59. **a.** $Zn(s)$

61. 0.807 mol orbitals

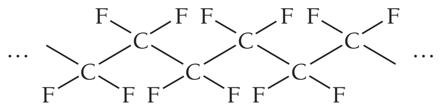
63. insulator

65. **a.** p-type

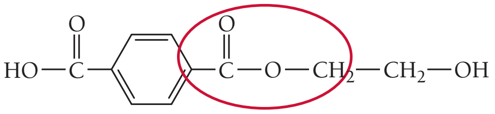
b. n-type

67. Yes, it has sufficient energy.

69.

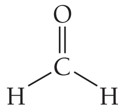


71.



73. $H—C \equiv C—H$

75.



77. CsCl has a higher melting point than AgI because of its higher coordination number. In CsCl, one anion bonds to eight cations (and vice versa), while in AgI, one anion bonds to only four cations.

79. **a.** $4r$

$c^2 = a^2 + b^2 \; c = 4r, a = l, b = l$

$(4r)^2 = l^2 + l^2$

$16r^2 = 2l^2$

b. $8r^2 = l^2$

$l = \sqrt[3]{8r^2}$

$l = 2\sqrt{2r}$

81. 8 atoms/unit

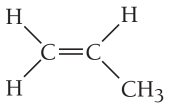
83. 55.843 g/mol

85. 2.00 g/cm^3

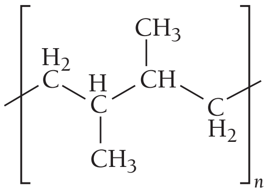
87. body diagonal $= \sqrt{6}r$,
radius $= (\sqrt{3} - \sqrt{2})r/\sqrt{2} = 0.2247r$

89. The higher-level electron transitions with their smaller energy gaps would not give off enough energy to create X-rays.

91. **a.**



b.



To obtain this structure, the monomer from part a would react in a head-to-head (or tail-to-tail) addition as opposed to the head-to-tail addition that leads to the structure shown in Table 12.3.

93. Because the structure is a face-centered cubic, there are therefore four C_{60} molecules per unit cell. Thus, there must be 3 × 4 = 12 Rb atoms per unit cell, and all sites (tetrahedral and octahedral) are occupied.

95. The liquid must be cooled quickly in order to prevent the formation of an organized crystal structure and instead achieve an amorphous product.

97. Both structures may be viewed as having essentially a face-centered cubic unit cell with half of the tetrahedral holes filled. Diamond, however, consists of only one type of atom (C) and is covalently bound, whereas zinc blende has S^{2-} ions at the face-centered cubic sites and Zn^{2+} ions in the tetrahedral holes, and is held together by ionic forces.

99. **d.** All of the above would likely lead to an increase in electrical conductivity.

105. **a.** 20% Cr and 80% Ni; 1405°

a. 97% Cr and 3% Ni; body-centered cubic

Chapter 14

29. **a.** hexane, toluene, or CCl_4; dispersion forces

b. water, methanol; dispersion, dipole–dipole, hydrogen bonding

c. hexane, toluene, or CCl_4; dispersion forces

d. water, acetone, methanol, ethanol; dispersion, ion–dipole

31. $HOCH_2CH_2CH_2OH$

33. **a.** water; dispersion, dipole–dipole, hydrogen bonding

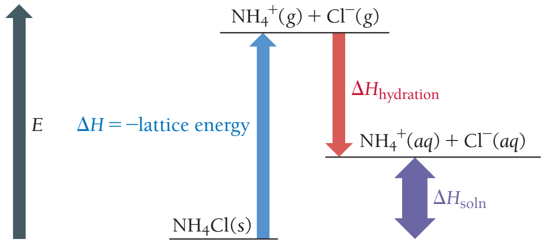
b. hexane; dispersion

c. water; dispersion, dipole–dipole

35. **a.** endothermic

b. The lattice energy is greater in magnitude than the heat of hydration.

c.



d. The solution forms because chemical systems tend toward greater entropy.

37. −797 kJ/mol

39. $\Delta H_{soln} = -6 \times 10^1$ kJ/mol, −7 kJ of energy evolved

41. unsaturated

43. About 31 g will precipitate.

45. Boiling water releases any O_2 dissolved in it. The solubility of gases decreases with increasing temperature.

47. As pressure increases, nitrogen will more easily dissolve in blood. To reverse this process, divers should ascend to lower pressures.

49. 1.1 g

51. 1.92 M, 2.0 *m*, 10.4%

53. 0.340 L

55. 1.6×10^2 g

57. 1.4×10^4 g

59. Add water to 7.31 mL of concentrated solution until a total volume of 1.15 L is acquired.

61. **a.** Add water to 3.73 g KCl to a volume of 100 mL.

b. Add 3.59 g KCl to 96.41 g H_2O.

c. Add 5.0 g KCl to 95 g H_2O.

63. **a.** 0.417 M **b.** 0.444 *m*

c. 7.41% by mass **d.** 0.00794

e. 0.794% by mole

65. 0.89 M

67. 15 *m*, 0.22

69. The level has decreased more in the beaker filled with pure water. The dissolved salt in the seawater decreases the vapor pressure and subsequently lowers the rate of vaporization.

71. 30.7 torr

73. **a.** $P_{\text{hep}} = 24.4$ torr, $P_{\text{oct}} = 5.09$ torr
b. 29.5 torr
c. 80.8% heptane by mass, 19.2% octane by mass
d. The vapor is richer in the more volatile component.

75. $P_{\text{chl}} = 51.9$ torr, $P_{\text{ace}} = 274$ torr, $P_{\text{tot}} = 326$ torr. The solution is not ideal. The chloroform–acetone interactions are stronger than the chloroform–chloroform and acetone–acetone interactions.

77. freezing point (fp) $= -1.27$ °C, bp $= 100.349$ °C

79. freezing point (fp) $= 1.0$ °C, boiling point(bp) $= 82.4$ °C

81. 1.8×10^2 g/mol

83. 26.1 atm

85. 6.36×10^3 g/mol

87. **a.** fp $= -0.558$ °C, bp $= 100.154$ °C
b. fp $= -1.98$ °C, bp $= 100.546$ °C
c. fp $= -2.5$ °C, bp $= 100.70$ °C

89. 157 g

91. **a.** −0.632 °C **b.** 5.4 atm **c.** 100.18 °C

93. 2.3

95. 3.4

97. 23.0 torr

99. Chloroform is polar and has stronger solute–solvent interactions than nonpolar carbon tetrachloride.

101. $\Delta H_{\text{soln}} = 51$ kJ/mol, −8.7 °C

103. 2.2×10^{-3} M/atm

105. 1.3×10^4 L

107. 0.24 g

109. −24 °C

111. **a.** 1.1% by mass/*V* **b.** 1.6% by mass/*V*
c. 5.3% by mass/*V*

113. 2.484

115. 0.229 atm

117. $\chi_{\text{CHCl}_3}(\text{original}) = 0.657$,
$P_{\text{CHCl}_3}(\text{condensed}) = 0.346$ atm

119. 1.74 M

121. $C_6H_{14}O_2$

123. 12 grams

125. 6.4×10^{-3} L

127. $2\underline{2}.4$ glucose by mass, $7\underline{7}.6$ sucrose by mass

129. $P_{\text{iso}} = 0.131$ atm, $P_{\text{pro}} = 0.068$ atm. The major intermolecular attractions are between the OH groups. The OH group at the end of the chain in propyl alcohol is more accessible than the one in the middle of the chain in isopropyl alcohol. In addition, the molecular shape of propyl alcohol is a straight chain of carbon atoms, while that of isopropyl alcohol is a branched chain and is more like a ball. The contact area between two ball-like objects is smaller than that of two chain-like objects. The smaller contact area in isopropyl alcohol means the molecules don't attract each other as strongly as do those of propyl alcohol. As a result of both of these factors, the vapor pressure of isopropyl alcohol is higher.

131. 0.005 *m*

133. Na_2CO_3 0.050 M, $NaHCO_3$ 0.075 M

135. The water should not be immediately cycled back into the river. As the water was warmed, dissolved oxygen would have been released, since the amount of a gas able to be dissolved into a liquid decreases as the temperature of the liquid increases. As such, the water returned to the river would lack dissolved oxygen if it was still hot. To preserve the dissolved oxygen necessary for the survival of fish and other aquatic life, the water must first be cooled.

137. **b.** NaCl

144. **a.** The salinity of seawater is generally higher near the equator and lower near the poles.
c. −2.3 °C

Chapter 15

25. **a.** $\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{HBr}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$
b. 1.8×10^{-3} M/s
c. 0.040 mol Br_2

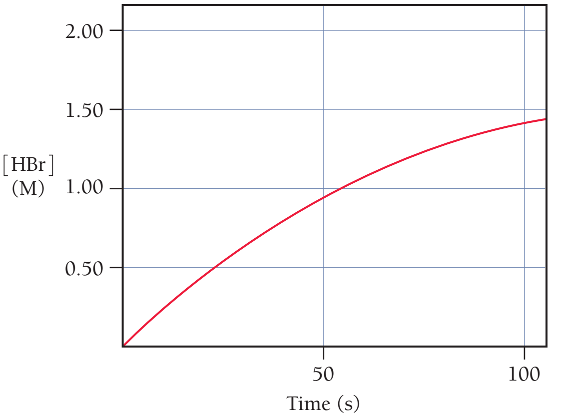
27. **a.** $\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{C}]}{\Delta t}$
b. $\frac{\Delta[\text{B}]}{\Delta t} = -0.0500\ \text{M/s}, \frac{\Delta[\text{C}]}{\Delta t} = 0.150\ \text{M/s}$

29.

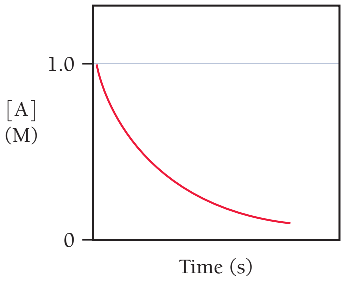
$\Delta[Cl_2]/\Delta t$	$\Delta[F_2]/\Delta t$	$\Delta[ClF_3]/\Delta t$	Rate
−0.012 M/s	−0.036 M/s	0.024 M/s	0.012 M/s

31. **a.** $0 \longrightarrow 10\ \text{s}: \text{Rate} = 8.7 \times 10^{-3}$ M/s
$40 \longrightarrow 50\ \text{s}: \text{Rate} = 6.0 \times 10^{-3}$ M/s
b. 1.4×10^{-2} M/s

33. **a.** **i.** 1.0×10^{-2} M/s **ii.** 8.5×10^{-3} M/s
iii. 0.013 M/s
b.



35. **a.** first order
b.



c. $\text{Rate} = k[\text{A}]^1, k = 0.010\ \text{s}^{-1}$

37. **a.** s^{-1} **b.** $M^{-1}\,s^{-1}$ **c.** $M \cdot s^{-1}$

39. **a.** Rate $= k[A][B]^2$ **b.** third order
c. 2 **d.** 4
e. 1 **f.** 8

41. second order, Rate $= 5.25\ M^{-1}\,s^{-1}[A]^2$

43. first order, Rate $= 0.065\ s^{-1}[A]$

45. Rate $= k[NO_2][F_2]$, $k = 2.57\ M^{-1}\,s^{-1}$, second order

47. **a.** zero order **b.** first order
c. second order

49. second order, $k = 2.25 \times 10^{-2}\ M^{-1}\,s^{-1}$, [AB] at 25 s = 0.619 M

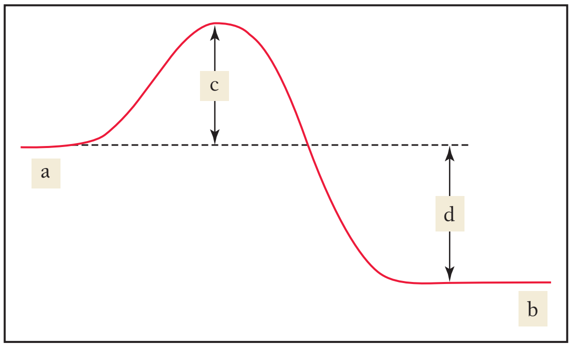
51. first order, $k = 1.12 \times 10^{-2}\ s^{-1}$, Rate $= 2.8 \times 10^{-3}$ M/s

53. **a.** $4.5 \times 10^{-3}\ s^{-1}$ **b.** Rate $= 4.5 \times 10^{-3}\ s^{-1}[A]$
c. 1.5×10^2 s **d.** $[A] = 0.0908$ M

55. **a.** 4.88×10^3 s **b.** 9.8×10^3 s
c. 1.7×10^3 s
d. 0.146 M at 200 s, 0.140 M at 500 s

57. 6.8×10^8 yr; 1.8×10^{17} atoms

59.



61. $17\ s^{-1}$

63. 61.90 kJ/mol

65. $E_a = 251$ kJ/mol, $A = 7.93 \times 10^{11}\ s^{-1}$

67. $E_a = 23.0$ kJ/mol, $A = 8.05 \times 10^{10}\ M^{-1}s^{-1}$

69. **a.** 122 kJ/mol
b. $0.101\ s^{-1}$

71. 47.85 kJ/mol

73. **a**

75. The mechanism is valid.

77. **a.** $Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$
b. $Cl(g)$, $CCl_3(g)$
c. Rate $= k[Cl_2]^{1/2}[CHCl_3]$

79. Heterogeneous catalysts require a large surface area because catalysis can only happen at the surface. A greater surface area means greater opportunity for the substrate to react, which results in a faster reaction.

81. 10^{12}

83. **a.** first order, $k = 0.0462\ hr^{-1}$
b. 15 hr
c. 5.0×10^1 hr

85. 0.0531 M/s

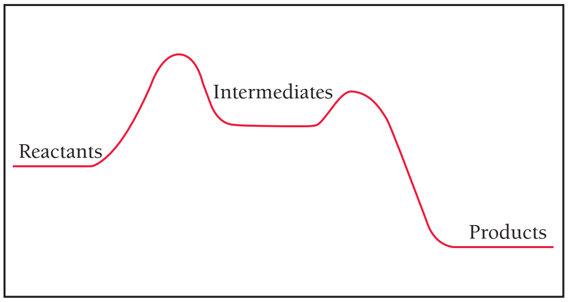
87. rate $= 4.5 \times 10^{-4}[CH_3CHO]^2$, $k = 4.5 \times 10^{-4}$, 0.37 atm

89. 219 torr

91. 1×10^{-7} s

93. 1.6×10^2 seconds

95. **a.** 2
b.



c. first step
d. exothermic

97. **a.** 5.41 s
b. 2.2 s for 25%, 5.4 s for 50%
c. 0.28 at 10 s, 0.077 at 20 s

99. **a.** $E_a = 89.5$ kJ/mol, $A = 4.22 \times 10^{11}\ s^{-1}$
b. $2.5 \times 10^{-5}\ M^{-1}\,s^{-1}$
c. 6.0×10^{-4} M/s

101. **a.** No
b. No bond is broken, and the two radicals attract each other.
c. Formation of diatomic gases from atomic gases

103. 1.35×10^4 years

105. **a.** Both are valid. For both, all steps sum to overall reaction, and the predicted rate law is consistent with experimental data.
b. Buildup of I(g)

107. rate $= k_2[(k_1/k_{-1})[Br_2]]^{1/2}[H_2]$ The rate law is 3/2 order overall.

109. **a.** 0% **b.** 25% **c.** 33%

111. 174 kJ

113. **a.** second order
b. $CH_3NC + CH_3NC \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3NC^* + CH_3NC$ (fast)

$CH_3NC^* \xrightarrow{k_3} CH_3CN$ (slow)

$$k_1[CH_3NC]^2 = k_2[CH_3NC^*][CH_3NC]$$

$$[CH_3NC^*] = \frac{k_1}{k_2}[CH_3NC]$$

$$\text{Rate} = k_3 \times \frac{k_1}{k_2}[CH_3NC]$$

$$\text{Rate} = k[CH_3NC]$$

115. Rate $= k[A]^2$

$$\text{Rate} = -\frac{d[A]}{dt}$$

$$\frac{d[A]}{dt} = -k[A]^2$$

$$2\frac{d[A]}{[A]^2} = k\,dt$$

$$\int_{[A]_0}^{[A]} -\frac{1}{[A]^2}d[A] = \int_0^t k\,dt$$

$$\left[\frac{1}{[A]}\right]_{[A]_0}^{[A]} = k[t]_0^t$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

117. $k = 3.20 \times 10^{-4}\ \mathrm{s}^{-1}$

119. b)

121. B is first order and A is second order. B will be linear if you plot ln[B] versus time; A will be linear if you plot 1/[A] versus time.

125. **a.** The reaction is first order in CH_4 and first order in O_3.
a. 1.7×10^{-18} M/s

Chapter 16

21. **a.** $K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]}$ **b.** $K = \frac{[NO]^2[Br_2]}{[BrNO]^2}$
c. $K = \frac{[CS_2][H_2]^4}{[CH_4][H_2S]^2}$ **d.** $K = \frac{[CO_2]^2}{[CO]^2[O_2]}$

23. The concentration of the reactants will be greater. No, this is not dependent on initial concentrations; it is dependent on the value of K_c.

25. **a.** figure v
b. The change in the decrease of reactants and increase of products would be faster.
c. No, catalysts affect kinetics, not equilibrium.

27. **a.** 4.42×10^{-5}, reactants favored
b. 1.50×10^{2}, products favored
c. 1.96×10^{-9}, reactants favored

29. 1.3×10^{-29}

31. **a.** 2.56×10^{-23} **b.** 1.3×10^{22}
c. 81.9

33. **a.** $K_c = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$ **b.** $K_c = [O_2]^3$
c. $K_c = \frac{[H_3O^+][F^-]}{[HF]}$ **d.** $K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$

35. 136

37.

T(K)	$[N_2]$	$[H_2]$	$[NH_3]$	K_c
500	0.115	0.105	0.439	1.45×10^3
575	0.110	0.249	0.128	9.6
775	0.120	0.140	4.39×10^{-3}	0.0584

39. 234 torr

41. 18

43. 3.3×10^2

45. 764

47. More solid will form.

49. Additional solid will not dissolve.

51. **a.** [A] = 0.20 M, [B] = 0.80 M
b. [A] = 0.33 M, [B] = 0.67 M
c. [A] = 0.38 M, [B] = 1.2 M

53. $[N_2O_4] = 0.0115$ M, $[NO_2] = 0.0770$ M

55. 0.199 M

57. 1.9×10^{-3} M

59. 7.84 torr

61. **a.** [A] = 0.38 M, [B] = 0.62 M, [C] = 0.62 M
b. [A] = 0.90 M, [B] = 0.095 M, [C] = 0.095 M
c. [A] = 1.0 M, [B] = 3.2×10^{-3} M, [C] = 3.2×10^{-3} M

63. **a.** shift left **b.** shift right
c. shift right

65. **a.** shift right **b.** no effect
c. no effect **d.** shift left

67. **a.** shift right **b.** shift left
c. no effect

69. Increase temperature → shift right, decrease temperature → shift left. Increasing the temperature will increase the equilibrium constant.

71. **b, d**

73. **a.** 1.7×10^2
b. $\frac{[Hb{-}CO]}{[Hb{-}O_2]} = 0.85$ or 17/20
CO is highly toxic, as it blocks O_2 uptake by hemoglobin. CO_2 at a level of 0.1% will replace nearly half of the O_2 in blood.

75. **a.** 1.68 atm **b.** 1.41 atm

77. 0.406 g

79. **b, c, d**

81. 0.0144 atm

83. 3.1×10^2 g, 20% yield

85. 0.12 atm

87. 0.72 atm

89. 0.017 g

91. 0.226

93. **a.** 29.3 **b.** 169 torr

95. $P_{NO} = P_{Cl_2} = 429$ torr

97. 1.27×10^{-2}

99. $K_P = 5.1 \times 10^{-2}$

101. Yes, because the volume affects Q.

103. $a = 1, b = 2$

105. $K_c = 1$

111. **a.** For system 1, $K_p = 0.011$; For system 2, $K_p = 91$.
c. System 1 is more likely.

Chapter 17

33. **a.** acid, $HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$
b. acid, $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$
c. base, $KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$
d. acid, $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$

35. **a.** $\underset{\text{acid}}{H_2CO_3(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conj. acid}}{H_3O^+(aq)} + \underset{\text{conj. base}}{HCO_3^-(aq)}$

b. $\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conj. acid}}{NH_4^+(aq)} + \underset{\text{conj. base}}{OH^-(aq)}$

c. $\underset{\text{acid}}{HNO_3(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conj. acid}}{H_3O^+(aq)} + \underset{\text{conj. base}}{NO_3^-(aq)}$

d. $\underset{\text{base}}{C_5H_5N(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conj. acid}}{C_5H_5NH^+(aq)} + \underset{\text{conj. base}}{OH^-(aq)}$

37. **a.** Cl^- **b.** HSO_3^- **c.** CHO_2^- **d.** F^-

39. $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

41. **a.** strong **b.** strong
c. strong **d.** weak, $K_a = \frac{[H_3O^+][HSO_3^-]}{[H_2SO_3]}$

43. **a, b, c**

45. **a.** F^- **b.** NO_2^- **c.** ClO^-

47. **a.** 8.3×10^{-7}, basic **b.** 1.2×10^{-10}, acidic
c. 2.9×10^{-13}, acidic

49. **a.** $\mathrm{pH} = 7.77, \mathrm{pOH} = 6.23$
b. $\mathrm{pH} = 7.00, \mathrm{pOH} = 7.00$
c. $\mathrm{pH} = 5.66, \mathrm{pOH} = 8.34$

51.

$[H_3O^+]$	$[OH^-]$	pH	Acidic or Basic
7.1×10^{-4}	1.4×10^{-11}	3.15	Acidic
3.7×10^{-9}	2.7×10^{-6}	8.43	Basic
7.9×10^{-12}	1.3×10^{-3}	11.1	Basic
6.3×10^{-4}	1.6×10^{-11}	3.20	Acidic

53. $[H_3O^+] = 1.5 \times 10^{-7}\,\mathrm{M}, \mathrm{pH} = 6.81$

55. $\mathrm{pH} = 1.36, 1.35, 1.34$. A difference of 1 in the second significant digit in a concentration value produces a difference of 0.01 in pH. Therefore, the second significant digit in value of the concentration corresponds to the hundredths place in a pH value.

57. **a.** $[H_3O^+] = 0.25\,\mathrm{M}, [OH^-] = 4.0 \times 10^{-14}\,\mathrm{M}, \mathrm{pH} = 0.60$
b. $[H_3O^+] = 0.015\,\mathrm{M}, [OH^-] = 6.7 \times 10^{-13}\,\mathrm{M}, \mathrm{pH} = 1.82$
c. $[H_3O^+] = 0.072\,\mathrm{M}, [OH^-] = 1.4 \times 10^{-13}\,\mathrm{M}, \mathrm{pH} = 1.14$
d. $[H_3O^+] = 0.105\,\mathrm{M}, [OH^-] = 9.5 \times 10^{-14}\,\mathrm{M}, \mathrm{pH} = 0.979$

59. **a.** 1.8 g **b.** 0.57 g **c.** 0.045 g

61. 2.21

63. $[H_3O^+] = 2.5 \times 10^{-13}\,\mathrm{M}, \mathrm{pH} = 2.59$

65. **a.** 1.82 (approximation valid)
b. 2.18 (approximation breaks down)
c. 2.72 (approximation breaks down)

67. 2.75

69. 6.8×10^{-6}

71. 0.0063%

73. **a.** 0.42% **b.** 0.60%
c. 1.3% **d.** 1.9%

75. 3.61×10^{-5}

77. **a.** $\mathrm{pH} = 1.88$, percent ionization $= 5.1\%$
b. $\mathrm{pH} = 2.10$, percent ionization $= 7.9\%$
c. $\mathrm{pH} = 2.26$, percent ionization $= 11\%$

79. **a.** 0.939 **b.** 1.07
c. 2.19 **d.** 3.02

81. **a.** $[OH^-] = 0.15\,\mathrm{M}, [H_3O^+] = 6.7 \times 10^{-14}\,\mathrm{M}, \mathrm{pH} = 13.17, \mathrm{pOH} = 0.83$
b. $[OH^+] = 0.003\,\mathrm{M}, [H_3O^+] = 3.3 \times 10^{-12}\,\mathrm{M}, \mathrm{pH} = 11.48, \mathrm{pOH} = 2.52$
c. $[OH^-] = 9.6 \times 10^{-4}\,\mathrm{M}, [H_3O^+] = 1.0 \times 10^{-11}\,\mathrm{M}, \mathrm{pH} = 10.98, \mathrm{pOH} = 3.02$
d. $[OH^-] = 8.7 \times 10^{-5}\,\mathrm{M}, [H_3O^+] = 1.1 \times 10^{-10}\,\mathrm{M}, \mathrm{pH} = 9.93, \mathrm{pOH} = 4.07$

83. 13.842

85. 0.104 L

87. **a.** $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$,
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$
b. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$,
$$K_b = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]}$$
c. $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$,
$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

89. $[OH^-] = 1.6 \times 10^{-3}\,\mathrm{M}, \mathrm{pOH} = 2.79, \mathrm{pH} = 11.21$

91. 7.48

93. 6.7×10^{-7}

95. **a.** neutral
b. basic, $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$
c. basic, $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$
d. neutral

97. $[OH^-] = 1.4 \times 10^{-6}\,\mathrm{M}, \mathrm{pH} = 8.16$

99. **a.** acidic, $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$
b. neutral
c. acidic, $Co(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Co(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$
d. acidic, $CH_2NH_3^+(aq) + H_2O(l) \rightleftharpoons CH_2NH_2(aq) + H_2O^+(aq)$

101. **a.** acidic **b.** basic
c. neutral **d.** acidic
e. acidic

103. $NaOH, NaHCO_3, NaCl, NH_4ClO_2, NH_4Cl$

105. **a.** 5.13 **b.** 8.87 **c.** 7.0

107. $[K^+] = 0.15\,\mathrm{M}, [F^-] = 0.15\,\mathrm{M}, [HF] = 1.5 \times 10^{-6}\,\mathrm{M}, [OH^-] = 1.5 \times 10^{-6}\,\mathrm{M}; [H_3O^+] = 6.7 \times 10^{-9}\,\mathrm{M}$

109. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$,
$$K_{a_1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$,
$$K_{a_2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$
$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$,
$$K_{a_3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

111. **a.** $[H_3O^+] = 0.048\,\mathrm{M}, \mathrm{pH} = 1.32$
b. $[H_3O^+] = 0.12\,\mathrm{M}, \mathrm{pH} = 0.92$

113. $[H_2SO_3] = 0.418\,\mathrm{M}$
$[HSO_3^-] = 0.082\,\mathrm{M}$
$[SO_3^{2-}] = 6.4 \times 10^{-8}\,\mathrm{M}$
$[H_3O^+] = 0.082\,\mathrm{M}$

115. **a.** $[H_3O^+] = 0.50\,\mathrm{M}, \mathrm{pH} = 0.30$
b. $[H_3O^+] = 0.11\,\mathrm{M}, \mathrm{pH} = 0.96$ (*x is small* approximation breaks down)
c. $[H_3O^+] = 0.059\,\mathrm{M}, \mathrm{pH} = 1.23$

117. **a.** HCl, weaker bond
b. HF, bond polarity
c. H_2Se, weaker bond

119. **a.** H_2SO_4, more oxygen atoms bonded to S
b. $HClO_2$ more oxygen atoms bonded to Cl
c. HClO, Cl has higher electronegativity
d. CCl_3COOH, Cl has higher electronegativity

121. S^{2-}; its conjugate acid (H_2S), is a weaker acid than H_2S.

123. **a.** Lewis acid **b.** Lewis acid
c. Lewis base **d.** Lewis base

125. **a.** acid: Fe^{3+}, base: H_2O
b. acid: Zn^{2+}, base: NH_3
c. acid: BF_3, base: $(CH_3)_3N$

127. **a.** weak **b.** strong
c. weak **d.** strong

129. If blood became acidic, the H^+ concentration would increase. According to Le Châtelier's principle, equilibrium would be shifted to the left and the concentration of oxygenated Hb would decrease.

131. All acid will be neutralized.

133. $[H_3O^+]$(Great Lakes) $= 3 \times 10^{-5}$ M,
$[H_3O^+]$(West Coast) $= 4 \times 10^{-6}$ M. The rain over the Great Lakes is about eight times more concentrated.

135. 2.7

137. **a.** 2.000 **b.** 1.52 **c.** 12.95
d. 11.12 **e.** 5.03

139. **a.** 1.260 **b.** 8.22 **c.** 0.824
d. 8.57 **e.** 1.171

141. **a.** $CN^-(aq) + H^+(aq) \rightleftharpoons HCN(aq)$
b. $NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$
c. $CN^-(aq) + NH_4^+(aq) \rightleftharpoons HCN(aq) + NH_3(aq)$
d. $HSO_4^-(aq) + C_2H_3O_2^-(aq) \rightleftharpoons SO_4^{2-}(aq) + HC_2H_3O_2(aq)$
e. no reaction between the major species

143. 0.794

145. $K_a = 1.4 \times 10^{-4}$

147. 6.79

149. 2.14

151. $[A^-] = 4.5 \times 10^{-5}$ M
$[H^+] = 2.2 \times 10^{-4}$ M
$[HA_2^-] = 1.8 \times 10^{-4}$ M

153. 9.28

155. 50.1 g $NaHCO_3$

157. **b**

159. $CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$

166. **a.** 9.2 g SO_2
c. $S_2O_5^{2-}(aq) + H_2O(l) \rightleftharpoons 2\,HSO_3^-(aq)$
e. 16 g for (a) and 15 g for (b)

Chapter 18

27. **d**

29. **a.** 3.62 **b.** 9.11

31. pure water: 2.1%, in $NaC_7H_5O_2$: 0.065%. The percent ionization in the sodium benzoate solution is much smaller because the presence of the benzoate ion shifts the equilibrium to the left.

33. **a.** 2.14 **b.** 8.32 **c.** 3.46

35. $HCl + NaC_2H_3O_2 \longrightarrow HC_2H_3O_2 + NaCl$
$NaOH + HC_2H_3O_2 \longrightarrow NaC_2H_3O_2 + H_2O$

37. **a.** 3.62 **b.** 9.11

39. **a.** 7.60 **b.** 11.18 **c.** 4.61

41. **a.** 3.86 **b.** 8.95

43. 3.5

45. 3.7 g

47. **a.** 4.74 **b.** 4.68 **c.** 4.81

49. **a.** initial 7.00 after 1.70
b. initial 4.71 after 4.56
c. initial 10.78 after 10.66

51. 1.2 g; 2.7 g

53. **a.** yes **b.** no **c.** yes
d. no **e.** no

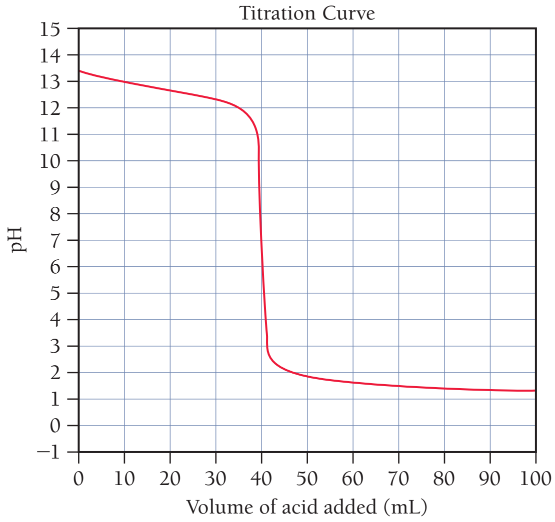
55. **a.** 7.4 **b.** 0.3 g **c.** 0.14 g

57. KClO/HClO = 0.79

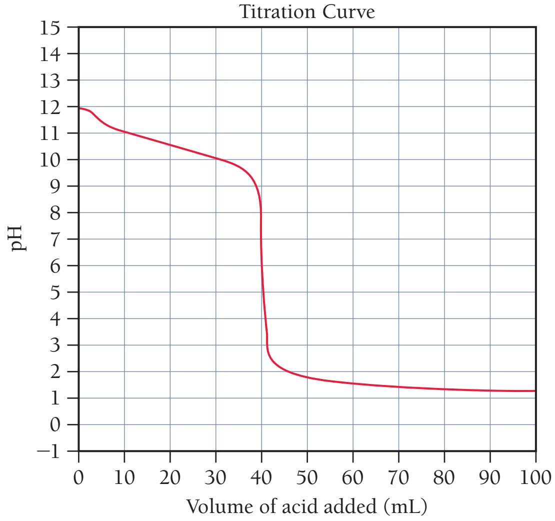
59. **a.** does not exceed capacity
b. does not exceed capacity
c. does not exceed capacity
d. does not exceed capacity

61. **i. a.** pH = 8
b. pH = 7
ii. a. weak acid
b. strong acid

63. **a.** 40.0 mL HI for both
b. KOH: neutral, CH_3NH_2: acidic
c. CH_3NH_2
d. Titration of KOH with HI:



Titration of CH_3NH_2 with HI:



65. **a.** pH = 9, added base = 30 mL
b. 0 mL **c.** 15 mL
d. 30 mL **e.** 30 mL

67. **a.** 0.757 **b.** 30.6 mL **c.** 1.038
d. 7 **e.** 12.15

69. **a.** 13.06 **b.** 28.8 mL **c.** 12.90
d. 7 **e.** 2.07

71. **a.** 2.86 **b.** 16.8 mL **c.** 4.37
d. 4.74 **e.** 8.75 **f.** 12.17

73. **a.** 11.94 **b.** 29.2 mL **c.** 11.33
d. 10.64 **e.** 5.87 **f.** 1.90

75. **i.** (a)
ii. (b)

77. $pK_a = 3{,}82$ g/mol

79. First equivalence: 22.7 mL
Second equivalence: 45.4 mL

81. The indicator will appear red. The pH range is 4 to 6.

83. **a.** phenol red, *m*-nitrophenol
b. alizarin, bromothymol blue, phenol red
c. alizarin yellow R

85. **a.** $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$, $K_{sp} = [Ba^{2+}][SO_4^{2-}]$
b. $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Br^-(aq)$, $K_{sp} = [Pb^{2+}][Br^-]^2$
c. $Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$, $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

87. **a.** 7.31×10^{-7} M **b.** 3.72×10^{-5} M
c. 3.32×10^{-4} M

89. **a.** 1.07×10^{-21} **b.** 7.14×10^{-7}
c. 7.44×10^{-11}

91. AX_2

93. 2.07×10^{-5} g/100 mL

95. **a.** 0.0183 M **b.** 0.00755 M
c. 0.00109 M

97. **a.** 5×10^{14} M **b.** 5×10^{8} M
c. 5×10^{4} M

99. **a.** more soluble, CO_3^{2-} is basic
b. more soluble, S^{2-} is basic
c. not, neutral
d. not, neutral

101. precipitate will form, CaF_2

103. precipitate will form, $Mg(OH)_2$

105. **a.** 0.018 M **b.** 1.4×10^{-7} M
c. 1.1×10^{-5} M

107. **a.** $BaSO_4$, 1.1×10^{-8} M
b. 3.0×10^{-8} M

109. 8.7×10^{-10} M

111. 5.6×10^{16}

113. 4.03

115. 3.57

117. HCl, 4.7 g

119. **a.** $NaOH(aq) + KHC_8H_4O_4(aq) \longrightarrow Na^+(aq) + K^+(aq) + C_8H_4O_4^{2-}(aq) + H_2O(l)$
b. 0.1046 M

121. 4.73

123. 176 g/mol; 1.0×10^{-4}

125. 14.2 L

127. 1.6×10^{-7} M

129. 8.0×10^{-8} M

131. 6.29

133. 0.172 M

135. The ratio by mass of dimethyl ammonium chloride to dimethyl amine needed is 3.6.

137. 0.18 M benzoic acid, 0.41 M sodium benzoate

139. 0.78 g $NaCO_3$

141. 1.8×10^{-11} (based on this data)

143. **a.** 5.5×10^{-25} M **b.** 5.5×10^{-4} M

145. 1.38 L

147. 12.97

149. **a.** $pH < pK_a$ **b.** $pH > pK_a$
c. $pH = pK_a$ **d.** $pH > pK_a$

151. **b**

153. **a.** no difference **b.** less soluble
c. more soluble

160. **a.** 30.0 mL **a.** 1.0×10^{2} g/mol
a. Trimethylamine

Chapter 19

27. **a, c**

29. System B has the greatest entropy. There is only one energetically equivalent arrangement for System A. However, the particles of System B may exchange positions for a second energetically equivalent arrangement.

31. 29.2 J/K

33. −24.7 J/K

35. **a.** $\Delta S > 0$ **b.** $\Delta S < 0$
c. $\Delta S < 0$ **d.** $\Delta S < 0$

37. **a.** $\Delta S_{sys} > 0$, $\Delta S_{surr} > 0$, spontaneous at all temperatures
b. $\Delta S_{sys} < 0$, $\Delta S_{surr} < 0$, nonspontaneous at all temperatures
c. $\Delta S_{sys} < 0$, $\Delta S_{surr} < 0$, nonspontaneous at all temperatures
d. $\Delta S_{sys} > 0$, $\Delta S_{surr} > 0$, spontaneous at all temperatures

39. **a.** 1.29×10^{3} J/K
b. 5.00×10^{3} J/K
c. -3.83×10^{2} J/K
d. -1.48×10^{3} J/K

41. **a.** −649 J/K, nonspontaneous
b. 649 J/K, spontaneous
c. 123 J/K, spontaneous
d. −76 J/K, nonspontaneous

43. **a.** 1.93×10^{5} J, nonspontaneous
b. -1.93×10^{5} J, spontaneous
c. -3.7×10^{4} J, spontaneous
d. 4.7×10^{4} J, nonspontaneous

45. -2.247×10^{6} J, spontaneous

47.

ΔH	ΔS	ΔG	Low Temperature	High Temperature
−	+	−	Spontaneous	Spontaneous
−	−	Temperature dependent	Spontaneous	Nonspontaneous
+	+	Temperature dependent	Nonspontaneous	Spontaneous
+	−	+	Nonspontaneous	Nonspontaneous

49. It increases.

51. **a.** $CO_2(g)$, greater molar mass and complexity
b. $CH_3OH(g)$, gas phase
c. $CO_2(g)$, greater molar mass and complexity
d. $SiH_4(g)$, greater molar mass
e. $CH_3CH_2CH_3(g)$, greater complexity
f. NaBr(*aq*), aqueous

53. **a.** He, Ne, SO_2, NH_3, CH_3CH_2OH From He to Ne there is an increase in molar mass; beyond that, the molecules increase in complexity.
b. $H_2O(s)$, $H_2O(l)$, $H_2O(g)$; increase in entropy in going from solid to liquid to gas phase.
c. CH_4, CF_4, CCl_4; increasing entropy with increasing molar mass.

55. **a.** −120.8 J/K, decrease in moles of gas
b. 133.9 J/K, increase in moles of gas
c. −42.0 J/K, small change because moles of gas stay constant
d. −390.8 J/K, decrease in moles of gas

57. −89.3 J/K, decrease in moles of gas

59. $\Delta H^\circ_{\text{rxn}} = -1277$ kJ, $\Delta S^\circ_{\text{rxn}} = 313.6$ J/K, $\Delta G^\circ_{\text{rxn}} = -1.370 \times 10^3$ kJ; yes

61. **a.** $\Delta H^\circ_{\text{rxn}} = 57.2$ kJ, $\Delta S^\circ_{\text{rxn}} = 175.8$ J/K, $\Delta G^\circ_{\text{rxn}} = 4.8 \times 10^3$ J/mol; nonspontaneous, becomes spontaneous at high temperatures
b. $\Delta H^\circ_{\text{rxn}} = 176.2$ kJ, $\Delta S^\circ_{\text{rxn}} = 285.1$ J/K, $\Delta G^\circ_{\text{rxn}} = 91.2$ KJ; nonspontaneous, becomes spontaneous at high temperatures
c. $\Delta H^\circ_{\text{rxn}} = 98.8$ kJ, $\Delta S^\circ_{\text{rxn}} = 141.5$ J/K, $\Delta G^\circ_{\text{rxn}} = 56.6$ KJ; nonspontaneous, becomes spontaneous at high temperatures
d. $\Delta H^\circ_{\text{rxn}} = -91.8$ kJ, $\Delta S^\circ_{\text{rxn}} = -198.1$ J/K, $\Delta G^\circ_{\text{rxn}} = -32.8$ kJ; spontaneous

63. **a.** 2.8 kJ **b.** 91.2 kJ **c.** 56.4 kJ **d.** −32.8 kJ
Values are comparable. The method using ΔH° and ΔS° can be used to determine how ΔG° changes with temperature.

65. **a.** −72.5 kJ, spontaneous
b. −11.4 kJ, spontaneous
c. 9.1 kJ, nonspontaneous

67. −29.4 kJ

69. **a.** 19.3 kJ **b.** **(i)** 2.9 kJ **(ii)** −2.9 kJ
c. The partial pressure of iodine is very low.

71. 11.9 kJ

73. **a.** 1.48×10^{90} **b.** 2.09×10^{-26}

75. **a.** −24.8 kJ **b.** 0 **c.** 9.4 kJ

77. **a.** 1.90×10^{47} **b.** 1.51×10^{-13}

79. $\Delta H^\circ = 50.6$ kJ $\Delta S^\circ = 226$ J·K

81. 4.8

83. **a.** + **b.** − **c.** −

85. **a.** $\Delta G^\circ = 175.2$ kJ, $K = 1.95 \times 10^{-31}$, nonspontaneous
b. 133 kJ, yes

87. Cl_2 : $\Delta H^\circ_{\text{rxn}} = -182.1$ kJ, $\Delta S^\circ_{\text{rxn}} = -134.4$ J/K, $\Delta G^\circ_{\text{rxn}} = -142.0$ kJ $K = 7.94 \times 10^{24}$
Br_2 : $\Delta H^\circ_{\text{rxn}} = -121.6$ kJ, $\Delta S^\circ_{\text{rxn}} = -134.2$ J/K, $\Delta G^\circ_{\text{rxn}} = -81.6$ kJ $K = 2.02 \times 10^{14}$
I_2 : $\Delta H^\circ_{\text{rxn}} = -48.3$ kJ, $\Delta S^\circ_{\text{rxn}} = -132.2$ J/K, $\Delta G^\circ_{\text{rxn}} = -8.9$ kJ $K = 37$
Cl_2 is the most spontaneous, and I_2 is the least. Spontaneity is determined by the standard enthalpy of formation of the dihalogenated ethane. Higher temperatures make the reactions less spontaneous.

89. **a.** 107.8 kJ **b.** 5.0×10^{-7} atm
c. spontaneous at higher temperatures, $T = 923.4$ K

91. **a.** 2.22×10^5 **b.** 94.4 mol

93. **a.** $\Delta G^\circ = -689.6$ kJ, ΔG° becomes less negative.
b. $\Delta G^\circ = -665.2$ kJ, ΔG° becomes less negative.
c. $\Delta G^\circ = -632.4$ kJ, ΔG° becomes less negative.
d. $\Delta G^\circ = -549.3$ kJ, ΔG° becomes less negative.

95. With one exception, the formation of any oxide of nitrogen at 298 K requires more moles of gas as reactants than are formed as products. For example, 1 mol of N_2O requires 0.5 mol of O_2 and 1 mol of N_2, 1 mol of N_2O_3 requires 1 mol of N_2 and 1.5 mol of O_2, and so on. The exception is NO, where 1 mol of NO requires 0.5 mol of O_2 and 0.5 mol of N_2:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$$

This reaction has a positive ΔS because what is essentially mixing of the N and O has taken place in the product.

97. 15.0 kJ

99. **a.** Positive, the process is spontaneous. It is slow unless a spark is applied.
b. Positive, although the change in the system is not spontaneous; the overall change, which includes such processes as combustion or water flow to generate electricity, is spontaneous.
c. Positive, the acorn-oak tree system is becoming more ordered, so the processes associated with growth are not spontaneous. But they are driven by spontaneous processes such as the generation of heat by the sun and the reactions that produce energy in the cell.

101. At 18.3 mmHg $\Delta G = 0$, at 760 mmHg $\Delta G^\circ = 55.4$ kJ

103. **a.** 3.24×10^{-3}
b.

$$\begin{array}{l} NH_3 + ATP + H_2O \longrightarrow NH_3{-}P_i + ADP \\ NH_3{-}P_i + C_5H_8O_4N^- \longrightarrow C_5H_9O_3N_2 + P_i + H_2O \\ \hline NH_3 + C_5H_8O_4N^- + ATP \longrightarrow C_5H_9O_3N_2 + ADP + P_i \end{array}$$

$\Delta G^\circ = -16.3$ kJ, $K = 7.20 \times 10^2$

105. **a.** −95.3 kJ/mol Since the number of moles of reactants and products is the same, the decrease in volume affects the entropy of both equally, so there is no change in ΔG.
b. 102.8 kJ/mol The entropy of the reactants (1.5 mol) is decreased more than the entropy of the product (1 mol). Since the product is relatively more favored at lower volume, ΔG is less positive.
c. 204.2 kJ/mol The entropy of the product (1 mol) is decreased more than the entropy of the reactant (0.5 mol). Since the product is relatively less favored, ΔG is more positive.

107. $\Delta H^\circ = -93$ kJ, $\Delta S^\circ = -2.0 \times 10^2$ J/K

109. ΔS_{vap} diethyl ether $= 86.1$ J/mol K,
ΔS_{vap} acetone $= 88.4$ J/mol K,

ΔS_{vap} benzene $= 87.3$ J/mol K,
ΔS_{vap} chloroform $= 88.0$ J/mol K. Because water and ethanol hydrogen bond, they are more ordered in the liquid and we expect ΔS_{vap} to be more positive.
Ethanol $38600/351.0 = 38600/351.0 = 110$ J/mol K,
$H_2O = 40700/373.2 = 109$ J/mol K

111. c

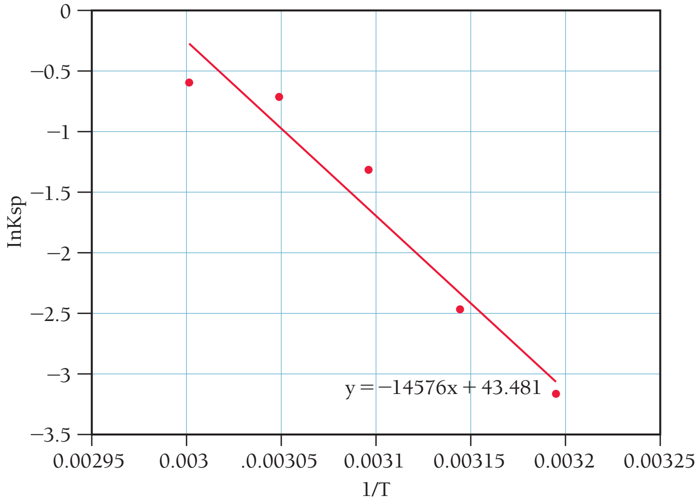
113. b

115. c

117. $\Delta G^\circ_{\text{rxn}}$ is negative and ΔG_{rxn} is positive.

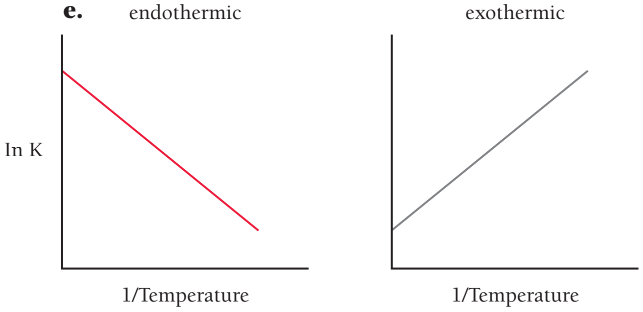
123.

a.



c. 362 J/K

e.



Chapter 20

37. **a.** $3\,K(s) + Cr^{3+}(aq) \longrightarrow Cr(s) + 3\,K^+(aq)$

b. $2\,Al(s) + 3\,Fe^{2+}(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,Fe(s)$

c. $2\,BrO_3^-(aq) + 3\,N_2H_4(g) \longrightarrow 2\,Br^-(aq) + 3\,N_2(g) + 6\,H_2O(l)$

39. **a.** $PbO_2(s) + 2\,I^-(aq) + 4\,H^+(aq) \longrightarrow Pb^{2+}(aq) + I_2(s) + 2\,H_2O(l)$

b. $5\,SO_3^{2-}(aq) + 2\,MnO_4^-(aq) + 6\,H^+(aq) \longrightarrow 5\,SO_4^{2-}(aq) + 2\,Mn^{2+}(aq) + 3\,H_2O(l)$

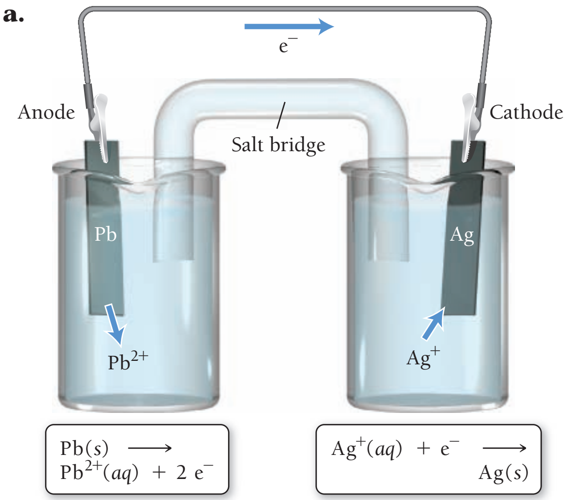
c. $S_2O_3^{2-}(aq) + 4\,Cl_2(g) + 5\,H_2O(l) \longrightarrow 2\,SO_4^{2-}(aq) + 8\,Cl^-(aq) + 10\,H^+(aq)$

41. **a.** $H_2O_2(aq) + 2\,ClO_2(aq) + 2\,OH^-(aq) \longrightarrow O_2(g) + 2\,ClO_2^-(aq) + 2\,H_2O(l)$

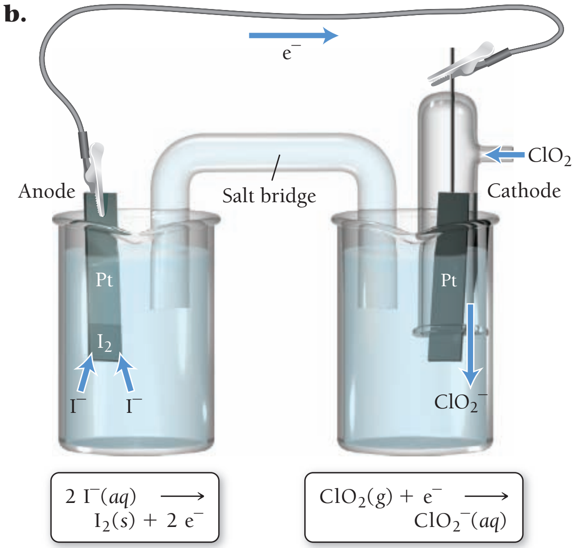
b. $Al(s) + MnO_4^-(aq) + 2\,H_2O(l) \longrightarrow Al(OH)_4^-(aq) + MnO_2(s)$

c. $Cl_2(g) + 2\,OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$

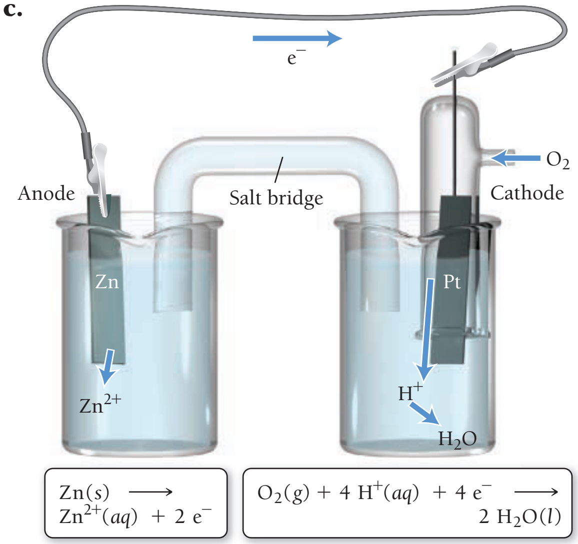
43. **a.**



b.

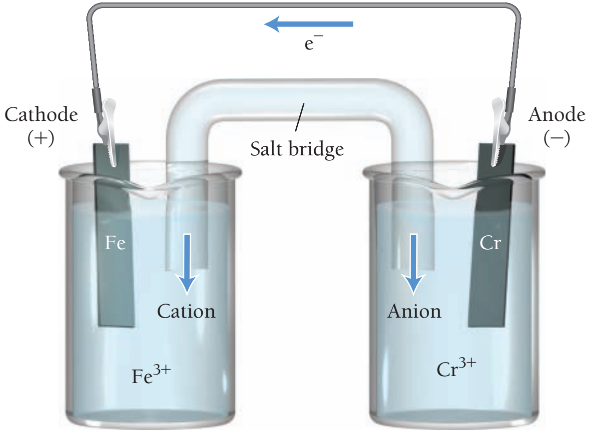


c.



45. **a.** 0.93 V **b.** 0.41 V **c.** 1.99 V

47. **a, c, d**



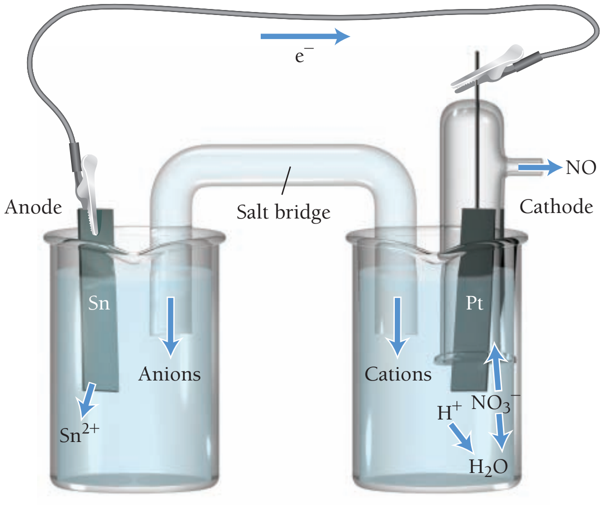
b. $Cr(s) + Fe^{3+}(aq) \longrightarrow Cr^{3+}(aq) + Fe(s)$, $E^{\circ}_{cell} = 0.69$ V

49. **a.** $Pb(s)|Pb^{2+}(aq)||Ag^{+}(aq)|Ag(s)$

b. $Pt(s), I_2(s)|I^{-}(aq)||ClO_2^{-}(aq)|ClO_2(g)|Pt(s)$

c. $Zn(s)|Zn^{2+}(aq)||H_2(O)(l)|H^{+}(aq)|O_2(g)|Pt(s)$

51.



$$3\,Sn(s) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \longrightarrow 3\,Sn^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l),\ E^{\circ}_{cell} = 1.10\ V$$

53. **b, c** occur spontaneously in the forward direction.

55. aluminum

57. **a.** yes, $2\,Al(s) + 6\,H^{+}(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)$

b. no

c. yes, $Pb(s) + 2\,H^{+}(aq) \longrightarrow Pb^{2+}(aq) + H_2(g)$

59. **a.** yes, $3\,Cu(s) + 2\,NO_3^{-}(aq) + 8\,H^{+}(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l)$

b. no

61. **a.** −1.70 V, nonspontaneous

b. 1.97 V, spontaneous

c. −1.51 V, nonspontaneous

63. **a**

65. **a.** −432 kJ **b.** 52 kJ

c. -1.7×10^{2} KJ

67. **a.** 5.31×10^{75} **b.** 7.7×10^{-10}

c. 6.3×10^{29}

69. 5.6×10^{5}

71. $\Delta G^{\circ} = -7.\underline{9}7$ kJ, $E^{\circ}_{cell} = 0.041$ V

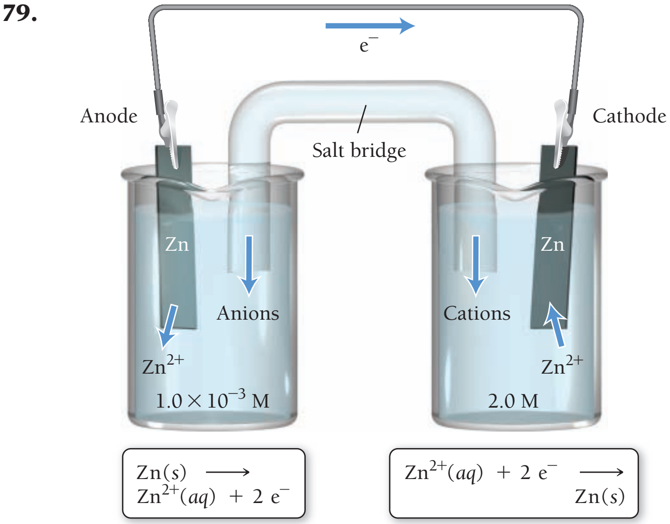
73. **a.** 1.04 V **b.** 0.97 V **c.** 1.11 V

75. 1.87 V

77. **a.** 0.56 V **b.** 0.52 V

c. $[Ni^{2+}] = 0.003$ M, $[Zn^{2+}] = 1.60$ M

79.



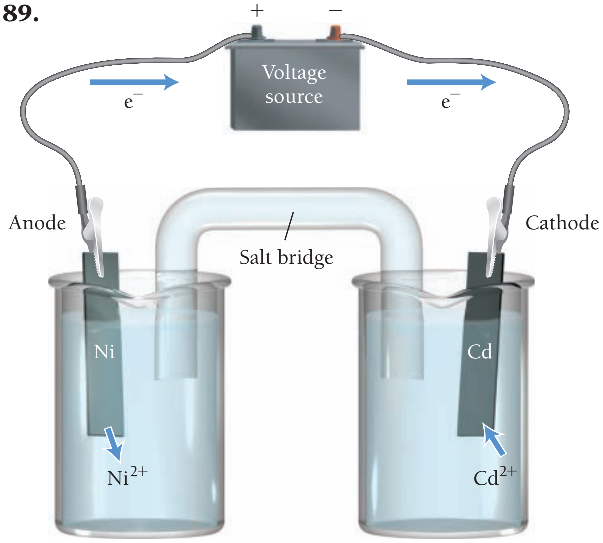
81. $\dfrac{[Sn^{2+}](ox)}{[Sn^{2+}](red)} = 4.2 \times 10^{-4}$

83. 0.3762

85. 1.038 V

87. **a, c** would prevent the corrosion of iron.

89.



minimum voltage = 0.17 V

91. oxidation: $2\,Br^{-}(l) \longrightarrow Br_2(g) + 2\,e^{-}$

reduction: $K^{+}(l) + e^{-} \longrightarrow K(l)$

93. oxidation: $2\,Br^{-}(l) \longrightarrow Br_2(g) + 2\,e^{-}$

reduction: $K^{+}(l) + e^{-} \longrightarrow K(l)$

95. **a.** anode: $2\,Br^{-} \longrightarrow Br_2(l) + 2\,e^{-}$

cathode: $2\,H_2O(l) + 2\,e^{-} \longrightarrow H_2(g) + 2\,OH^{-}(aq)$

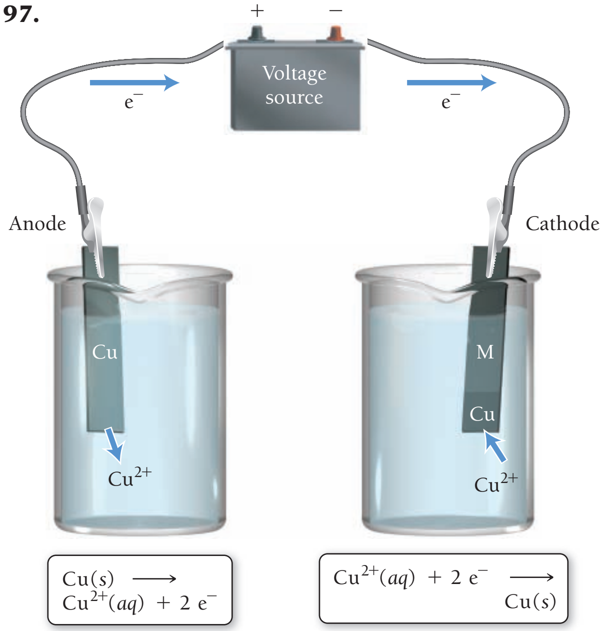
b. anode: $2\,I^{-}(aq) \longrightarrow I_2(s) + 2\,e^{-}$

cathode: $Pb^{2+}(aq) + 2\,e^{-} \longrightarrow Pb(s)$

c. anode: $2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^{+}(aq) + 4\,e^{-}$

cathode: $2\,H_2O(l) + 2\,e^{-} \longrightarrow H_2(g) + 2\,OH^{-}(aq)$

97.



99. 1.8×10^2 s

101. 1.2×10^3 A $E_{cell} = 0.0725$ V, K = 282

103.

$[B^{2+}]$	$[A^{2+}]$	Q	E_{cell}	ΔG_{rxn}
1.00	1.0	1.0	0.0725 V	−14.0 kJ
1.00	1.00×10^{-4}	1.00×10^{-4}	0.191	−36.8 kJ
1.00×10^{-4}	1.0	1.00×10^4	−0.0458	8.82 kJ
3.52×10^{-3}	1.0	284	0	0

105. $2\,MnO_4^-(aq) + 5\,Zn(s) + 16\,H^+(aq) \longrightarrow 2\,Mn^{2+}(aq) + 5\,Zn^{2+}(aq) + 8\,H_2O(l)$ 34.9 mL

107. The drawing should show that several Al atoms dissolve into solution as Al^{3+} ions and that several Cu^{2+} ions are deposited on the Al surface as solid Cu.

109. **a.** 68.3 mL
b. cannot be dissolved
c. cannot be dissolved

111. 0.25

113. There are no paired reactions that produce more than about 5 or 6 V.

115. **a.** 2.83 V **b.** 2.71 V **c.** 16 hr

117. 176 hr

119. 0.71 V

121. **a.** $\Delta G^\circ = 461$ kJ, $K = 1.4 \times 10^{-81}$
b. $\Delta G^\circ = 2.7 \times 10^2$ kJ, $K = 2.0 \times 10^{-48}$

123. MCl_4

125. 51.3%

127. pH = 0.85

129. 0.83 M

131. 4.1×10^5 L

133. 435 s

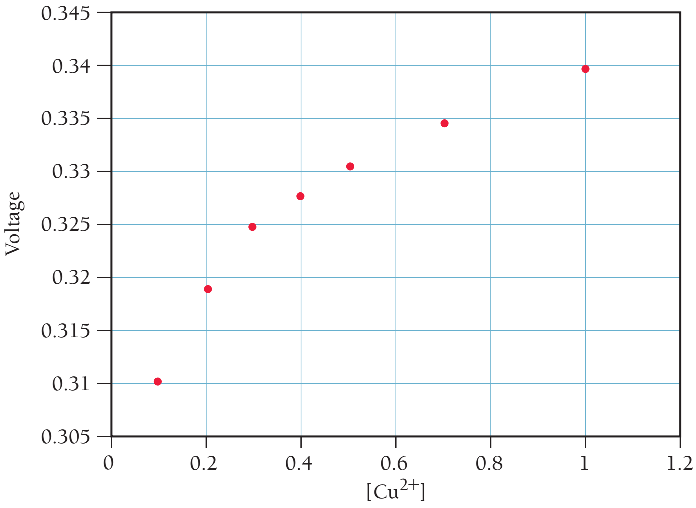
135. 8.39% U

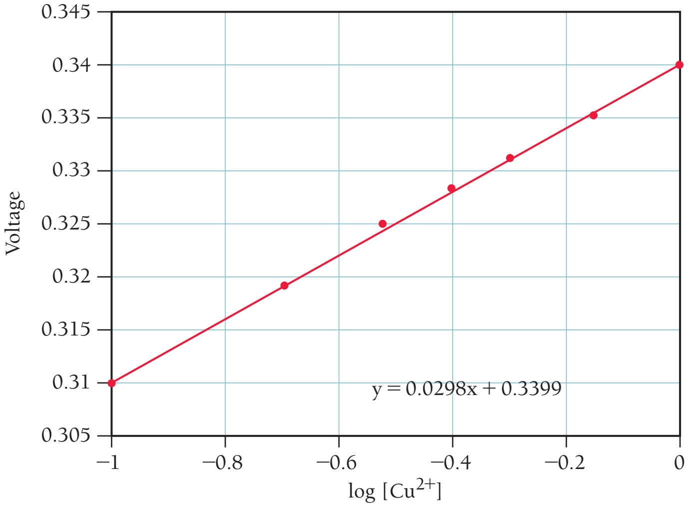
137. The overall cell reaction for both cells is $2\,Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$. The difference in E° is because $n = 1$ for the first cell and $n = 2$ for the second cell. For both cells, $\Delta G^\circ = -35.1$ kJ.

139. **a**

141. ΔG°_{rxn} is positive and E^0_{cell} is negative.

147. **a.**





e. Slope = 0.0298; intercept = 0.340; yes, the slope should be $0.0592/n$ and the intercept should be E^0_{cell}.

Chapter 21

31. **a.** ${}^{234}_{92}U \longrightarrow {}^{4}_{2}He + {}^{230}_{90}Th$
b. ${}^{230}_{90}Th \longrightarrow {}^{4}_{2}He + {}^{226}_{88}Ra$
c. ${}^{214}_{82}Pb \longrightarrow {}^{0}_{-1}e + {}^{214}_{83}Bi$
d. ${}^{13}_{7}N \longrightarrow {}^{0}_{+1}e + {}^{13}_{6}C$
e. ${}^{51}_{24}Cr + {}^{0}_{-1}e \longrightarrow {}^{51}_{23}V$

33. ${}^{232}_{90}Th \longrightarrow {}^{4}_{2}He + {}^{228}_{88}Ra$
${}^{228}_{88}Ra \longrightarrow {}^{0}_{-1}e + {}^{228}_{89}Ac$
${}^{228}_{89}Ac \longrightarrow {}^{0}_{-1}e + {}^{228}_{90}Th$
${}^{228}_{90}Th \longrightarrow {}^{4}_{2}He + {}^{224}_{88}Ra$

35. **a.** ${}^{221}_{87}Fr$ **b.** ${}^{0}_{-1}e$ **c.** ${}^{0}_{+1}e$ **d.** ${}^{0}_{-1}e$

37. **a.** stable; N/Z ratio is close to 1, acceptable for low Z atoms.
b. not stable; N/Z ratio is much too high for low Z atom.
c. not stable; N/Z ratio is less than 1, much too low.
d. stable; N/Z ratio is acceptable for this Z.

39. Sc, V, and Mn; each have odd numbers of protons. Atoms with an odd number of protons typically have less stable isotopes than those with an even number of protons.

41. **a.** beta decay
b. positron emission
c. positron emission
d. positron emission

43. **a.** Cs-125 **b.** Fe-62

45. 2.34×10^9 years

47. 0.57 g

49. 10.8 hr

51. 2.66×10^3 yr

53. 2.4×10^4 yr

55. 2.7×10^9 yr

57. $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{144}_{54}Xe + ^{90}_{38}Sr + 2\,^{1}_{0}n$

59. $^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n$

61. $^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U$
$^{239}_{92}U \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$
$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + ^{0}_{-1}e$

63. $^{249}_{98}Cf + ^{12}_{6}C \longrightarrow ^{257}_{104}Rf + 4\,^{1}_{0}n$

65. 9.0×10^{13} J

67. **a.** mass defect = 0.13701 amu binding energy = 7.976 MeV/nucleon
b. mass defect = 0.54369 amu binding energy = 8.732 MeV/nucleon
c. mass defect = 1.16754 amu binding energy = 8.431 MeV/nucleon

69. 7.228×10^{10} J/g U—235

71. 7.84×10^{10} J/g H—2

73. radiation: 25 J, fall: 370 J

75. 68 mi

77. **a.** $^{1}_{1}p + ^{9}_{4}Be \longrightarrow ^{6}_{3}Li + ^{4}_{2}He$ 1.03×10^{11} J/mol
b. $^{209}_{83}Bi + ^{64}_{28}Ni \longrightarrow ^{272}_{111}Rg + ^{1}_{0}n$ 1.141×10^{13} J/mol
c. $^{179}_{74}W + ^{0}_{-1}e \longrightarrow ^{179}_{73}Ta$ 7.59×10^{10} J/mol

79. **a.** $^{114}_{44}Ru \longrightarrow ^{0}_{-1}e + ^{114}_{45}Rh$
b. $^{216}_{88}Ra \longrightarrow ^{0}_{+1}e + ^{216}_{87}Fr$
c. $^{58}_{30}Zn \longrightarrow ^{0}_{11}e + ^{58}_{29}Cu$
d. $^{31}_{10}Ne \longrightarrow ^{0}_{-1}e + ^{31}_{11}Na$

81. 2.9×10^{21} beta emissions, 3700 Ci

83. 1.6×10^{-5} L

85. 4.94×10^{7} kJ/mol

87. 7.72 MeV

89. ^{14}N

91. 0.15%

93. 1.24×10^{21} atoms

95. 2.42×10^{-12} m

97. −0.7 MeV; there is no coulombic barrier for collision with a neutron.

99. **a.** 1.164×10^{10} kJ
b. 0.1299 g

101. U-235 forms Pb-207 in seven α-decays and four β-decays, and Th-232 forms Pb-208 in six α-decays and four β-decays.

103. 3.0×10^2 K

105. $^{21}_{9}F \longrightarrow ^{21}_{10}Ne + ^{0}_{-1}e$

107. Nuclide A is more dangerous because the half-life is shorter (18.5 days) and so it decays faster.

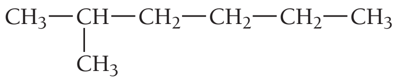
109. Iodine is used by the thyroid gland to make hormones. Normally, we ingest iodine in foods, especially iodized salt. The thyroid gland cannot tell the difference between stable and radioactive iodine and will absorb both. KI tablets work by blocking radioactive iodine from entering the thyroid. When a person takes KI, the stable iodine in the tablet gets absorbed by the thyroid. Because KI contains so much stable iodine, the thyroid gland becomes "full" and cannot absorb any more iodine—either stable or radioactive—for the next 24 hours.

115. **a.** 0.34 g at 200 minutes; 0.23 g at 400 minutes
c. 0.63 μg

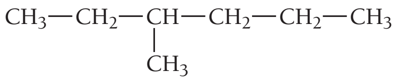
Chapter 22

33. **a.** alkane
b. alkene
c. alkyne
d. alkene

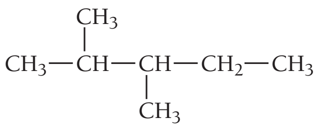
35. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$



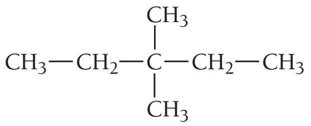
$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$



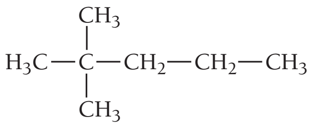
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2-CH_3$



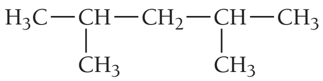
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$



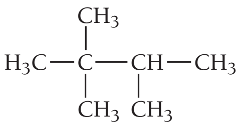
$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3$



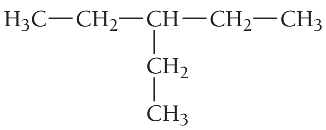
$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2-CH_3$



$H_3C-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$



$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$



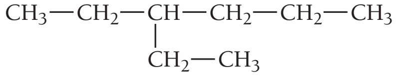
$H_3C-CH_2-\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{\displaystyle CH_2}}{|}}{CH}-CH_2-CH_3$

37. **a.** no **b.** yes **c.** yes **d.** no

39. **a.** enantiomers **b.** same **c.** enantiomers

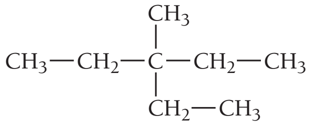
41. **a.** pentane
b. 2-methylbutane
c. 4-isopropyl-2-methylheptane
d. 4-ethyl-2-methylhexane

43. **a.**



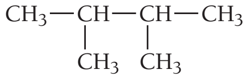
$CH_3{-}CH_2{-}\underset{CH_2{-}CH_3}{CH}{-}CH_2{-}CH_2{-}CH_3$

b.



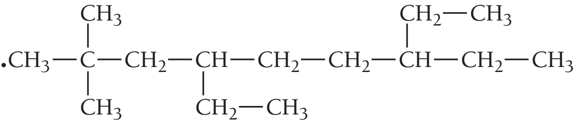
$CH_3{-}CH_2{-}\overset{CH_3}{\underset{CH_2{-}CH_3}{C}}{-}CH_2{-}CH_3$

c.



$CH_3{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}CH_3$

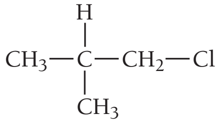
d.



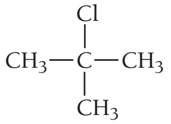
$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\underset{CH_2{-}CH_3}{CH}{-}CH_2{-}CH_2{-}\overset{CH_2{-}CH_3}{CH}{-}CH_2{-}CH_3$

45. **a.** $CH_3CH_2CH_3 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$
b. $CH_3CH_2CH = CH_2 + 6\,O_2 \longrightarrow 4\,CO_2 + 4\,H_2O$
c. $2\,CH{\equiv}CH + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$

47. **a.** CH_3CH_2Br
b. $CH_3CH_2CH_2Cl$, $CH_3CHClCH_3$
c.



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



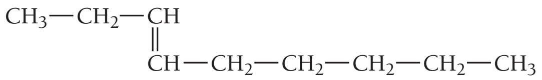
$CH_3{-}\overset{Cl}{\underset{CH_3}{C}}{-}CH_3$

49. $CH_2{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$
$CH_3{-}CH{-}CH{-}CH_2{-}CH_2{-}CH_3$
$CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3$

51. **a.** 1-butene
b. 3,4-dimethyl-2-pentene
c. 3-isopropyl-1-hexene
d. 2,4-dimethyl-3-hexene

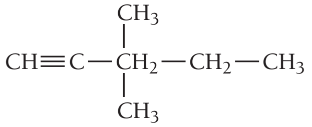
53. **a.** 2-butyne
b. 4,4-dimethyl-2-hexyne
c. 3-isopropyl-1-hexyne
d. 3,6-dimethyl-4-nonyne

55. **a.** $CH_3{-}CH_2{-}CH{-}C{\equiv}C{-}CH_2{-}CH_2{-}CH_3$
b.



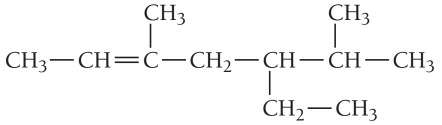
$CH_3{-}CH_2{-}\underset{\underset{CH{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3}{\|}}{CH}$

c.



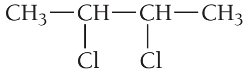
$CH{\equiv}C{-}\overset{CH_3}{\underset{CH_3}{CH_2}}{-}CH_2{-}CH_3$

d.



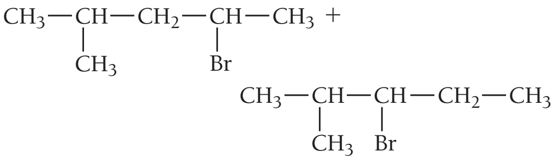
$CH_3{-}CH{=}\overset{CH_3}{C}{-}CH_2{-}\underset{CH_2{-}CH_3}{CH}{-}\overset{CH_3}{CH}{-}CH_3$

57. **a.**



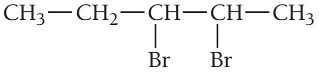
$CH_3{-}\underset{Cl}{CH}{-}\underset{Cl}{CH}{-}CH_3$

b.



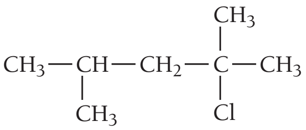
$CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\underset{Br}{CH}{-}CH_3 + CH_3{-}\underset{CH_3}{CH}{-}\underset{Br}{CH}{-}CH_2{-}CH_3$

c.



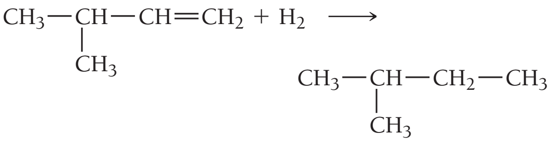
$CH_3{-}CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH}{-}CH_3$

d.



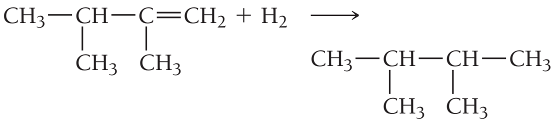
$CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}\overset{CH_3}{\underset{Cl}{C}}{-}CH_3$

59. **a.** $CH_2{=}CH{-}CH_3 + H_2 \longrightarrow CH_3{-}CH_2{-}CH_3$
b.



$CH_3{-}\underset{CH_3}{CH}{-}CH{=}CH_2 + H_2 \longrightarrow CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}CH_3$

c.



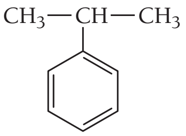
$CH_3{-}\underset{CH_3}{CH}{-}\underset{CH_3}{C}{=}CH_2 + H_2 \longrightarrow CH_3{-}\underset{CH_3}{CH}{-}\underset{CH_3}{CH}{-}CH_3$

61. **a.** methylbenzene or toluene
b. bromobenzene
c. chlorobenzene

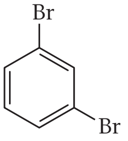
63. **a.** 3,5-dimethyl-7-phenylnonane
b. 2-phenyl-3-octene
c. 4,5-dimethyl-6-phenyl-2-octyne

65. **a.** 1,4-dibromobenzene or *p*-dibromobenzene
b. 1,3-diethylbenzene or *m*-diethylbenzene
c. 1-chloro-2-fluorobenzene or *o*-chlorofluorobenzene

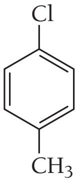
67. **d.**



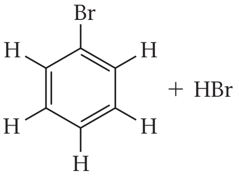
e.



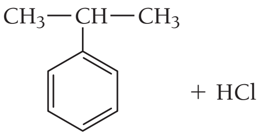
f.



69. **g.**



h.



71. **a.** 1-propanol

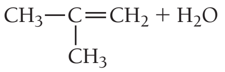
b. 4-methyl-2-hexanol

c. 2,6-dimethyl-4-heptanol

d. 3-methyl-3-pentanol

73. **a.** $CH_3CH_2CH_2Br + H_2O$

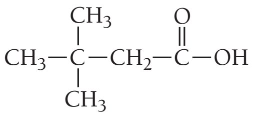
b.



$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2 + H_2O$

c. $CH_3CH_2ONa + \frac{1}{2}H_2$

d.



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

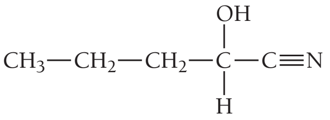
75. **a.** butanone

b. pentanal

c. 3,5,5-trimethylhexanal

d. 4-methyl-2-hexanone

77.



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

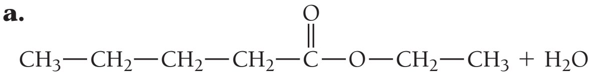
79. **a.** methylbutanoate

b. propanoic acid

c. 5-methylhexanoic acid

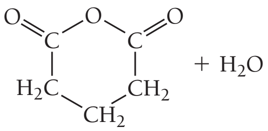
d. ethylpentanoate

81. **a.**



$CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$

b.



83. **a.** ethyl propyl ether

b. ethyl pentyl ether

c. dipropyl ether

d. butyl ethyl ether

85. **a.** diethylamine

b. methylpropylamine

c. butylmethylpropylamine

87. **a.** acid–base, $(CH_3)_2NH_2^+(aq) + Cl^-(aq)$

b. condensation, $CH_3CH_2CONHCH_2CH_3(aq) + H_2O$

c. acid–base, $CH_3NH_3^+(aq) + HSO_4^-(aq)$

89. **a.** ester, methyl 3-methylbutanoate

b. ether, ethyl 2-methylbutyl ether

c. aromatic, 1-ethyl-3-methylbenzene or *m*-ethylmethylbenzene

d. alkyne, 5-ethyl-4-methyl-2-heptyne

e. aldehyde, butanal

f. alcohol, 2-methyl-1-propanol

91. **a.** 5-isobutyl-3-methylnonane

b. 5-methyl-3-hexanone

c. 3-methyl-2-butanol

d. 4-ethyl-3,5-dimethyl-1-hexyne

93. **a.** isomers **b.** isomers

c. same

95. 558 g

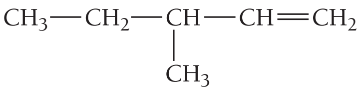
97. **a.** combustion

b. alkane substitution

c. alcohol elimination

d. aromatic substitution

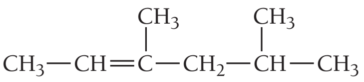
99. **a.**



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

Can exist as a stereoisomer

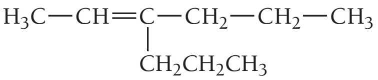
b.



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

Can exist as a stereoisomer

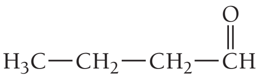
c.



$H_3C-CH=\underset{CH_2CH_2CH_3}{\underset{|}{C}}-CH_2-CH_2-CH_3$

Can exist as a stereoisomer

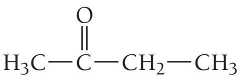
101. **1.**



$H_3C-CH_2-CH_2-\overset{O}{\overset{\|}{CH}}$

Aldehyde

2.



$H_3C-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

Ketone

3. $H_3C-CH=CH-O-CH_3$

Alkene, ether

4. $H_2C=CH-O-CH_2-CH_3$

Alkene, ether

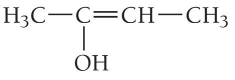
5. $H_2C=CH-CH_2-O-CH_3$

Alkene, ether

6. $H_3C-CH=CH-CH_2-OH$

Alkene, alcohol

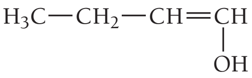
7.



$H_3C-\underset{OH}{\underset{|}{C}}=CH-CH_3$

Alkene, alcohol

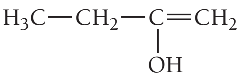
8.



$H_3C-CH_2-CH=\underset{OH}{\underset{|}{CH}}$

Alkene, alcohol

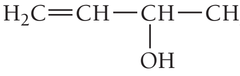
9.



$H_3C-CH_2-\underset{OH}{\underset{|}{C}}=CH_2$

Alkene, alcohol

10.



$H_2C=CH-\underset{OH}{\underset{|}{CH}}-CH_3$

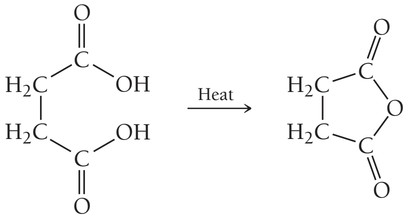
Alkene, alcohol

11. $H_2C=CH-CH_2-CH_2-OH$

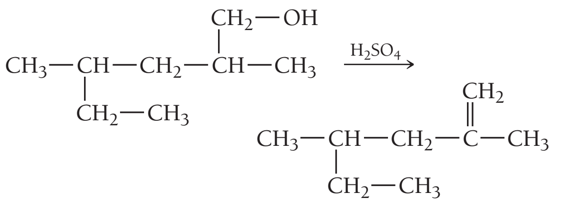
Alkene, alcohol

103. In the acid form of the carboxylic acid, electron withdrawal by the C=O enhances acidity. The conjugate base, the carboxylate anion, is stabilized by resonance, so the two O atoms are equivalent and bear the negative charge equally.

105. **a.**

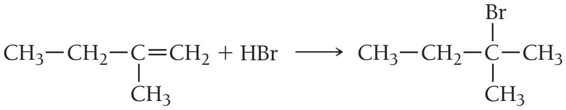


b.



$CH_3-CH(CH_2-CH_3)-CH_2-CH(CH_2-OH)-CH_3 \xrightarrow{H_2SO_4} CH_3-CH(CH_2-CH_3)-CH_2-C(=CH_2)-CH_3$

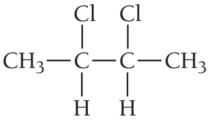
c.



$CH_3-CH_2-C(CH_3)=CH_2 + HBr \longrightarrow CH_3-CH_2-CBr(CH_3)-CH_3$

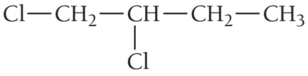
107. **a.** 3:1
b. 2° hydrogen atoms are more reactive. The reactivity of 2° hydrogens to 1° hydrogens is 11:3.

109.



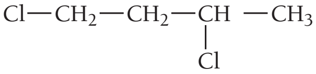
$CH_3-CHCl-CHCl-CH_3$

Chiral



$Cl-CH_2-CH(Cl)-CH_2-CH_3$

Chiral



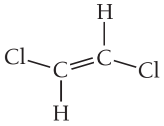
$Cl-CH_2-CH_2-CH(Cl)-CH_3$

Chiral

111. The first propagation step for F is very rapid and exothermic because of the strength of the H—F bond that forms. For I the first propagation step is endothermic and slow because the H—I bond that forms is relatively weak.

113.

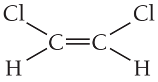
$Cl-C\equiv C-Cl$ trans



$ClCH_2-CH_2Cl$

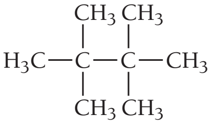
No dipole moment

cis



Cl_2CHCH_3 Dipole moment

115.



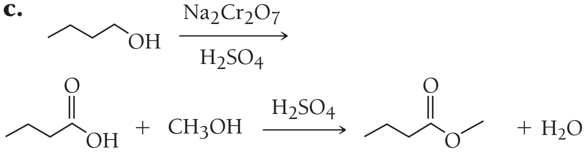
$H_3C-C(CH_3)_2-C(CH_3)_2-CH_3$

2,2,3,3-tetramethylbutane

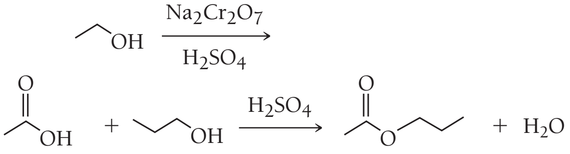
121. **a.** Apple: methylbutanoate; Pear: propyl ethanoate (or propyl acetate); Pineapple: ethyl butanoate

c.

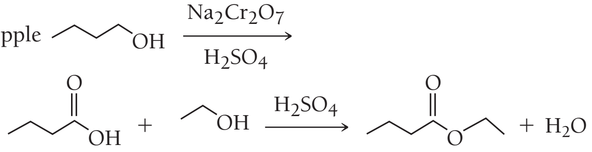
Apple



Pear



Pineapple

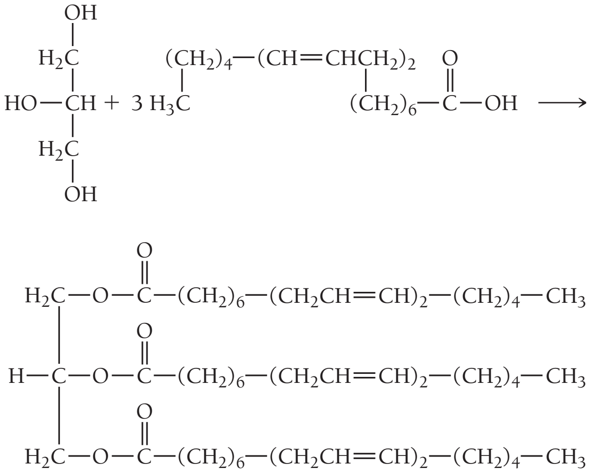


Chapter 23

31. **a.** saturated fatty acid
b. steroid

33. **a.** saturated fatty acid
b. not a fatty acid
c. not a fatty acid
d. monounsaturated fatty acid

35.



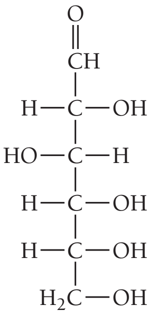
Triglyceride is expected to be an oil.

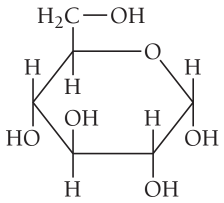
37. **a.** monosaccharide **c.** disaccharide

39. **a.** aldose, hexose **b.** aldose, pentose
c. ketose, tetrose **d.** aldose, tetrose

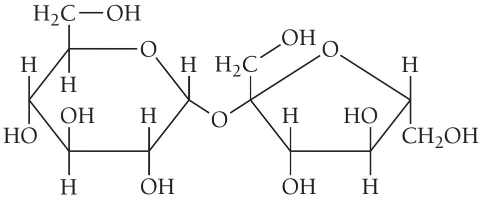
41. **a.** 5 **b.** 3 **c.** 1 **d.** 3

43.



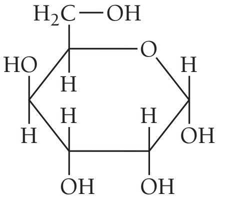


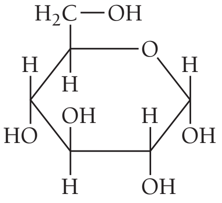
45.



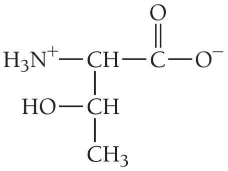
Glucose Fructose

47.



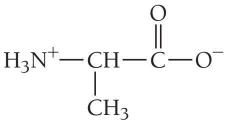


49. **a.**



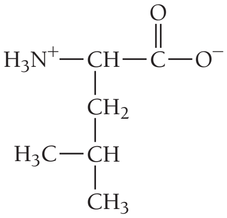
$H_3N^+-CH(CH(OH)CH_3)-C(=O)-O^-$

b.



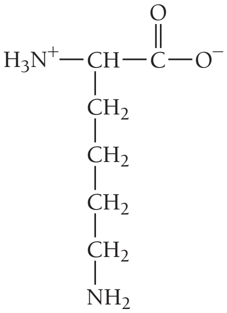
$H_3N^+{-}CH(CH_3){-}C(=O){-}O^-$

c.



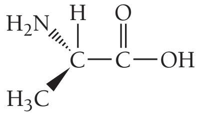
$H_3N^+{-}CH(CH_2CH(CH_3)CH_3){-}C(=O){-}O^-$

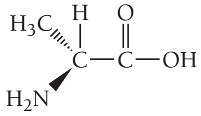
d.



$H_3N^+{-}CH(CH_2CH_2CH_2CH_2NH_2){-}C(=O){-}O^-$

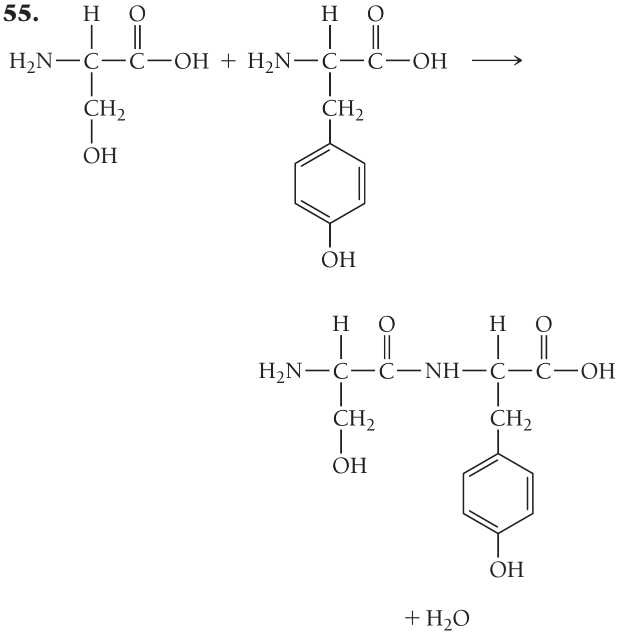
51.



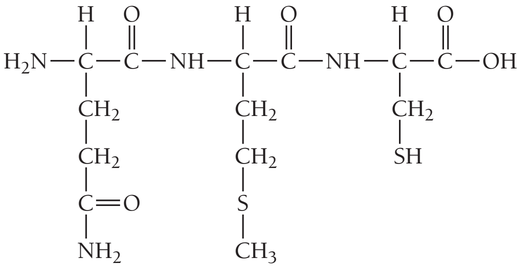


53. 6, Ser-Gly-Cys, Ser-Cys-Gly, Gly-Ser-Cys, Gly-Cys-Ser, Cys-Ser-Gly, Cys-Gly-Ser

55.

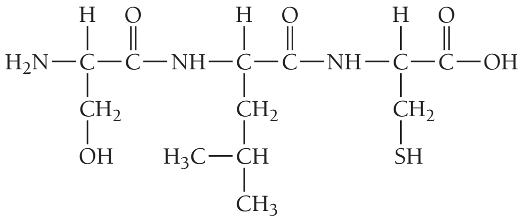


57. **a.**



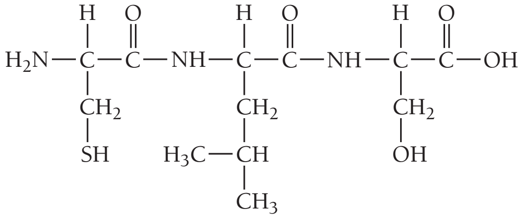
$H_2N{-}CH(CH_2CH_2C(=O)NH_2){-}C(=O){-}NH{-}CH(CH_2CH_2SCH_3){-}C(=O){-}NH{-}CH(CH_2SH){-}C(=O){-}OH$

b.



$H_2N{-}CH(CH_2OH){-}C(=O){-}NH{-}CH(CH_2CH(CH_3)CH_3){-}C(=O){-}NH{-}CH(CH_2SH){-}C(=O){-}OH$

c.



$H_2N{-}CH(CH_2SH){-}C(=O){-}NH{-}CH(CH_2CH(CH_3)CH_3){-}C(=O){-}NH{-}CH(CH_2OH){-}C(=O){-}OH$

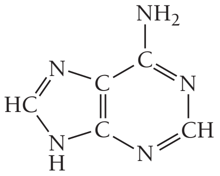
59. tertiary

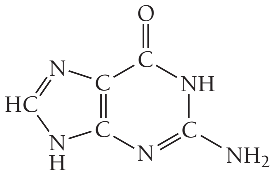
61. primary

63. **a.** A

b. T

65.





67. A C A T G C G

69. 154 codons, 462 nucleotides

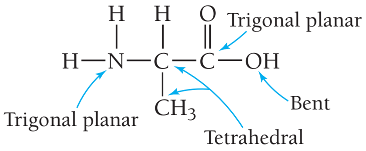
71. **a.** protein

b. carbohydrate

c. lipid

73. A codon is composed of three nucleotides. A codon codes for a specific amino acid, while a gene codes for an entire protein.

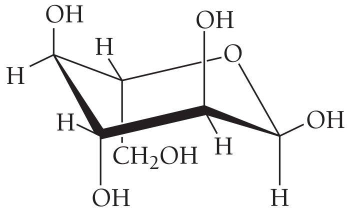
75.



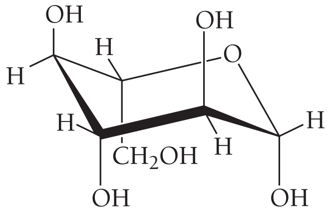
77. valine, leucine, isoleucine, phenylalanine

79. Gly-Arg-Ala-Leu-Phe-Gly-Asn-Lys-Trp-Glu-Cys

81.



a.



b.

83. As the temperature increases, the favorable entropy for uncoiling a chain becomes dominant. On cooling, the favorable enthalpy of forming hydrogen bonds between paired bases is dominant.

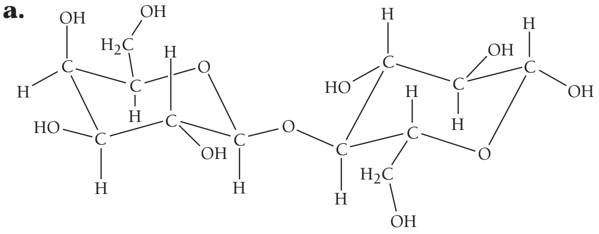
85. When the fake thymine nucleotide is added to the replicating DNA, the chain cannot continue to form because the $-N = N^+ = NH$ group on the sugar prevents future phosphate linkages.

87. $V_{max} = 47.6, K_t = 1.68$

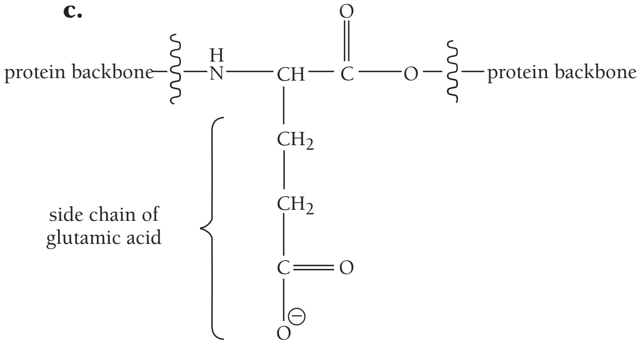
89. $H_3N^+CH_2COO^- + H^+ \rightleftharpoons$ $(H_3N^+CH_2COOH[HA]/[A^-] = 2,$ $H_3N^+CH_2COO^- \rightleftharpoons H_2NCH_2COO^- + H^+[HA]/[A^-] = 0.4, pH = 6.0$

91. A three-base codon codes for a single amino acid. If there are only three bases, there could be 27 different three-base codon arrangements. Therefore, you could theoretically code for the 20 different amino acids needed.

98. **a.**



c.



Chapter 24

15. **a.** +4 **b.** +4 **c.** +4

17. $Ca_3Al_2(SiO_4)_3$

19. 4

21. tetrahedrons stand alone, orthosilicates

23. amphibole or double-chain structure; $Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}$

25. 950 g

27. NCl_3 has a lone pair that BCl_3 lacks, giving it a trigonal pyramidal shape, as opposed to BCl_3's trigonal planar shape.

29. **a.** 6 vertices, 8 faces
b. 12 vertices, 20 faces

31. *closo*-Boranes have the formula $B_nH_n^{2-}$ and form fully closed polyhedra, *nido*-boranes have the formula B_nH_{n+4} and consist of a cage missing a corner, and *arachno*-boranes have the formula B_nH_{n+6} and consist of a cage missing two or three corners.

33. Activated charcoal consists of fine particles, rather than a lump of charcoal, and subsequently has a much higher surface area.

35. Ionic carbides are composed of carbon, generally in the form of the carbide ion, C_2^{2-}, and low-electronegativity metals, such as the alkali and alkaline earth metals. Covalent carbides are composed of carbon and low-electronegativity nonmetals or metalloids, such as silicon.

37. **a.** solid ⟶ gas
b. gas ⟶ liquid ⟶ solid
c. solid ⟶ gas

39. **a.** $CO(g) + CuO(s) \longrightarrow CO_2(g) + Cu(s)$
b. $SiO_2(s) + 3\,C(s) \longrightarrow SiC(s) + 2\,CO(g)$
c. $S(s) + CO(g) \longrightarrow COS(g)$

41. **a.** +2 **b.** +4 **c.** +4/3

43. Fixing nitrogen refers to converting N_2 to a nitrogen-containing compound.

45. White phosphorus consists of P_4 molecules in a tetrahedral shape with the atoms at the corners of the tetrahedron. This allotrope is unstable because of the strain from the bond angles. Red phosphorus is much more stable because one bond of the tetrahedron is broken, allowing the phosphorus atoms to make chains with bond angles that are less strained.

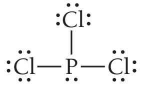
47. saltpeter: 13.86% N by mass Chile saltpeter: 16.48% N by mass

49. HN_3 has a positive ΔG_f°, meaning that it spontaneously decomposes into H_2 and N_2 at room temperature. There are no temperatures at which HN_3 will be stable. ΔH_f is positive and ΔS_f is negative, so ΔG_f will always be negative.

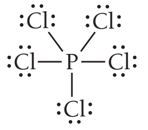
51. **a.** $NH_4NO_3(aq) + \text{heat} \longrightarrow N_2O(g) + 2\,H_2O(l)$
b. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(l) + NO(g)$
c. $2\,PCl_3(l) + O_2(g) \longrightarrow 2\,POCl_3(l)$

53. $NO_3^-, NO_2^-, N_3^-, N_2H_5^+, NH_4^+$

55.



Trigonal pyramidal



Trigonal bipyramidal

57. $CO(NH_2)_2 + 2\,H_2O \longrightarrow (NH_4)_2CO_3$
14g

59. P_4O_6 forms if there is only a limited amount of oxygen available, while P_4O_{10} will form with greater amounts of oxygen.

61. The major source of oxygen is the fractionation of air by which air is cooled and liquefied and oxygen is separated from the other components.

63. **a.** superoxide **b.** oxide
c. peroxide

65. Initially, liquid sulfur becomes less viscous when heated because the S_8 rings have greater thermal energy, which overcomes intermolecular forces. Above 150 °C the rings break and the broken rings entangle one another, causing greater viscosity.

67. **a.** 4×10^{-22} g
b. 4.0×10^{-19} g

69. $2\ FeS_2(s) \xrightarrow{heat} 2\ FeS(s) + S_2(g)$
510 L

71. **a.** +2, linear
b. +6, octahedral
c. +6, square pyramidal

73. $Cl_2(g) + 2\ Br^-(aq) \longrightarrow 2\ Cl^-(aq) + Br_2(l)$
Oxidizing agent: Cl_2
Reducing agent: Br^-

75. No, there is not enough HF to dissolve all of the SiO_2. HF is the limiting reagent. $\underline{1}.6$ g SiO_2.

77. 8 kg from lignite, 40 kg from bituminous

79. Chlorine is much more electronegative than iodine, allowing it to withdraw an electron and ionize in solution much more easily.

81. **a.** $rate_{HCl}/rate_{Cl_2} = 1.395$
b. $rate_{HCl}/rate_{HF} = 0.7407$
c. $rate_{HCl}/rate_{HI} = 1.873$

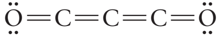
83. $4\ Na_2O_2 + 3\ Fe \longrightarrow 4\ Na_2O + Fe_3O_4$

85. The bond length of the O_2 species increases as electrons are added because they are added to the π^* antibonding orbital. O_2^{2-} is diamagnetic.

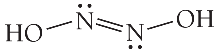
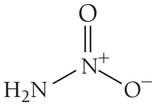
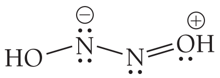
87. 2.0 mol of C—C bonds, 715 kJ/mol, 6.9×10^2 kJ/mol. This value calculated from the bond energy is too low because it doesn't include van der Waals attractions between C atoms not directly bonded to each other.

89. −50 kJ/mol

91. **a.** −13.6 kJ/mol **b.** −11.0 kJ/mol
c. −24.8 kJ/mol
Fe_2O_3 is the most exothermic because it has the highest oxidation state and is therefore able to oxidize the most CO per mol Fe.

93. **a.**

$\ddot{\underset{..}{O}}=C=C=C=\ddot{\underset{..}{O}}$
b. *sp*
c. −92 kJ/mol

95. **a.** 7.6×10^{-22} **b.** 1.2×10^{-8}
c. $[N_2H_4] = 0.009\ M$, $[N_2H_5^+] = 0.0025\ M$, $[N_2H_6^{2+}] = 7.0 \times 10^{-13}\ M$

97. The acid is
a.

and the base is
b.

The acid is weaker than nitrous acid because of electron donation by resonance in contributing structures such as
c.

The base is weaker than ammonia because of electron withdrawal by the electronegative nitro group.

99. The triple bond in nitrogen is much stronger than the double bond in oxygen, so it is much harder to break. This makes it less likely that the bond in nitrogen will be broken.

101. Sodium dinitrogen phosphate (NaH_2PO_4) can act as a weak base or a weak acid. A buffer can be made by mixing it with either Na_2HPO_4 or with Na_3PO_4, depending on the desired pH of the buffer solution.

103. F is extremely small, and so there is a huge driving force to fill the octet by adding an electron, giving a −1 oxidation state. Other halogens have access to *d* orbitals, which allows for more hybridization and oxidation state options.

105. SO_3 cannot be a reducing agent because the oxidation state of S is +6, the highest possible oxidation state for S. Reducing agents need to be able to be oxidized. SO_2 can be a reducing agent or an oxidizing agent because the oxidation state of S is +4.

112. **a.** The solubility of H_2S in water decreases as temperature increases.
c. No
e. Copper(II)
f. 4.8 g CuS

Chapter 25

15. Metals are typically opaque, are good conductors of heat and electricity, and are ductile and malleable, meaning they can be drawn into wires and flattened into sheets.

17. aluminum, iron, calcium, magnesium, sodium, potassium

19. Fe: hematite (Fe_2O_3), magnetite (Fe_3O_4)
Hg: cinnabar (HgS)
V: vanadite [$Pb_5(VO_4)Cl$], carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3\ H_2O$]
Nb: columbite [$Fe(NbO_3)_2$]

21. $MgCO_3(s) + heat \longrightarrow MgO(s) + CO_2(g)$
$Mg(OH)_2(s) + heat \longrightarrow MgO(s) + H_2O(g)$

23. The flux is a material that will react with the gangue to form a substance with a low melting point. MgO is the flux.

25. Hydrometallurgy is used to separate metals from ores by selectively dissolving the metal in a solution, filtering out impurities, and then reducing the metal to its elemental form.

27. The Bayer process is a hydrometallurgical process by which Al_2O_3 is selectively dissolved, leaving other oxides as solids. The soluble form of aluminum is $Al(OH)_4^-$.

29. Sponge-powdered iron contains many small holes in the iron particles due to the escaping of the oxygen when the iron is reduced. Water-atomized powdered iron has much smoother and denser particles as the powder is formed from molten iron.

31. **a.** 50% Cr, 50% V by moles; 50.5% Cr, 49.5% V by mass
b. 25% Fe, 75% V by moles; 26.8% Fe, 73.2% V by mass
c. 25% Cr, 25% Fe, 50% V by moles; 24.8% Cr, 26.6% Fe, 48.6% V by mass

33. Cr and Fe are very close to each other in mass, so their respective atomic radii are probably close enough to form an alloy. Also, they both form body-centered cubic structures.

35. A: solid, 20% Cr, 80% Fe
B: liquid, 50% Cr, 50% Fe

37. A: solid (20% Co and 80% Cu overall. Two phases; one is the Cu structure with 4% Co, and the other is the Co structure with 7% Cu. There will be more of the Cu structure).
B: solid (Co structure), 90% Co, 10% Cu

39. C would fill interstitial holes; Mn and Si would substitute for Fe.

41. **a.** Mo_2N **b.** CrH_2

43. **a.** zinc **b.** copper
c. manganese

45. -19.4 kJ/mol

47. When Cr is added to steel, it reacts with oxygen in steel to prevent it from rusting. A Cr steel alloy would be used in any situation where the steel might be easily oxidized, such as when it comes in contact with water.

49. rutile: 33.3% Ti by moles, 59.9% Ti by mass ilmenite: 20.0% Ti by moles, 31.6% Ti by mass

51. Titanium must be arc-melted in an inert atmosphere because the high temperature and flow of electrons would cause the metal to oxidize in a normal atmosphere.

53. TiO_2 is the most important industrial product of titanium, and it is often used as a pigment in white paint.

55. The Bayer process is a hydrometallurgical process used to separate Al_2O_3 from other oxides. The Al_2O_3 is selectively dissolved by hot, concentrated NaOH. The other oxides are removed as solids, and the Al_2O_3 precipitates out of solution when the solution is neutralized.

57. cobalt and tungsten

59. 3.3 kg Fe, 2.0 kg Ti

61. Four atoms surround a tetrahedral hole, and six atoms surround an octahedral hole. The octahedral hole is larger because it is surrounded by a greater number of atoms.

63. Mn has one more electron orbital available for bonding than does chromium.

65. Ferromagnetic atoms, like paramagnetic ones, have unpaired electrons. However, in ferromagnetic atoms, these electrons align with their spin oriented in the same direction, resulting in a permanent magnetic field.

67. The nuclear charge of the last three is relatively high because of the lanthanide series in which the 4*f* subshell falls between them and the other six metals of the group.

69. **a.** 16.0 cm **b.** 4.95 cm **c.** 14%

71. 92%

73. 5.4×10^7

75. First, roast to form the oxide.

$$4\,CoAsS(s) + 9\,O_2(g) \longrightarrow 4\,CoO(s) + 4\,SO_2(g) + As_4O_6(s)$$

Then reduce the oxide with coke.

$$CoO(s) + C(s) \longrightarrow Co(s) + Co(g)$$

The oxides of arsenic are relatively volatile and can be separated, but they are poisonous.

77. Au and Ag are found in elemental form because of their low reactivity. Na and Ca are group 1 and group 2 metals, respectively, and are highly reactive as they readily lose their valence electrons to obtain octets.

84. **a.** Because they are stronger and harder.
c. Tin, 232 °C; Lead 328 °C
e. Because the melting range is neither too sharp nor too broad. It has a pasty range that helps it to set, but it then hardens quickly.

Chapter 26

17. **a.** $[Ar]\,4s^2 3d^8, [Ar]\,3d^8$
b. $[Ar]\,4s^2 3d^5, [Ar]\,3d^3$
c. $[Kr]\,5s^2 4d^1, [Kr]\,5s^1 4d^1$
d. $[Xe]\,6s^2 4f^{14} 5d^3, [Xe]\,4f^{14} 5d^3$

19. **a.** +5 **b.** +7 **c.** +4

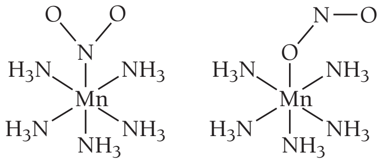
21. **a.** +3, 6 **b.** +2, 6
c. +2, 4 **d.** +1, 2

23. **a.** hexaaquachromium(III)
b. tetracyanocuprate(II)
c. pentaaminebromoiron(III) sulfate
d. aminetetraaquahydroxycobalt(III) chloride

25. **a.** $[Cr(NH_3)_6]^{3+}$
b. $K_3[Fe(CN)_6]$
c. $[Cu(en)(SCN)_2]$
d. $[Pt(H_2O)_4][PtCl_6]$

27. **a.** $[Co(NH_3)_3(CN)_3]$, triaminetricyanocobalt(III)
b. $[Cr(en)_3]^{3+}$, tris(ethylenediamine)chromium(III)

29.

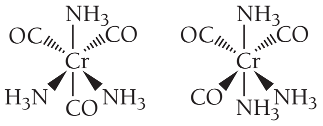


31. $[Fe(H_2O)_5Cl]Cl \cdot H_2O$ pentaaquachloroiron(II) chloride monohydrate
$[Fe(H_2O)_4Cl_2] \cdot 2\,H_2O$, tetraaquadichloroiron(II) dihydrate

33. **b, c, e**

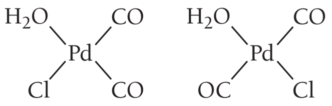
35. **a.** 3
b. No geometric isomers.

37. **a.**



Fac Mer

b.



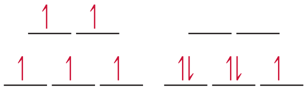
Cis Trans

39. *cis* isomer is optically active.

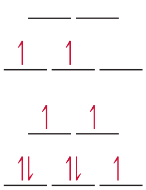
41. **a.**

b.

c.



d.



43. 163 kJ/mol

45. $[Co(CN)_6]^{3-} \longrightarrow$ 290 nm, colorless
$[Co(NH_3)_6]^{3+} \longrightarrow$ 440 nm, yellow
$[CoF_6]^{3-} \longrightarrow$ 770 nm, green

47. weak

49. **a.** 4 **b.** 3 **c.** 1

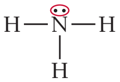
51. 3

53. porphyrin

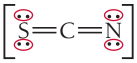
55. Water is a weak-field ligand that forms a high-spin complex with hemoglobin. Because deoxyhemoglobin is a weak field, it absorbs large-wavelength light and appears blue. Oxyhemoglobin is a low-spin complex and absorbs small-wavelength light, so O_2 must be a strong-field ligand.

57. **a.** $[Ar]4s^13d^5$, $[Ar]3d^5$, $[Ar]3d^4$, $[Ar]3d^3$
b. $[Ar]\ 4s^13d^{10}$, $[Ar]\ 3d^{10}$, $[Ar]\ 3d^9$

59. **a.**



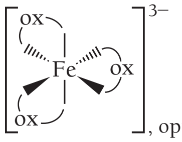
b.



c.

61. $[MA_2B_2C_2]$ all cis; A trans and B and C cis; B trans and A and C cis; C trans and A and B cis; all trans.
$[MA_2B_3C]$ will have fac–mer isomers.
$[MAB_2C_3]$ will have fac–mer isomers.
$[MAB_3C_2]$ will have fac–mer isomers.
$[MA_3B_2C]$ will have fac–mer isomers.
$[MA_2BC_3]$ will have fac–mer isomers.
$[MA_3BC_2]$ will have fac–mer isomers.
$[MABC_2]$ will have AB cis–trans isomers.
$[MAB_4C]$ will have AC cis–trans isomers.
$[MA_4BC]$ will have BC cis–trans isomers.
$[MABC_4]$ will have AB cis–trans isomers.

63.



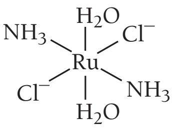
, optical isomers

65.

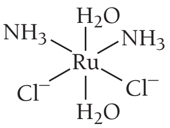
, paramagnetic

67.

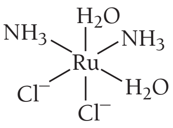
1.



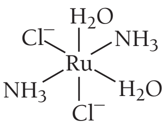
2.



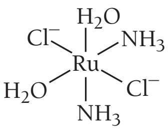
3.



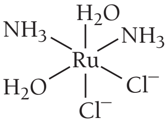
4.



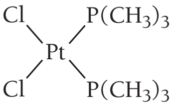
5.



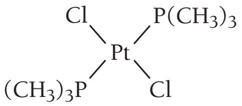
Only structure 3. is chiral. This is its mirror image.



69.

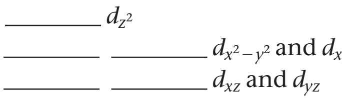


cis-dichlorobis (trimethyl phosphine) platinum(II)



trans-dichlorobis (trimethyl phosphine) platinum(II)

71.



73. **a.** 2×10^{-8} M
b. 6.6×10^{-3} M
c. NiS will dissolve more easily in the ammonia solution because the formation of the complex ion is favorable, removing Ni^{2+} ions from the solution and allowing more NiS to dissolve.

75. Prepare a solution that contains both $[MCl_6]^{3-}$ and $[MBr_6]^{3-}$ and see if any complex ions that contain both Cl and Br form. If they do, it would demonstrate that these complexes are labile.

77. pH = 10.1

79. Au

86. **a.** red
c. smaller (because it absorbs at longer wavelengths)
e. The crystal fields splitting energies of the two complexes must be similar (because they have the same color).

APPENDIX IV

Answers to In-Chapter Practice Problems

Chapter 1

1.1. **a.** The composition of the copper is not changing; thus, being hammered flat is a physical change that signifies a physical property.

b. The dissolution and color change of the nickel indicate that it is undergoing a chemical change and exhibiting a chemical property.

c. Sublimation is a physical change indicative of a physical property.

d. When a match ignites, a chemical change begins as the match reacts with oxygen to form carbon dioxide and water. Flammability is a chemical property.

1.2. **a.** 29.8 °C

b. 302.9 K

1.3. 21.4 g/cm^3. This matches the density of platinum.

1.3. *For More Practice* 4.50 g/cm^3 The metal is titanium.

1.4. The thermometer shown has markings every 1 °F; thus, the first digit of uncertainty is 0.1. The answer is 103.1 °F.

1.5. **a.** Each figure in this number is significant by rule 1: three significant figures.

b. This is a defined quantity that has an unlimited number of significant figures.

c. Both 1's are significant (rule 1), and the interior zero is significant as well (rule 2): three significant figures.

d. Only the two 9's are significant, the leading zeroes are not (rule 3): two significant figures.

e. There are five significant figures because the 1, 4, and 5 are nonzero (rule 1) and the trailing zeroes are after a decimal point so they are significant as well (rule 4).

f. The number of significant figures is ambiguous because the trailing zeroes occur before an implied decimal point (rule 4).

1.6. **a.** 0.381

b. 121.0

c. 1.174

d. 8

1.7. 3.15 yd

1.8. 2.446 gal

1.9. 1.61×10^6 cm^3

1.9. *For More Practice* 3.23×10^3 kg

1.10. 1.03 kg

1.10. *For More Practice* 2.9×10^{-2} cm^3

1.11. 0.855 cm

1.12. 2.70 g/cm^3

1.13. 0.33 ppm/yr; The rate is lower because less fossil fuel was being burned in that era.

Chapter 2

2.1. For the first sample:

$$\frac{\text{mass of oxygen}}{\text{mass of carbon}} = \frac{17.2\text{ g O}}{12.9\text{ g C}} = 1.33 \text{ or } 1.33:1$$

For the second sample:

$$\frac{\text{mass of oxygen}}{\text{mass of carbon}} = \frac{10.5\text{ g O}}{7.88\text{ g C}} = 1.33 \text{ or } 1.33:1$$

The ratios of oxygen to carbon are the same in the two samples of carbon monoxide, so these results are consistent with the law of definite proportions.

2.2. Mass of hydrogen to 1 g of oxygen in water/mass of hydrogen to 1 g of oxygen in hydrogen peroxide $= 0.125/0.0625 = 2.00$.

The ratio of the mass of hydrogen from one compound to the mass of hydrogen in the other is equal to 2. This is a simple whole number and therefore consistent with the law of multiple proportions.

2.3. **a.** $Z = 6, A = 13, {}^{13}_{6}\text{C}$

b. 19 protons, 20 neutrons

2.4. **a.** N^{3-}

b. Rb^{+}

2.5. 24.31 amu

2.5. *For More Practice* 70.92 amu

2.6. 4.65×10^{-2} mol Ag

2.7. 0.563 mol Cu

2.7. *For More Practice* 22.6 g Ti

2.8. 1.3×10^{22} C atoms

2.8. *For More Practice* 6.87 g W

2.9. $l = 1.72$ cm

2.9. *For More Practice* 2.90×10^{24} Cu atoms

Chapter 3

3.1. **a.** C_5H_{12}

b. HgCl

c. CH_2O

3.2. **a.** molecular element

b. molecular compound

c. atomic element

d. ionic compound

e. ionic compound

3.3. K_2S

3.4. AlN

3.5. silver nitride

3.5. *For More Practice* Rb_2S

3.6. iron(II) sulfide

3.6. *For More Practice* RuO_2

3.7. tin(II) chlorate

3.7. *For More Practice* $Co_3(PO_4)_2$
3.8. dinitrogen pentoxide
3.8. *For More Practice* PBr_3
3.9. hydrofluoric acid
3.10. nitrous acid
3.10. *For More Practice* $HClO_4$
3.11. sulfurous acid
3.12. 164.10 amu
3.13. 5.839×10^{20} $C_{13}H_{18}O_2$ molecules
3.13. *For More Practice* 1.06 g H_2O
3.14. 53.29%
3.14. *For More Practice* 74.19% Na
3.15. 83.9 g Fe_2O_3
3.15. *For More Practice* 8.6 g Na
3.16. 4.0 g O
3.16. *For More Practice* 3.60 g C
3.17. CH_2O
3.18. $C_{13}H_{18}O_2$
3.19. C_6H_6
3.19. *For More Practice* $C_2H_8N_2$
3.20. C_2H_5
3.21. C_2H_4O

Chapter 4

4.1. $SiO_2(s) + 3\,C(s) \longrightarrow SiC(s) + 2\,CO(g)$
4.2. $2\,C_2H_6(g) + 7\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(g)$
4.3. $Pb(NO_3)_2(aq) + 2\,KCl(aq) \longrightarrow PbCl_2(s) + 2\,KNO_3(aq)$
4.4. 4.08 g HCl
4.5. 22 kg HNO_3
4.6. H_2 is the limiting reagent, since it produces the least amount of NH_3. Therefore, 29.4 kg NH_3 is the theoretical yield.
4.7. CO is the limiting reagent, since it only produces 114 g Fe. Therefore, 114 g Fe is the theoretical yield: percentage yield = 63.4% yield.
4.8. $2\,C_2H_5SH(l) + 9\,O_2(g) \longrightarrow 4\,CO_2(g) + 2\,SO_2(g) + 6\,H_2O(g)$
4.9. **a.** $2\,Al(s) + 3\,Cl_2(g) \longrightarrow 2\,AlCl_3(s)$
  b. $2\,Li(s) + 2\,H_2O(l) \longrightarrow 2\,Li^+(aq) + 2\,OH^-(aq) + H_2(g)$
  c. $H_2(g) + Br_2(l) \longrightarrow 2\,HBr(g)$

Chapter 5

5.1. 0.214 M $NaNO_3$
5.1. *For More Practice* 44.6 g KBr
5.2. 402 g $C_{12}H_{22}O_{11}$
5.2. *For More Practice* 221 mL of KCl solution
5.3. 667 mL
5.3. *For More Practice* 0.105 L
5.4. 51.4 mL HNO_3 solution
5.4. *For More Practice* 0.170 g CO_2
5.5. **a.** insoluble
  b. insoluble
  c. soluble
  d. soluble
5.6. $NH_4Cl(aq) + Fe(NO_3)_3(aq) \longrightarrow$ NO REACTION
5.7. $2\,NaOH(aq) + CuBr_2(aq) \longrightarrow Cu(OH)_2(s) + 2\,NaBr(aq)$
5.8. $2\,H^+(aq) + 2\,I^-(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l) + Ba^{2+}(aq) + 2\,I^-(aq) H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
5.9. Molecular equation:
  $HBr(aq) + LiOH(aq) \longrightarrow H_2O(l) + LiBr(aq)$
  Net ionic equation:
  $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$
5.10. $HCHO_2(aq) + OH^-(aq) \longrightarrow H_2O(l) + CHO_2^-(aq)$
5.11. 9.03×10^{-2} M H_2SO_4
5.11. *For More Practice* 24.5 mL NaOH solution
5.12. $2\,HBr(aq) + K_2SO_3(aq) \longrightarrow H_2O(l) + SO_2(g) + 2\,KBr(aq)$
5.12. *For More Practice* $2\,H^+(aq) + S^{2-}(aq) \longrightarrow H_2S(g)$
5.13. **a.** Cr = 0
  b. $Cr^{3+} = +3$
  c. $Cl^- = -1$, C = +4
  d. Br = −1, Sr = +2
  e. O = −2, S = +6
  f. O = −2, N = +5
5.14. Sn is oxidized and N is reduced.
5.14. *For More Practice* **b.** Reaction b is the only redox reaction. Al is oxidized and O is reduced.
5.15. **a.** This is a redox reaction in which Li is the reducing agent (it is oxidized) and Cl_2 is the oxidizing reagent (it is reduced).
  b. This is a redox reaction in which Al is the reducing agent and Sn^{2+} is the oxidizing agent.
  c. This is not a redox reaction because no oxidation states change.
  d. This is a redox reaction in which C is the reducing agent and O_2 is the oxidizing agent.
5.16. **a.** Yes
  b. No

Chapter 6

6.1. 15.0 psi
6.1. *For More Practice* 80.6 kPa
6.2. 2.1 atm at a depth of approximately 11 m
6.3. 123 mL
6.4. 11.3 L
6.5. 1.63 atm, 23.9 psi
6.6. 16.1 L
6.6. *For More Practice* 976 mmHg
6.7. $d = 4.91$ g/L
6.7. *For More Practice* 44.0 g/mol
6.8. 70.7 g/mol
6.9. 0.0610 mol H_2
6.10. 4.2 atm
6.11. 12.0 mg H_2
6.12. 82.3 g Ag_2O
6.12. *For More Practice* 7.10 g Ag_2O
6.13. 6.53 L O_2
6.14. $u_{rms} = 238$ m/s
6.15. $\dfrac{\text{rate}_{H_2}}{\text{rate}_{Kr}} = 6.447$

Chapter 7

7.1. $\Delta E = 71\ \mathrm{J}$

7.2. $C_s = 0.38 \dfrac{\mathrm{J}}{\mathrm{g} \cdot {}^\circ\mathrm{C}}$

The specific heat capacity of gold is $0.128\ \mathrm{J/g \cdot {}^\circ C}$; therefore, the rock cannot be pure gold.

7.2. *For More Practice* $T_f = 42.1\ {}^\circ\mathrm{C}$

7.3. 37.8 grams Cu

7.4. $-122\ \mathrm{J}$

7.4. *For More Practice* $\Delta E = -998\ \mathrm{J}$

7.5. $\Delta E_{\mathrm{reaction}} = -3.91 \times 10^3\ \mathrm{kJ/mol}\ C_6H_{14}$

7.5. *For More Practice* $C_{\mathrm{cal}} = 4.55 \dfrac{\mathrm{kJ}}{{}^\circ\mathrm{C}}$

7.6. **a.** endothermic, positive ΔH

b. endothermic, positive ΔH

c. exothermic, negative ΔH

7.7. $-2.06 \times 10^3\ \mathrm{kJ}$

7.7. *For More Practice* 33 g C_4H_{10}

99 g CO_2

7.8. $\Delta H_{\mathrm{rxn}} = -68\ \mathrm{kJ}$

7.9. $N_2O(g) + NO_2(g) \longrightarrow 3\,NO(g),\ \Delta H_{\mathrm{rxn}} = +157.6\ \mathrm{kJ}$

7.9. *For More Practice*

$3\,H_2(g) + O_3(g) \longrightarrow 3\,H_2O(g),\ \Delta H_{\mathrm{rxn}} = -868.1\ \mathrm{kJ}$

7.10. **d.** $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow$

$NaCl(s),\ \Delta H_f^\circ = -411.2\ \mathrm{kJ/mol}$

e. $Pb(s) + N_2(g) + 3\,O_2(g) \longrightarrow$

$Pb(NO_3)_2(s),\ \Delta H_f^\circ = -451.9\ \mathrm{kJ/mol}$

7.11. $\Delta H_{\mathrm{rxn}}^\circ = -851.5\ \mathrm{kJ}$

7.12. $\Delta H_{\mathrm{rxn}}^\circ = -1648.4\ \mathrm{kJ}$

111 kJ emitted (-111 kJ)

7.13. $1.2 \times 10^2\ \mathrm{kg}\ CO_2$

Chapter 8

8.1. $5.83 \times 10^{14}\ \mathrm{s}^{-1}$

8.2. 2.64×10^{20} photons

8.2. *For More Practice* 435 nm

8.3. **a.** blue < green < red

b. red < green < blue

c. red < green < blue

8.4. $6.1 \times 10^6\ \mathrm{m/s}$

8.5. For the 5*d* orbitals:

$n = 5$

$l = 2$

$m_l = -2, -1, 0, 1, 2$

The five integer values for m_l signify that there are five 5*d* orbitals.

8.6. **a.** l cannot equal 3 if $n = 3$. $l = 2$

b. m_l cannot equal -2 if $l = -1$. Possible values for $m_l = -1, 0,$ or 1

c. l cannot be 1 if $n = 1$. $l = 0$

8.7. 397 nm

8.7. *For More Practice* $n = 1$

Chapter 9

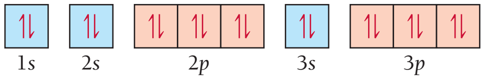
9.1. **a.** Cl $1s^22s^22p^63s^23p^5$ or $[\mathrm{Ne}]3s^23p^5$

b. Si $1s^22s^22p^63s^23p^2$ or $[\mathrm{Ne}]3s^23p^2$

c. Sr $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$ or $[\mathrm{Kr}]5s^2$

d. O $1s^22s^22p^4$ or $[\mathrm{He}]2s^22p^4$

9.2. There are no unpaired electrons.



9.3. $1s^22s^22p^63s^23p^3$ or $[\mathrm{Ne}]3s^23p^3$. The 5 electrons in the $3s^23p^3$ orbitals are the valence electrons, while the 10 electrons in the $1s^22s^22p^6$ orbitals belong to the core.

9.4. $[\mathrm{Xe}]6s^24f^{14}5d^{10}6p^3$

9.4. *For More Practice* $[\mathrm{Kr}]5s^24d^{10}5p^5$

9.5. **a.** Sn

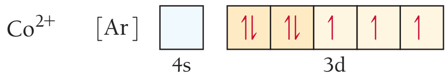
b. cannot predict

c. W

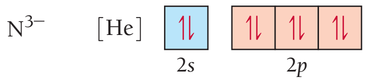
d. Se

9.5. *For More Practice* Rb > Ca > Si > S > F

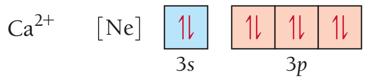
9.6. **a.** $[\mathrm{Ar}]4s^03d^7$. Co^{2+} is paramagnetic.



b. $[\mathrm{He}]2s^22p^6$. N^{3-} is diamagnetic.



c. $[\mathrm{Ne}]3s^23p^6$. Ca^{2+} is diamagnetic.



9.7. **a.** K **b.** F^- **c.** Cl^-

9.8. **a.** I **b.** Ca

c. cannot predict **d.** F

9.8. *For More Practice* F > S > Si > Ca > Rb

9.9. **a.** Sn

b. cannot predict based on simple trends (Po is larger)

c. Bi

d. B

9.9. *For More Practice* Cl < Si < Na < Rb

Chapter 10

10.1. Mg_3N_2

10.2. KI < LiBr < CaO

10.2. *For More Practice* $MgCl_2$

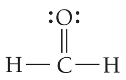
10.3. **a.** pure covalent

b. ionic

c. polar covalent

10.4. $:\mathrm{C}\equiv\mathrm{O}:$

10.5.



$$\mathrm{H{-}\overset{\overset{:\ddot{O}:}{\|}}{C}{-}H}$$

10.6. $\left[:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}:\right]^-$

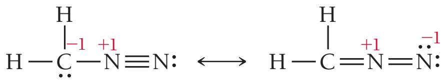
10.7. $\left[\ddot{\underset{}{O}}{=}\ddot{N}{-}\ddot{\underset{..}{O}}:\right]^- \longleftrightarrow \left[:\ddot{\underset{..}{O}}{-}\ddot{N}{=}\ddot{O}:\right]^-$

10.8.

Structure	A			B			C		
	$:\ddot{N}{=}N{=}\ddot{O}:$			$:N{\equiv}N{-}\ddot{\underset{..}{O}}:$			$:\ddot{\underset{..}{N}}{-}N{\equiv}O:$		
number of valence e⁻	5	5	6	5	5	6	5	5	6
number of nonbonding e⁻	−4	−0	−4	−2	−0	−6	−6	−0	−2
$\frac{1}{2}$ (number of bonding e⁻)	−2	−4	−2	−3	−4	−1	−1	−4	−3
Formal charge	−1	−1	0	0	+1	−1	−2	+1	+1
Structure B contributes the most to the correct overall structure of N_2O									

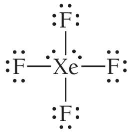
10.8. *For More Practice* The nitrogen is +1, the singly bonded oxygen atoms are −1, and the double-bonded oxygen atom has no formal charge.

10.9.



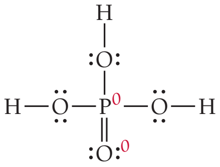
$$\mathrm{H{-}\overset{\overset{H}{|}}{\underset{..}{C}}{-}N{\equiv}N:} \longleftrightarrow \mathrm{H{-}\overset{\overset{H}{|}}{C}{=}N{=}\ddot{N}:}$$

10.10.



$$:\ddot{\underset{..}{F}}{-}\overset{\overset{:\ddot{F}:}{|}}{\underset{\underset{:\underset{..}{F}:}{|}}{Xe}}{-}\ddot{\underset{..}{F}}:$$

10.10. *For More Practice*



$$\mathrm{H{-}\ddot{\underset{..}{O}}{-}\overset{\overset{\overset{H}{|}}{\overset{:\ddot{O}:}{|}}}{\underset{\underset{:\ddot{O}:}{\|}}{P^0}}{-}\ddot{\underset{..}{O}}{-}H}$$

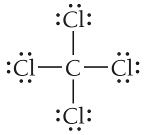
10.11. $CH_3OH(g) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$

$\Delta H_{rxn} = -641\ \text{kJ}$

10.11. *For More Practice* $\Delta H_{rxn} = -8.0 \times 10^1\ \text{kJ}$

Chapter 11

11.1. tetrahedral



$$:\ddot{\underset{..}{Cl}}{-}\overset{\overset{:\ddot{Cl}:}{|}}{\underset{\underset{:\underset{..}{Cl}:}{|}}{C}}{-}\ddot{\underset{..}{Cl}}:$$

11.2. bent

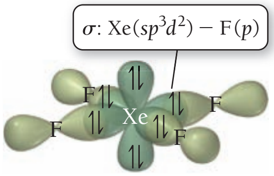
11.3. linear

11.4.

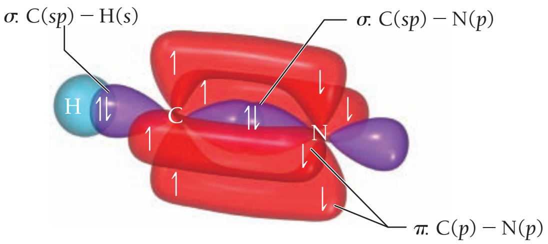
Atom	Number of Electron Groups	Number of Lone Pairs	Molecular Geometry
Carbon (left)	4	0	Tetrahedral
Carbon (right)	3	0	Trigonal planar
Oxygen	4	2	Bent

11.5. The molecule is nonpolar.

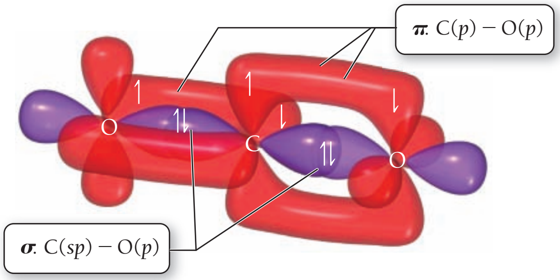
11.6. The xenon atom has six electron groups and therefore has an octahedral electron geometry. An octahedral electron geometry corresponds to sp^3d^2 hybridization (refer to Table 11.3).



11.7. Since there are only two electron groups around the central atom (C), the electron geometry is linear. According to Table 11.3, the corresponding hybridization on the carbon atom is *sp*.



11.8. Since there are only two electron groups about the central atom (C), the electron geometry is linear. The hybridization on C is *sp* (refer to Table 11.3).

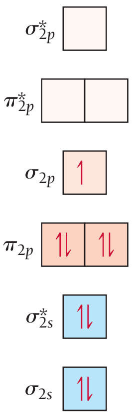


11.8. *For More Practice* There are five electron groups about the central atom (I); therefore, the electron geometry is trigonal bipyramidal and the corresponding hybridization of I is sp^3d (refer to Table 11.3).

11.9. H_2^+ bond order $= +\frac{1}{2}$

Since the bond order is positive, the H_2^+ ion should be stable; however, the bond order of H_2^+ is lower than the bond order of H_2 (bond order $= 1$). Therefore, the bond in H_2^+ is weaker than in H_2.

11.10. The bond order of N_2^+ is 2.5, which is lower than that of the N_2 molecule (bond order $= 3$); therefore, the bond is weaker. The MO diagram shows that the N_2^+ ion has one unpaired electron and is therefore paramagnetic.



11.10. *For More Practice* The bond order of Ne_2 is 0, which indicates that dineon does not exist.

11.11. The bond order of NO is +2.5. The MO diagram shows that the ion has one unpaired electron and is therefore paramagnetic.

Chapter 12

12.1. **b**, **c**

12.2. HF has a higher boiling point than HCl because, unlike HCl, HF is able to form hydrogen bonds. The hydrogen bond is the strongest of the intermolecular forces and requires more energy to break.

12.3. 5.83×10^3 kJ

12.3. *For More Practice* 49 °C

12.4. 33.8 KJ/mol

12.5. 7.04×10^3 torr

Chapter 13

13.1. 29.4°

13.2. 78.5%

13.3. 3.24×10^{-23} cm^3

13.4. $7.18 \frac{g}{cm^3}$

13.5. Metallic

Chapter 14

14.1. **a.** not soluble
- **b.** soluble
- **c.** not soluble
- **d.** not soluble

14.2. 2.7×10^{-4} M

14.3. 42.5 g $C_{12}H_{22}O_{11}$

14.3. *For More Practice* 3.3×10^4 L

14.4. **a.** $M = 0.415$ M
- **b.** $m = 0.443$ m
- **c.** % by mass $= 13.2\%$
- **d.** $\chi_{C_{12}H_{22}O_{11}} = 0.00793$
- **e.** mole percent $= 0.793\%$

14.5. 0.600 M

14.5. *For More Practice* 0.651 *m*

14.6. 22.5 torr

14.6. *For More Practice* 0.144

14.7. **a.** $P_{\text{benzene}} = 26.6$ torr
$P_{\text{toluene}} = 20.4$ torr
- **b.** 47.0 torr
- **c.** 52.5% benzene; 47.5% toluene The vapor will be richer in the more volatile component, which in this case is benzene.

14.8. $T_f = -4.8$ °C

14.9. 101.84 °C

14.10. 11.8 atm

14.11. −0.60 °C

14.12. 0.014 mol NaCl

Chapter 15

15.1. $\frac{\Delta[H_2O_2]}{\Delta t} = -4.40 \times 10^{-3}$ M/s

$\frac{\Delta[I_3^-]}{\Delta t} = 4.40 \times 10^{-3}$ M/s

15.2. **a.** Rate $= k[CHCl_3][Cl_2]^{1/2}$. (Fractional-order reactions are not common but are occasionally observed.)
- **b.** $3.5\ M^{-1/2} \cdot s^{-1}$

15.3. 5.78×10^{-2} M

15.4. 0.0277 M

15.5. 1.64×10^{-3} M

15.6. 79.2 s

15.7. $2.07 \times 10^{-5} \frac{L}{mol \cdot s}$

15.8. $6.13 \times 10^{-4} \frac{L}{mol \cdot s}$

15.9. $2\,A + B \longrightarrow A_2B$
Rate $= k[A]^2$

Chapter 16

16.1. $K = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$

16.2. 2.1×10^{-13}

16.2. *For More Practice* 1.4×10^2

16.3. 6.2×10^2

16.4. $K_c = \frac{[Cl_2]^2}{[HCl]^4[O_2]}$

16.5. 9.4

16.6. 1.1×10^{-6}

16.7. $Q_c = 0.0196$
Reaction proceeds to the left.

16.8. 0.033 M

16.9. $[N_2] = 4.5 \times 10^{-3}$ M
$[O_2] = 4.5 \times 10^{-3}$ M
$[NO] = 1.1 \times 10^{-3}$ M

16.10. $[N_2O_4] = 0.005$ M
$[NO_2] = 0.041$ M

16.11. $P_{I_2} = 0.0027$ atm
$P_{Cl_2} = 0.0027$ atm
$P_{ICl_2} = 0.246$ atm

16.12. 1.67×10^{-7} M

16.13. 6.78×10^{-6} M

16.14. Adding Br_2 increases the concentration of Br_2, causing a shift to the left (away from the Br_2). Adding BrNO increases the concentration of BrNO, causing a shift to the right.

16.15. Decreasing the volume causes the reaction to shift right. Increasing the volume causes the reaction to shift left.

16.16. If we increase the temperature, the reaction shifts to the left. If we decrease the temperature, the reaction shifts to the right.

Chapter 17

17.1. a. H_2O donates a proton to C_5H_5N, making it the acid. The conjugate base is therefore OH^-. Since C_5H_5N accepts the proton, it is the base and becomes the conjugate acid $C_5H_5NH^+$.
b. Since HNO_3 donates a proton to H_2O, it is the acid, making NO_3^- the conjugate base. Since H_2O is the proton acceptor, it is the base and becomes the conjugate acid, H_3O^+.

17.2. a. Since $[H_3O^+] < [OH^-]$, the solution is basic.
b. $[H_3O^+] = 1.0 \times 10^{-7}$ M
Neutral solution.
c. $[H_3O^+] = 1.2 \times 10^{-5}$ M
Since $[H_3O^+] > [OH^-]$, the solution is acidic.

17.3. a. 8.02 (basic)
b. 11.85 (basic)

17.4. 4.3×10^{-9} M

17.5. 0.013 M

17.6. 3.28

17.7. 2.72

17.8. 1.8×10^{-6}

17.9. 0.85%

17.10. 2.0×10^{-7} M

17.11. $[OH^-] = 0.020$ M pH = 12.30

17.12. $[OH^-] = 1.2 \times 10^{-2}$ M pH = 12.08

17.13. a. weak base
b. pH-neutral

17.14. 9.07

17.15. a. pH-neutral
b. weak acid
c. weak acid

17.16. a. basic
b. acidic
c. pH-neutral
d. acidic

17.17. 3.83

17.18. $[SO_4^{2}] = 0.00386$ M
pH = 1.945

17.19. 5.6×10^{-11} M

Chapter 18

18.1. 4.44

18.1. *For More Practice* 3.44

18.2. 9.14

18.3. 4.87

18.3. *For More Practice* 4.65

18.4. 9.68

18.4. *For More Practice* 9.56

18.5. hypochlorous acid (HClO); 2.4 g NaClO

18.6. 1.74

18.7. 8.08

18.8. 2.30×10^{-6} M

18.9. 5.3×10^{-13}

18.10. 1.21×10^{-5} M

18.11. $FeCO_3$ will be more soluble in an acidic solution than $PbBr_2$ because the CO_3^{2-} ion is a basic anion, whereas Br^- is the conjugate base of a strong acid (HBr) and is therefore pH-neutral.

18.12. $Q > K_{sp}$; therefore, a precipitate forms.

18.13. 2.9×10^{-6} M

18.14. a. AgCl precipitates first; $[NaCl] = 7.1 \times 10^{-9}$ M
b. $[Ag^+]$ is 1.5×10^{-8} M when $PbCl_2$ begins to precipitate, and $[Pb^{2+}]$ is 0.085 M.

18.15. 9.6×10^{-6} M

Chapter 19

19.1. a. positive
b. negative
c. positive

19.2. 15.2 J/K

19.3. a. −548 J/K
b. ΔS_{sys} is negative.
c. ΔS_{univ} is negative, and the reaction is not spontaneous.

19.3. *For More Practice* 375 K

19.4. $\Delta G = -101.6 \times 10^3$ J
Therefore, the reaction is spontaneous. Since both ΔH and ΔS are negative, as the temperature increases ΔG will become more positive.

19.5. −153.2 J/K

19.6. $\Delta G^\circ_{rxn} = -36.3$ kJ
Since ΔG°_{rxn} is negative, the reaction is spontaneous at this temperature.

19.7. $\Delta G^\circ_{rxn} = -42.1$ kJ
Since the value of ΔG°_{rxn} at the lowered temperature is more negative (or less positive) (which is −36.3 kJ), the reaction is more spontaneous.

19.8. $\Delta G^\circ_{\text{rxn}} = -689.6\text{ kJ}$
Since $\Delta G^\circ_{\text{rxn}}$ is negative, the reaction is spontaneous at this temperature.

19.8. *For More Practice* $\Delta G^\circ_{\text{rxn}} = -689.7\text{ kJ}$ (at 25°)
The value calculated for $\Delta G^\circ_{\text{rxn}}$ from the tabulated values (-689.6 kJ) is the same, to within 1 in the least significant digit, as the value calculated using the equation for $\Delta G^\circ_{\text{rxn}}$
$\Delta G^\circ_{\text{rxn}} = -649.7\text{ kJ}$ (at 500.0 K)
You could not calculate $\Delta G^\circ_{\text{rxn}}$ at 500.0 K using tabulated $\Delta G^\circ_{\text{f}}$ values because the tabulated values of free energy are calculated at a standard temperature of 298 K, much lower than 500 K.

19.9. +107.1 kJ

19.10. $\Delta G_{\text{rxn}} = -129\text{ kJ}$
The reaction is more spontaneous under these conditions than under standard conditions because ΔG_{rxn} is more negative than $\Delta G^\circ_{\text{rxn}}$.

19.11. -10.9 kJ

Chapter 20

20.1. $2\,\text{Cr}(s) + 4\,\text{H}^+(aq) \longrightarrow 2\,\text{Cr}^{2+}(aq) + 2\,\text{H}_2(g)$

20.2. $\text{Cu}(s) + 4\,\text{H}^+(aq) + 2\,\text{NO}_3^-(aq) \longrightarrow \text{Cu}^{2+}(aq) + 2\,\text{NO}_2(g) + 2\,\text{H}_2\text{O}(l)$

20.3. $3\,\text{ClO}^-(aq) + 2\,\text{Cr(OH)}_4^-(aq) + 2\,\text{OH}^-(aq) \longrightarrow 3\,\text{Cl}^-(aq) + 2\,\text{CrO}_4^{2-}(aq) + 5\,\text{H}_2\text{O}(l)$

20.4. +0.60 V

20.5. **a.** The reaction *will* be spontaneous as written.
b. The reaction *will not* be spontaneous as written.

20.6. $\Delta G^\circ = -3.63 \times 10^5\text{ J}$
Since ΔG° is negative, the reaction is spontaneous.

20.7. 4.5×10^3

20.8. 1.08 V

20.9. *Anode*: $2\,\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\,\text{H}^+(aq) + 4\,\text{e}^-$
Cathode: $2\,\text{H}_2\text{O}(l) + 2\,\text{e}^- \longrightarrow \text{H}_2(g) + 2\,\text{OH}^-(aq)$

20.10. 6.0×10^1 min

Chapter 21

21.1. ${}^{216}_{84}\text{Po} \longrightarrow {}^{212}_{82}\text{Pb} + {}^{4}_{2}\text{He}$

21.2. **a.** ${}^{235}_{92}\text{U} \longrightarrow {}^{231}_{90}\text{Th} + {}^{4}_{2}\text{He}$
${}^{231}_{91}\text{Th} \longrightarrow {}^{231}_{91}\text{Pa} + {}^{0}_{-1}\text{e}$
${}^{231}_{91}\text{Pa} \longrightarrow {}^{227}_{89}\text{Ac} + {}^{4}_{2}\text{He}$
b. ${}^{22}_{11}\text{Na} \longrightarrow {}^{22}_{10}\text{Ne} + {}^{0}_{+1}\text{e}$
c. ${}^{76}_{36}\text{Kr} + {}^{0}_{-1}\text{e} \longrightarrow {}^{76}_{35}\text{Br}$

21.2. *For More Practice* Positron emission (${}^{40}_{19}\text{K} \longrightarrow {}^{40}_{18}\text{Ar} + {}^{0}_{+1}\text{e}$) or electron capture (${}^{40}_{19}\text{K} + {}^{0}_{+1}\text{e} \longrightarrow {}^{40}_{18}\text{Ar}$)

21.3. **a.** positron emission
b. beta decay
c. positron emission

21.4. 10.7 yr

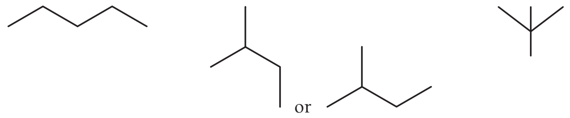
21.5. $t = 964$ yr
No, the C-14 content suggests that the scroll is from about A.D. 1000, not 500 B.C.

21.6. 1.0×10^9 yr

21.7. Mass defect = 1.934 amu
Nuclear binding energy = 7.569 MeV/nucleon

Chapter 22

22.1.



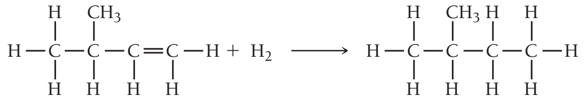
22.2. 3-methylhexane

22.3. 3,5-dimethylheptane

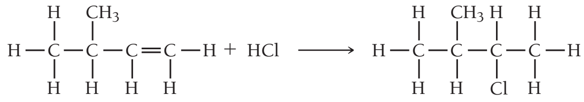
22.4. 2,3,5-trimethylhexane

22.5. **a.** 4,4-dimethyl-2-pentyne
b. 3-ethyl-4,6-dimethyl-1-heptene

22.6. **a.** 2-methylbutane



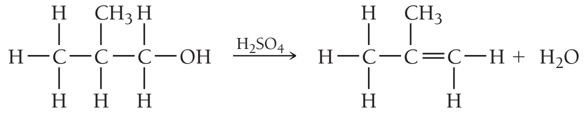
b. 2-chloro-3-methylbutane



22.7. **a.** Alcohol reacting with an active metal.

$$\text{CH}_3\text{CH}_2\text{OH} + \text{Na} \longrightarrow \text{CH}_3\text{CH}_2\text{ONa} + \frac{1}{2}\text{H}_2$$

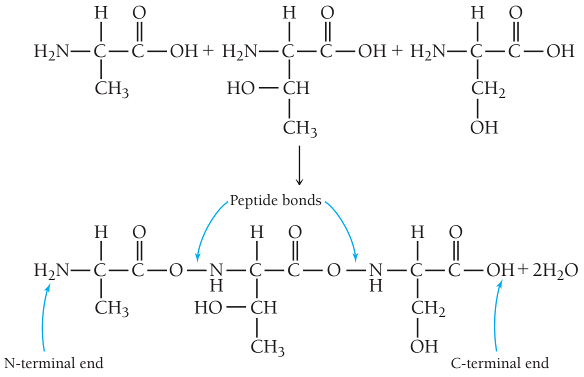
b. dehydration reaction



Chapter 23

23.1. Fructose exhibits optical isomerism. It contains three chiral carbons.

23.2.



Chapter 24

24.1. $KAlSi_3O_8$

24.2. $x = 2$

24.3. Orthosilicate (or neosilicate): each of the two Be ions has a charge of 2+ for a total of 4+, and the SiO_4 unit has a charge of 4–.

24.4. Inosilicate (or pyroxene): Ca and Mg each have a charge of 2+ for a total of 4+, and the Si_2O_6 unit has a charge of 4– (two SiO_3^{2-} units).

24.5. $2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(g) + SO_2(g)$
S changes from the −2 to +4 oxidation state.

24.6. The oxidation state for Cl is +7 in ClO_4^- and −1 in Cl^-.

24.7. $I_2(s) + 5\,F_2(g) \longrightarrow 2\,IF_5(g)$

24.8. The electron geometry is tetrahedral, and the shape is bent for ICl_2^+.

24.9. The electron geometry is octahedral for BrF_5, and the molecular geometry is square pyramidal.

24.10. The oxidation number changes from −1 to 0 for the oxidation of the Cl in HCl to Cl_2 and from +5 to +4 for the reduction of the Cl in $NaClO_3$ to ClO_2. The oxidizing agent is $NaClO_3$, and the reducing agent is HCl.

Chapter 25

25.1. At 50 mol% Ni and 1000 °C, this is a solid phase with half of the atoms each Ni and Cu.

25.2. At 50 mol% Ni and 1400 °C, this is a liquid phase with half of the atoms each Ni and Cu.

25.3. At 900 °C and 60 mol% Cr, this is a two-phase region with more Ni-rich face-centered cubic crystals than Cr-rich body-centered cubic crystals. The Ni-rich phase is about 42 mol% Cr and 58 mol% Ni. The Cr-rich phase is about 94 mol% Cr and 6 mol% Ni.

25.4. At 900 °C and 98 mol% Cr, this is a single-phase region with 100 mol% of the Cr-rich body-centered cubic crystals that contains 2% Ni.

Chapter 26

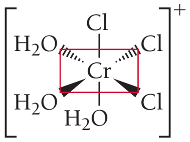
26.1. $[Xe]6s^24f^{14}5d^6$

26.2. $[Kr]5s^04d^3$ or $[Kr]4d^3$

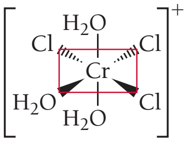
26.3. pentaamminecarbonylmanganese(II) sulfate

26.4. sodium tetrachloroplatinate(II)

26.5. The complex ion $[Cr(H_2O)_3Cl_3]^+$ fits the general formula MA_3B_3, which results in fac and mer isomers.

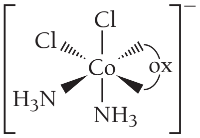


Fac

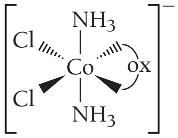


Mer

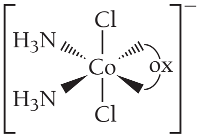
26.6. The oxalate ligand is a small bidentate ligand, so it will have to occupy two adjacent (cis) positions of the octahedron. There are three ways to arrange the two NH_3 and two Cl^- ligands in the four remaining positions. One has both NH_3 and both Cl^- in cis positions (cis isomer). Another has the NH_3 ligands in a trans arrangement with both Cl^- in cis positions (*trans*-ammine isomer). The third has both NH_3 ligands cis and Cl^- ligands trans (*trans*-chloro isomer).



Cis isomer



Trans (in NH_3)



Trans (in Cl^-)

26.7. Both the fac and mer isomers are superimposable (by rotating 180°) on their mirror images, so neither one is optically active.

26.8. 288 kJ/mol

26.9. five unpaired electrons

26.10. one unpaired electron