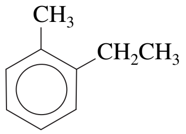
27. a. $CH_3CH_2CH=CHCH_2CH_3$; **b.** $CH_3CH=CHCH=CHCH_2CH_3$;

c.

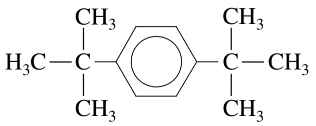


$CH_3\underset{CH_3}{\underset{|}{C}}HCH=CHCH_2CH_2CH_2CH_3$

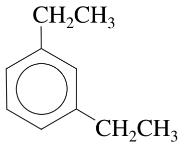
29. a.



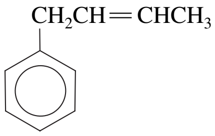
b.



c.

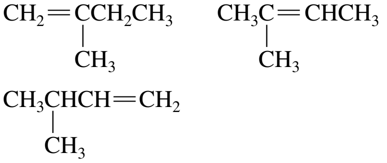


d.



31. a. 1,3-dichlorobutane; **b.** 1,1,1-trichlorobutane; **c.** 2,3-dichloro-2,4-dimethylhexane; **d.** 1,2-difluoroethane; **33.** CH_2Cl-CH_2Cl,1-2-dichloroethane: There is free rotation about the C—C single bond that doesn't lead to different compounds. $CHCl=CHCl$, 1-2-dichloroethene: There is no rotation about the C=C double bond. This creates the *cis* and *trans* isomers, which are different compounds. **35.** [25], compounds b and c; [27], all compounds

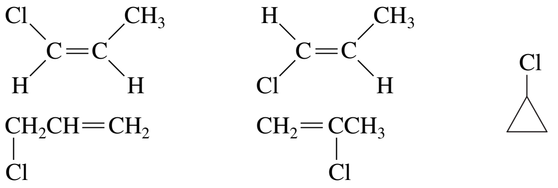
37. $CH_2=CHCH_2CH_2CH_3$ $CH_3CH=CHCH_2CH_3$



$CH_2=\underset{CH_3}{\underset{|}{C}}CH_2CH_3$ $CH_3\underset{CH_3}{\underset{|}{C}}=CHCH_3$

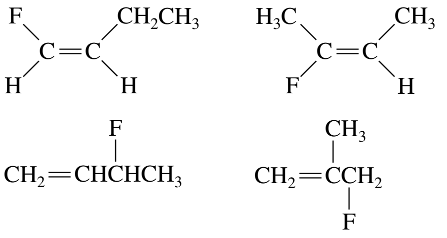
$CH_3\underset{CH_3}{\underset{|}{C}}HCH=CH_2$

39.

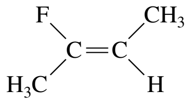


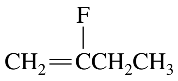
$\underset{Cl}{\underset{|}{CH_2}}CH=CH_2$ $CH_2=\underset{Cl}{\underset{|}{C}}CH_3$

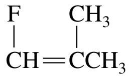
41.

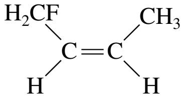


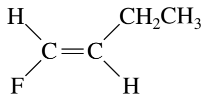
$CH_2=CH\overset{F}{\overset{|}{C}}HCH_3$ $CH_2=\overset{CH_3}{\overset{|}{C}}\underset{F}{\underset{|}{CH_2}}$

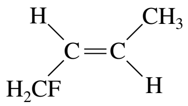


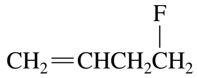

$CH_2{=}\overset{\overset{F}{|}}{C}CH_2CH_3$


$\overset{\overset{F}{|}}{CH}{=}\overset{\overset{CH_3}{|}}{C}CH_3$

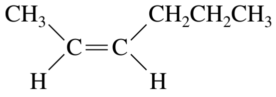




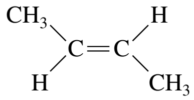



$CH_2{=}CHCH_2\overset{\overset{F}{|}}{C}H_2$

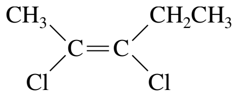
43. a.



b.

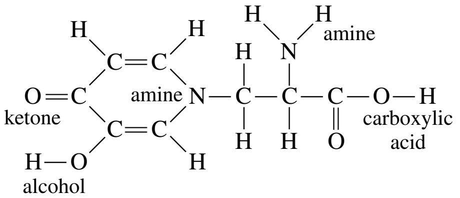


c.



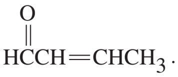
45. a. 3 monochloro isomers of *n*-pentane; **b.** 4 monochloro isomers of 2-methylbutane; **c.** 3 monochloro isomers of 2,4-dimethylpentane; **d.** 4 monochloro isomers of methylcyclobutane **47. a.** ketone; **b.** aldehyde; **c.** carboxylic acid; **d.** amine

49. 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 **51. a.** 3-chloro-1-butanol, primary: **b.** 3-methyl-3-hexanol, tertiary; **c.** 2-methylcyclopentanol, secondary **53.** 1-pentanol; 2-pentanol; 3-pentanol; 2-methyl-1-butanol; 2-methyl-2-butanol; 3-methyl-2-butanol; 3-methyl-1-butanol; 2,2-dimethyl-1-propanol; 6 ethers **55. a.** 4,5-dichloro-3-hexanone; **b.** 2,3-dimethylpentanal; **c.** 3-methylbenzaldehyde or *m*-methylbenzaldehyde **57. a.** 4-chlorobenzoic acid or *p*-chlorobenzoic acid; **b.** 3-ethyl-2-methylhexanoic acid; **c.** methanoic acid (common name = formic acid) **59.** Only statement d is false.

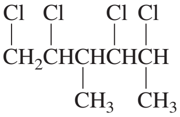
2-butenal:


$H\overset{\overset{O}{\|}}{C}CH{=}CHCH_3$.

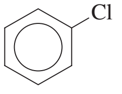
The formula of 2-butenal is C_4H_6O, while the ether has a formula of C_4H_8O.

61. a. $CH_3CH_2CH_2CH_3$

b.


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

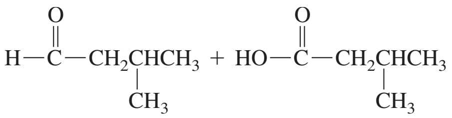
c.


+ HCl

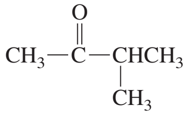
d. $C_4H_8(g) + 6O_2(g) \longrightarrow 4CO_2(g) + 4H_2O(g)$

63. For the iron-catalyzed reaction, one of the *ortho* or *para* hydrogens in benzene is replaced by chlorine. When an iron catalyst is not present, then the benzene hydrogens are unreactive, which is seen for the light-catalyzed reaction where one of the methyl hydrogens is replaced by chlorine.

65. a.

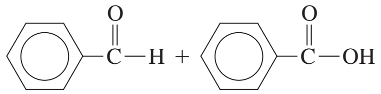

$H-\overset{\overset{O}{\|}}{C}-CH_2\underset{\underset{CH_3}{|}}{C}HCH_3 + HO-\overset{\overset{O}{\|}}{C}-CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

b.

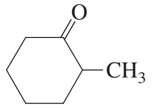

$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}HCH_3$

c. No reaction

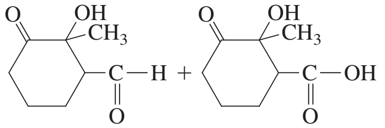
d.



e.

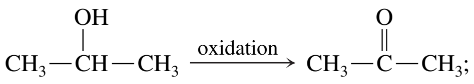


f.

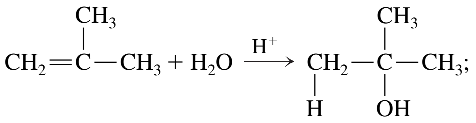


67. a. $CH_3CH{=}CH_2$ + $Br_2 \rightarrow CH_3CHBrCH_2Br$;

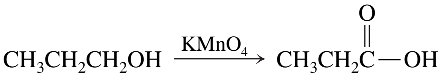
b.


$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{oxidation}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3;$

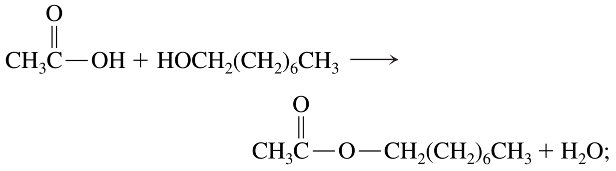
c.


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

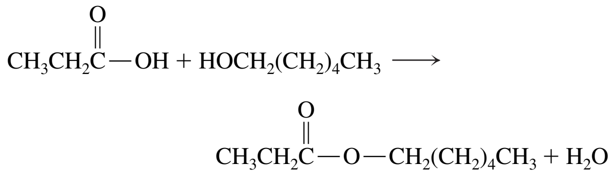
d.


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

69. a.

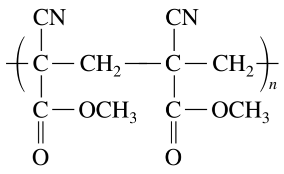

$CH_3\overset{\overset{O}{\|}}{C}-OH + HOCH_2(CH_2)_6CH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-O-CH_2(CH_2)_6CH_3 + H_2O;$

b.

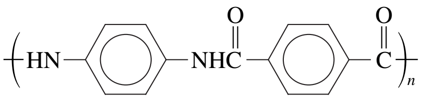

$CH_3CH_2\overset{\overset{O}{\|}}{C}-OH + HOCH_2(CH_2)_4CH_3 \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}-O-CH_2(CH_2)_4CH_3 + H_2O$

71. $CFCl{=}CF_2$

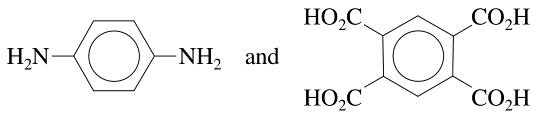
73.



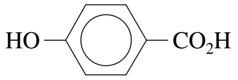
75.



77.

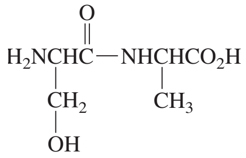


79. Divinylbenzene inserts itself into two adjacent polymer chains and bonds them together. The chains cannot move past each other because of the crosslinks making the polymer more rigid. **81. a.** The polymer from 1,2-diaminoethane and terephthalic acid is stronger because of the possibility of hydrogen bonding between chains. **b.** The polymer of



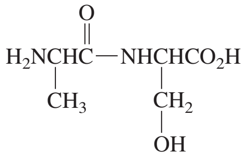
is more rigid because the chains are stiffer due to the rigid benzene rings in the chains. **c.** Polyacetylene is $n\mathrm{HC{\equiv}CH} \rightarrow \mathrm{+\!(CH{=}CH)\!+}_n$. Polyacetylene is more rigid because the double bonds in the chains make the chains stiffer. **83. a.** serine; tyrosine; threonine; **b.** aspartic acid; glutamic acid; **c.** histidine; lysine; arginine; tryptophan; **d.** glutamine; asparagine **85. a.** aspartic acid and phenylalanine; **b.** Aspartame contains the methyl ester of phenylalanine. This ester can hydrolyze to form methanol, $\mathrm{R{-}CO_2CH_3 + H_2O \rightleftharpoons RCO_2H + CH_3OH}$.

87.



$\mathrm{H_2NCH(CH_2OH)C({=}O){-}NHCH(CH_3)CO_2H}$

ser–ala

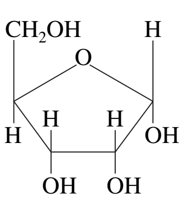


$\mathrm{H_2NCH(CH_3)C({=}O){-}NHCH(CH_2OH)CO_2H}$

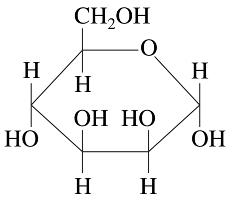
ala–ser

89. 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 **91.** Ionic: his, lys, or arg with asp or glu; hydrogen bonding: ser, glu, tyr, his, arg, asn, thr, asp, gln, or lys with any amino acid; covalent: cys with cys; London dispersion: all amino acids with nonpolar R groups (gly, ala, pro, phe, ile, trp, met, leu, val); dipole–dipole: tyr, thr, and ser with each other **93.** Glutamic acid has a polar R group and valine has a nonpolar R group. The change in polarity of the R groups could affect the tertiary structure of hemoglobin and affect the ability of hemoglobin to bond to oxygen.

95.

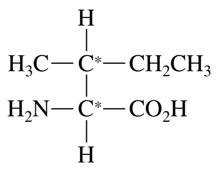


D-Ribose

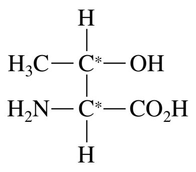


D-Mannose

97. aldohexose: glucose, mannose, galactose; aldopentose: ribose, arabinose; ketohexose: fructose; ketopentose; ribulose **99.** They differ in the orientation of a hydroxy group on a particular carbon. Starch is composed from α-D-glucose, and cellulose is composed from β-D-glucose.
101. The chiral carbons are marked with asterisks.

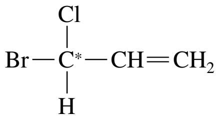


Isoleucine



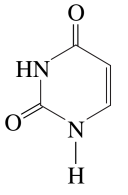
Threonine

103.

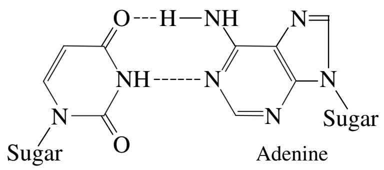


$\mathrm{Br{-}C^{*}(Cl)(H){-}CH{=}CH_2}$

is optically active. The chiral carbon is marked with an asterisk. **105.** C–C–A–G–A–T–A–T–G **107.** Uracil will H-bond to adenine.



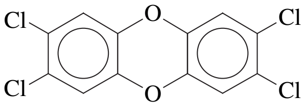
Uracil



Adenine

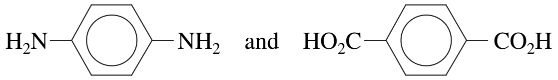
109. a. glu: CTT, CTC; val: CAA, CAG, CAT, CAC; met: TAC; trp: ACC; phe: AAA, AAG; asp: CTA, CTG; **b.** ACC–CTT–AAA–TAC or ACC–CTC–AAA–TAC or ACC–CTT–AAG–TAC or ACC–CTC–AAG– TAC; **c.** four (see answer in part b); **d.** met–asp–phe **e.** TAC–CTA–AAG; TAC–CTA–AAA; TAC–CTG–AAA **111. a.** 2,3,5,6-tetramethyloctane; **b.** 2,2,3,5-tetramethylheptane; **c.** 2,3,4-trimethylhexane; **d.** 3-methyl-1-pentyne

113.

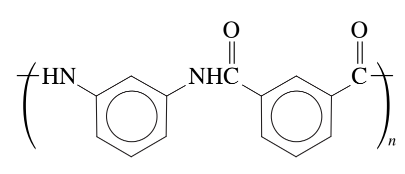


There are many possibilities for isomers. Any structure with four chlorines replacing four hydrogens in any of the numbered positions would be an isomer; i.e., 1,2,3,4-tetrachloro-dibenzo-*p*-dioxin is a possible isomer. **115.** −23°C: $\mathrm{CH_3{-}O{-}CH_3}$; 78.5°C: $\mathrm{CH_3{-}CH_2{-}OH}$ **117.** Alcohols consist of two parts, the polar OH group and the nonpolar hydrocarbon chain attached to the OH group. As the length of the nonpolar hydrocarbon chain increases, the solubility of the alcohol decreases. In methyl alcohol (methanol), the polar OH group can override the effect of the nonpolar CH_3 group, and methyl alcohol is soluble in water. In stearyl alcohol, the molecule consists mostly of the long nonpolar hydrocarbon chain, so it is insoluble in water. **119.** *n*-hexane, 69°C; pentanal, 103°C; 1-pentanol, 137°C; butanoic acid, 164°C. **121.** 1-butene **123.** ethanoic acid **125.** In nylon, hydrogen-bonding interactions occur due to the presence of N—H bonds in the polymer. For a given polymer chain length, there are more N—H groups in nylon-46 as compared to nylon-6. Hence, nylon-46 forms a stronger polymer compared to nylon-6 due to the increased hydrogen-bonding interactions.

127. a.



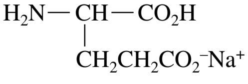
b. Repeating unit:



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. **129. a.** The bond angles in the ring are about 60°. VSEPR predicts bond angles close to 109°. The bonding electrons are much closer together than they prefer, resulting in strong electron–electron repulsions. Thus ethylene oxide is unstable (reactive). **b.** The ring opens up during polymerization and the monomers link together through the formation of O—C bonds.

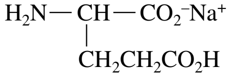
$$\mathrm{+\!O{-}CH_2CH_2{-}O{-}CH_2CH_2{-}O{-}CH_2CH_2\!+}_n$$

131.



$\mathrm{H_2N{-}CH(CH_2CH_2CO_2^{-}Na^{+}){-}CO_2H}$

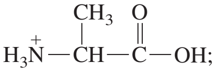
or

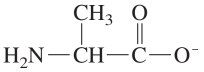


$\mathrm{H_2N{-}CH(CH_2CH_2CO_2H){-}CO_2^{-}Na^{+}}$

The first structure is MSG, which is impossible for you to predict. **133.** In the reaction, P—O and O—H bonds are broken and P—O and O—H bonds are formed. Thus $\Delta H \approx 0$. $\Delta S < 0$, since two molecules are going to form one molecule. Thus $\Delta G > 0$, not spontaneous.

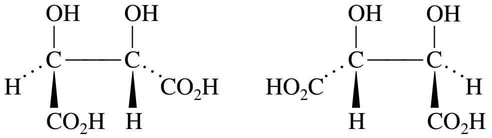
135.

1.0 M H^+: 
$H_3\overset{+}{N}-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-OH$;

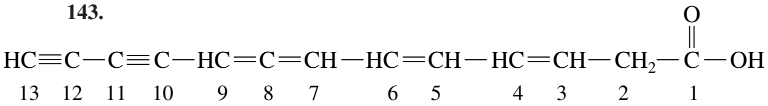
1.0 M OH^-: 
$H_2N-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^-$

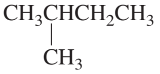
137. Both ΔH and ΔS are positive values. **139.** 6.07 **141. a.** No; the mirror image is superimposable.

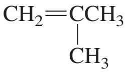
b.

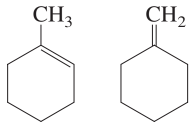


143.

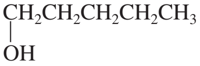

$HC{\equiv}C-C{\equiv}C-HC{=}C{=}CH-HC{=}CH-HC{=}CH-CH_2-\overset{O}{\overset{\|}{C}}-OH$
13 12 11 10 9 8 7 6 5 4 3 2 1

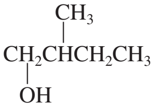
145. a. 
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_3$

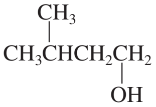
b. 
$CH_2{=}\underset{\underset{CH_3}{|}}{C}CH_3$

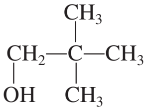
c. 

d. $CH_2{=}CHCH_3$

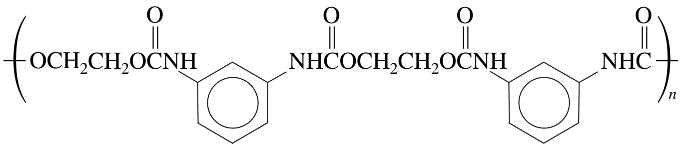
e. 
$\underset{\underset{OH}{|}}{CH_2}CH_2CH_2CH_2CH_2CH_3$


$\underset{\underset{OH}{|}}{CH_2}\overset{\overset{CH_3}{|}}{CH}CH_2CH_3$


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


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

147.



149. a. The temperature of the rubber band increases when it is stretched; **b.** exothermic (heat is released); **c.** As the chains are stretched, they line up more closely resulting in stronger dispersion forces between the chains. Heat is released as the strength of the intermolecular forces increases. **d.** ΔG is positive and ΔS is negative; **e.** The structure of the stretched polymer chains is more ordered than in unstretched rubber. Disorder decreases as the rubber band is stretched. **151.** 0.11% **153.** 5 **155. a.** 37.50%; **b.** The hybridization changes from sp^2 to sp^3; **c.** 3,4-dimethyl-3-hexanol