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Assignment 1. Questions from chapters 1 and 2 of McMurry and Fay
Question numbers are from the fourth edition.

Chapter 1. Chemistry: Matter and Measurement

1.1 (a) Cd (b) Sb (c) Am

1.2 (a) silver (b) rhodium (c) rhenium (d) cesium (e) argon (f) arsenic

1.3 (a) Ti, metal (b) Te, semimetal (c) Se, nonmetal
(d) Sc, metal (e) At, semimetal (f) Ar, nonmetal

1.4 The three Acoinage metals@ are copper (Cu), silver (Ag), and gold (Au).

1.5 (a) The decimal point must be shifted ten places to the right so the exponent is S10. The result is 3.72×10^{S10} m.
(b) The decimal point must be shifted eleven places to the left so the exponent is 11. The result is 1.5×10^{11} m.

1.6 (a) microgram (b) decimeter (c) picosecond
(d) kiloampere (e) millimole

1.7 $^{o}C = \frac{5}{9} \times (^{o}F - 32) = \frac{5}{9} \times (98.6 - 32) = 37.0^{o}C$

$K = {}^{o}C + 273.15 = 37.0 + 273.15 = 310.2\ K$

1.8 (a) $K = {}^{o}C + 273.15 = S78 + 273.15 = 195.15\ K = 195\ K$

(b) $^{o}F = (\frac{9}{5} \times {}^{o}C) + 32 = (\frac{9}{5} \times 158) + 32 = 316.4^{o}F = 316^{o}F$

(c) $^{o}C = K\ S\ 273.15 = 375\ S\ 273.15 = 101.85^{o}C = 102^{o}C$

$^{o}F = (\frac{9}{5} \times {}^{o}C) + 32 = (\frac{9}{5} \times 101.85) + 32 = 215.33^{o}F = 215^{o}F$

1.9 $d = \frac{m}{V} = \frac{27.43\ g}{12.40\ cm^3} = 2.212\ \ g/cm^3$

1.10 $\text{volume} = 9.37\ g \times \frac{1\ mL}{1.483\ g} = 6.32\ mL$

1.11 The actual mass of the bottle and the acetone = 38.0015 g + 0.7791 g = 38.7806 g. The measured values are 38.7798 g, 38.7795 g, and 38.7801 g. These values are both close to each other and close to the actual mass. Therefore the results are both precise and accurate.

1.12 (a) 76.600 kg has 5 significant figures because zeros at the end of a number and after the decimal point are always significant.
(b) 4.502 00 x 10^3 g has 6 significant figures because zeros in the middle of a number are significant and zeros at the end of a number and after the decimal point are always significant.
(c) 3000 nm has 1, 2, 3, or 4 significant figures because zeros at the end of a number and before the decimal point may or may not be significant.
(d) 0.003 00 mL has 3 significant figures because zeros at the beginning of a number are not significant and zeros at the end of a number and after the decimal point are always significant.
(e) 18 students has an infinite number of significant figures since this is an exact number.
(f) 3 x 10^{s5} g has 1 significant figure.
(g) 47.60 mL has 4 significant figures because a zero at the end of a number and after the decimal point is always significant.
(h) 2070 mi has 3 or 4 significant figures because a zero in the middle of a number is significant and a zero at the end of a number and before the decimal point may or may not be significant.

1.13 (a) Since the digit to be dropped (the second 4) is less than 5, round down. The result is 3.774 L.
(b) Since the digit to be dropped (0) is less than 5, round down. The result is 255 K.
(c) Since the digit to be dropped is equal to 5 with nothing following, round down. The result is 55.26 kg.

1.14 (a)
$$\begin{array}{r} 24.567\ \text{g} \\ +\ 0.044\,78\ \text{g} \\ \hline 24.611\,78\ \text{g} \end{array}$$
This result should be expressed with 3 decimal places. Since the digit to be dropped (7) is greater than 5, round up. The result is 24.612 g (5 significant figures).

(b) 4.6742 g / 0.003 71 L = 1259.89 g/L
0.003 71 has only 3 significant figures so the result of the division should have only 3 significant figures. Since the digit to be dropped (first 9) is greater than 5, round up. The result is 1260 g/L (3 significant figures), or 1.26 x 10^3 g/L.

(c)
$$\begin{array}{r} 0.378\ \text{mL} \\ +\ 42.3\ \text{mL} \\ -\ 1.5833\ \text{mL} \\ \hline 41.0947\ \text{mL} \end{array}$$
This result should be expressed with 1 decimal place. Since the digit to be dropped (9) is greater than 5, round up. The result is 41.1 mL (3 significant figures).

1.15 The level of the liquid in the thermometer is just past halfway between the 32°C and 33°C

marks on the thermometer. The temperature is 32.6°C (3 significant figures).

1.16 (a) Calculation: $^{o}F = (\frac{9}{5} \text{ x } ^{o}C) + 32 = (\frac{9}{5} \text{ x } 1064) + 32 = 1947^{o}F$

Ballpark estimate: ^{o}F . 2 x ^{o}C if ^{o}C is large. The melting point of gold . 2000°F.

(b) r = d/2 = 3 x 10^{s6} m = 3 x 10^{s4} cm; h = 2 x 10^{s6} m = 2 x 10^{s4} cm

Calculation: volume = $\pi r^2 h$ = (3.1416)(3 x 10^{s4} cm)^2(2 x 10^{s4} cm) = 6 x 10^{s11} cm^3

Ballpark estimate: volume = $\pi r^2 h$. 3$r^2 h$. 3(3 x 10^{s4} cm)^2(2 x 10^{s4} cm) . 5 x 10^{s11} cm^3

1.17 1 carat = 200 mg = 200 x 10^{s3} g = 0.200 g

$$\text{Mass of Hope Diamond in grams} = 44.4 \text{ carats x } \frac{0.200 \text{ g}}{1 \text{ carat}} = 8.88 \text{ g}$$

1 ounce = 28.35 g

$$\text{Mass of Hope Diamond in ounces} = 8.88 \text{ g x } \frac{1 \text{ ounce}}{28.35 \text{ g}} = 0.313 \text{ ounces}$$

1.18 An LD_{50} value is the amount of a substance per kilogram of body weight that is a lethal dose for 50% of the test animals.

1.19 $$\text{mass of salt} = 155 \text{ lb} \text{ x } \frac{453.6 \text{ g}}{1 \text{ lb}} \text{ x } \frac{1 \text{ kg}}{1000 \text{ g}} \text{ x } \frac{4 \text{ g}}{1 \text{ kg}} = 281.2 \text{ g or } 300 \text{ g}$$

Understanding Key Concepts

1.20

1.21

1.22 red B gas; blue B 42; green B sodium

1.23 The element is americium (Am) with atomic number = 95. It is in the actinide series.

1.24 (a) Darts are clustered together (good precision) but are away from the bullseye (poor accuracy).
(b) Darts are clustered together (good precision) and hit the bullseye (good accuracy).
(c) Darts are scattered (poor precision) and are away from the bullseye (poor accuracy).

1.25 (a) 34.2 mL (3 significant figures) (b) 2.68 cm (3 significant figures)

1.26

The 5 mL graduated cylinder is marked every 0.2 mL and can be read to ∀ 0.02 mL. The 50 mL graduated cylinder is marked every 2 mL and can only be read to ∀ 0.2 mL. The 5 mL graduated cylinder will give more accurate measurements.

1.27 A liquid that is less dense than another will float on top of it. The most dense liquid is mercury, and it is at the bottom of the cylinder. Because water is less dense than mercury but more dense than vegetable oil, it is the middle liquid in the cylinder. Vegetable oil is the least dense of the three liquids and is the top liquid in the cylinder.

Additional Problems
Elements and the Periodic Table

1.28 114 elements are presently known. About 90 elements occur naturally.

1.29 The rows are called periods, and the columns are called groups.

1.30 There are 18 groups in the periodic table. They are labeled as follows:
1A, 2A, 3B, 4B, 5B, 6B, 7B, 8B (3 groups), 1B, 2B, 3A, 4A, 5A, 6A, 7A, 8A

1.31 Elements within a group have similar chemical properties.

1.32

1.33

1.34

A semimetal is an element with properties that fall between those of metals and nonmetals.

1.35 (a) The alkali metals are shiny, soft, low-melting metals that react rapidly with water to form products that are alkaline.
(b) The noble gases are gases of very low reactivity.
(c) The halogens are nonmetallic and corrosive. They are found in nature only in

combination with other elements.

1.36 Li, Na, K, Rb, and Cs

1.37 Be, Mg, Ca, Sr, and Ba

1.38 F, Cl, Br, and I

1.39 He, Ne, Ar, Kr, Xe, and Rn

1.40 (a) gadolinium, Gd (b) germanium, Ge (c) technetium, Tc (d) arsenic, As

1.41 (a) cadmium, Cd (b) iridium, Ir (c) beryllium, Be (d) tungsten, W

1.42 (a) Te, tellurium (b) Re, rhenium (c) Be, beryllium
(d) Ar, argon (e) Pu, plutonium

1.43 (a) B, boron (b) Rh, rhodium (c) Cf, californium
(d) Os, osmium (e) Ga, gallium

1.44 (a) Tin is Sn: Ti is titanium. (b) Manganese is Mn: Mg is magnesium.
(c) Potassium is K: Po is polonium. (d) The symbol for helium is He. The second letter is lowercase.

1.45 (a) The symbol for carbon is C. (b) The symbol for sodium is Na.
(c) The symbol for nitrogen is N. (d) The symbol for chlorine is Cl.

Units and Significant Figures

1.46 Mass measures the amount of matter in an object, whereas weight measures the pull of gravity on an object by the earth or other celestial body.

1.47 There are only seven fundamental (base) SI units for scientific measurement. A derived SI unit is some combination of two or more base SI units.
Base SI unit: Mass, kg; Derived SI unit: Density, kg/m^3

1.48 (a) kilogram, kg (b) meter, m (c) kelvin, K (d) cubic meter, m^3

1.49 (a) kilo, k (b) micro, Φ (c) giga, G (d) pico, p (e) centi, c

1.50 A Celsius degree is larger than a Fahrenheit degree by a factor of $\frac{9}{5}$.

1.51 A kelvin and Celsius degree are the same size.

1.52 The volume of a cubic decimeter (dm^3) and a liter (L) are the same.

1.53 The volume of a cubic centimeter (cm^3) and a milliliter (mL) are the same.

1.54 Only (a) is exact because it is obtained by counting. (b) and (c) are not exact because they result from measurements.

1.55
$$\begin{array}{r} 4.8673\,\text{g} \\ -\ 4.8\,\text{g} \\ \hline 0.0673\,\text{g} \end{array}$$

The result should contain only 1 decimal place. Since the digit to be dropped (6) is greater than 5, round up. The result is 0.1 g.

1.56 cL is centiliter (10^{-2} L)

1.57 (a) deciliter (10^{-1} L) (b) decimeter (10^{-1} m)
(c) micrometer (10^{-6} m) (d) nanoliter (10^{-9} L)

1.58 1 mg = 1 x 10^{-3} g and 1 pg = 1 x 10^{-12} g

$$\frac{1 \times 10^{-3}\ \text{g}}{1\,\text{mg}} \times \frac{1\ \text{pg}}{1 \times 10^{-12}\ \text{g}} = 1 \times 10^{9}\ \text{pg/mg}$$

35 ng = 35 x 10^{-9} g

$$\frac{35 \times 10^{-9}\ \text{g}}{35\ \text{ng}} \times \frac{1\ \text{pg}}{1 \times 10^{-12}\ \text{g}} = 3.5 \times 10^{4}\ \text{pg} / 35\ \text{ng}$$

1.59 1 μL = 10^{-6} L $\quad \frac{1\ \mu\text{L}}{10^{-6}\ \text{L}} = 10^{6}\ \mu\text{L/L}$

20 mL = 20 x 10^{-3} L $\quad \frac{20 \times 10^{-3}\ \text{L}}{20\,\text{mL}} \times \frac{1\ \mu\text{L}}{10^{-6}\ \text{L}} = 2 \times 10^{4}\ \mu\text{L} / 20\ \text{mL}$

1.60 (a) 5 pm = 5 x 10^{-12} m

$$5 \times 10^{-12}\ \text{m} \times \frac{100\ \text{cm}}{1\ \text{m}} = 5 \times 10^{-10}\ \text{cm}$$

$$5 \times 10^{-12}\ \text{m} \times \frac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 5 \times 10^{-3}\ \text{nm}$$

(b) $$8.5\ \text{cm}^3 \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 = 8.5 \times 10^{-6}\ \text{m}^3$$

$$8.5\ \text{cm}^3 \times \left(\frac{10\ \text{mm}}{1\ \text{cm}}\right)^3 = 8.5 \times 10^3\ \text{mm}^3$$

(c) $$65.2\ \text{mg} \times \frac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} = 0.0652\ \text{g}$$

$$65.2\ \text{mg} \times \frac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} \times \frac{1\ \text{pg}}{1 \times 10^{-12}\ \text{g}} = 6.52 \times 10^{10}\ \text{pg}$$

1.61 (a) A liter is just slightly larger than a quart.
(b) A mile is about twice as long as a kilometer.
(c) An ounce is about 30 times larger than a gram.
(d) An inch is about 2.5 times larger than a centimeter.

1.62 (a) 35.0445 g has 6 significant figures because zeros in the middle of a number are significant.
(b) 59.0001 cm has 6 significant figures because zeros in the middle of a number are significant.
(c) 0.030 03 kg has 4 significant figures because zeros at the beginning of a number are not significant and zeros in the middle of a number are significant.
(d) 0.004 50 m has 3 significant figures because zeros at the beginning of a number are not significant and zeros at the end of a number and after the decimal point are always significant.
(e) 67,000 m^2 has 2, 3, 4, or 5 significant figures because zeros at the end of a number and before the decimal point may or may not be significant.

(f) 3.8200×10^3 L has 5 significant figures because zeros at the end of a number and after the decimal point are always significant.

1.63 (a) $130.95 is an exact number and has an infinite number of significant figures.
(b) 2000.003 has 7 significant figures because zeros in the middle of a number are significant.
(c) The measured quantity, 5 ft 3 in., has 2 significant figures. The 5 ft is certain and the 3 in. is an estimate.

1.64 To convert 3,666,500 m^3 to scientific notation, move the decimal point 6 places to the left and include an exponent of 10^6. The result is 3.6665×10^6 m^3.

1.65 Since the digit to be dropped (3) is less than 5, round down. The result to 4 significant figures is 7926 mi or 7.926×10^3 mi.
Since the digit to be dropped (2) is less than 5, round down. The result to 2 significant figures is 7900 mi or 7.9×10^3 mi.

1.66 (a) To convert 453.32 mg to scientific notation, move the decimal point 2 places to the left and include an exponent of 10^2. The result is 4.5332×10^2 mg.

(b) To convert 0.000 042 1 mL to scientific notation, move the decimal point 5 places to the right and include an exponent of 10^{s5}. The result is 4.21 x 10^{s5} mL.
(c) To convert 667,000 g to scientific notation, move the decimal point 5 places to the left and include an exponent of 10^5. The result is 6.67 x 10^5 g.

1.67 (a) Since the exponent is a negative 3, move the decimal point 3 places to the left to get 0.003 221 mm.
(b) Since the exponent is a positive 5, move the decimal point 5 places to the right to get 894,000 m.
(c) Since the exponent is a negative 12, move the decimal point 12 places to the left to get 0.000 000 000 001 350 82 m^3.
(d) Since the exponent is a positive 2, move the decimal point 2 places to the right to get 641.00 km.

1.68 (a) Since the digit to be dropped (0) is less than 5, round down. The result is 3.567 x 10^4 or 35,670 m (4 significant figures).
Since the digit to be dropped (the second 6) is greater than 5, round up. The result is 35,670.1 m (6 significant figures).
(b) Since the digit to be dropped is 5 with nonzero digits following, round up. The result is 69 g (2 significant figures).
Since the digit to be dropped (0) is less than 5, round down. The result is 68.5 g (3 significant figures).
(c) Since the digit to be dropped is 5 with nothing following, round down. The result is 4.99 x 10^3 cm (3 significant figures).
(d) Since the digit to be dropped is 5 with nothing following, round down. The result is 2.3098 x 10^{s4} kg (5 significant figures).

1.69 (a) Since the digit to be dropped (1) is less than 5, round down. The result is 7.000 kg.
(b) Since the digit to be dropped is 5 with nothing following, round down. The result is 1.60 km.
(c) Since the digit to be dropped (1) is less than 5, round down. The result is 13.2 g/cm^3.
(d) Since the digit to be dropped (1) is less than 5, round down. The result is 2,300,000. or 2.300 000 x 10^6.

1.70 (a) 4.884 x 2.05 = 10.012
The result should contain only 3 significant figures because 2.05 contains 3 significant figures (the smaller number of significant figures of the two). Since the digit to be dropped (1) is less than 5, round down. The result is 10.0.

(b) 94.61 / 3.7 = 25.57
The result should contain only 2 significant figures because 3.7 contains 2 significant figures (the smaller number of significant figures of the two). Since the digit to be dropped (second 5) is 5 with nonzero digits following, round up. The result is 26.

(c) 3.7 / 94.61 = 0.0391
The result should contain only 2 significant figures because 3.7 contains 2 significant

figures (the smaller number of significant figures of the two). Since the digit to be dropped (1) is less than 5, round down. The result is 0.039.

(d)
$$\begin{array}{r} 5502.3 \\ 24 \\ +\ 0.01 \\ \hline 5526.31 \end{array}$$

This result should be expressed with no decimal places. Since the digit to be dropped (3) is less than 5, round down. The result is 5526.

(e)
$$\begin{array}{r} 86.3 \\ +\ 1.42 \\ -\ 0.09 \\ \hline 87.63 \end{array}$$

This result should be expressed with only 1 decimal place. Since the digit to be dropped (3) is less than 5, round down. The result is 87.6.

(f) $5.7 \times 2.31 = 13.167$

The result should contain only 2 significant figures because 5.7 contains 2 significant figures (the smaller number of significant figures of the two). Since the digit to be dropped (second 1) is less than 5, round down. The result is 13.

1.71 (a) $\dfrac{3.41 - 0.23}{5.233} \times 0.205 = \dfrac{3.18}{5.233} \times 0.205 = 0.12457 = 0.125$

Complete the subtraction first. The result has 2 decimal places and 3 significant figures. The result of the multiplication and division must have 3 significant figures. Since the digit to be dropped is 5 with nonzero digits following, round up.

(b) $\dfrac{5.556 \times 2.3}{4.223 - 0.08} = \dfrac{5.556 \times 2.3}{4.143} = 3.08 = 3.1$

Complete the subtraction first. The result of the subtraction should have 2 decimal places and 3 significant figures (an extra digit is being carried until the calculation is completed). The result of the multiplication and division must have 2 significant figures. Since the digit to be dropped (8) is greater than 5, round up.

Unit Conversions

1.72 (a) $0.25 \text{ lb} \times \dfrac{453.59 \text{ g}}{1 \text{ lb}} = 113.4 \text{ g} = 110 \text{ g}$

(b) $1454\ \text{ft} \times \frac{12\ \text{in}}{1\ \text{ft}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 443.2\ \text{m}$

(c) $2{,}941{,}526\ \text{mi}^2 \times \left(\frac{1.6093\ \text{km}}{1\ \text{mi}}\right)^2 \times \left(\frac{1000\ \text{m}}{1\ \text{km}}\right)^2 = 7.6181 \times 10^{12}\ \text{m}^2$

1.73 (a) $5.4\ \text{in} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{1\ \text{m}}{100\ \text{cm}} = 0.14\ \text{m}$

(b) $66.31\ \text{lb} \times \frac{1\ \text{kg}}{2.2046\ \text{lb}} = 30.08\ \text{kg}$

(c) $0.5521\ \text{gal} \times \frac{3.7854\ \text{L}}{1\ \text{gal}} \times \frac{1 \times 10^{-3}\ \text{m}^3}{1\ \text{L}} = 2.090 \times 10^{-3}\ \text{m}^3$

(d) $65\ \frac{\text{mi}}{\text{h}} \times \frac{1.6093\ \text{km}}{1\ \text{mi}} \times \frac{1000\ \text{m}}{1\ \text{km}} \times \frac{1\ \text{h}}{60\ \text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 29\ \frac{\text{m}}{\text{s}}$

(e) $978.3\ \text{yd}^3 \times \left(\frac{1\ \text{m}}{1.0936\ \text{yd}}\right)^3 = 748.0\ \text{m}^3$

(f) $2.380\ \text{mi}^2 \times \left(\frac{1.6093\ \text{km}}{1\ \text{mi}}\right)^2 \times \left(\frac{1000\ \text{m}}{1\ \text{km}}\right)^2 = 6.164 \times 10^6\ \text{m}^2$

1.74 (a) $1\ \text{acre-ft} \times \frac{1\ \text{mi}^2}{640\ \text{acres}} \times \left(\frac{5280\ \text{ft}}{1\ \text{mi}}\right)^2 = 43{,}560\ \text{ft}^3$

(b) $116\ \text{mi}^3 \times \left(\frac{5280\ \text{ft}}{1\ \text{mi}}\right)^3 \times \frac{1\ \text{acref-ft}}{43{,}560\ \text{ft}^3} = 3.92 \times 10^8\ \text{acre-ft}$

1.75 (a) $18.6\ \text{hands} \times \frac{1/3\ \text{ft}}{1\ \text{hand}} \times \frac{12\ \text{in}}{1\ \text{ft}} \times \frac{2.54\ \text{cm}}{1\ \text{in}} = 189\ \text{cm}$

(b) $(6 \times 2.5 \times 15)\ \text{hands}^3 \times \left(\frac{1/3\ \text{ft}}{1\ \text{hand}}\right)^3 \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^3 \times \left(\frac{2.54\ \text{cm}}{1\ \text{in}}\right)^3 \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^3 = 0.2\ \text{m}^3$

1.76 (a) $\frac{200\ \text{mg}}{100\ \text{mL}} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 2000\ \text{mg/L}$

(b) $\frac{200\ \text{mg}}{100\ \text{mL}} \times \frac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} \times \frac{1\ \mu\text{g}}{1 \times 10^{-6}\ \text{g}} = 2000\ \mu\text{g/mL}$

(c) $\frac{200\ \text{mg}}{100\ \text{mL}} \times \frac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 2\ \text{g/L}$

(d) $\frac{200\ \text{mg}}{100\ \text{mL}} \times \frac{1 \times 10^{-3}\ \text{g}}{1\ \text{mg}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{1\ \text{ng}}{1 \times 10^{-9}\ \text{g}} \times \frac{1 \times 10^{-6}\ \text{L}}{1\ \mu\text{L}} = 2000\ \text{ng/}\mu\text{L}$

(e) $2\ \text{g/L} \times 5\ \text{L} = 10\ \text{g}$

1.77 $8.65 \text{ stones} \times \frac{14 \text{ lb}}{1 \text{ stone}} = 121 \text{ lb}$

1.78 $55 \frac{\text{mi}}{\text{h}} \times \frac{5280 \text{ ft}}{1 \text{ mi}} \times \frac{12 \text{ in}}{1 \text{ ft}} \times \frac{2.54 \text{ cm}}{1 \text{ in}} \times \frac{1 \text{ h}}{3600 \text{ s}} \times \frac{2.5 \times 10^{-4} \text{ s}}{1 \text{ shake}} = 0.61 \frac{\text{cm}}{\text{shake}}$

1.79 $160 \text{ lb} \times \frac{1 \text{ kg}}{2.2046 \text{ lb}} = 72.6 \text{ kg}$

$72.6 \text{ kg} \times \frac{20 \text{ } \mu\text{g}}{1 \text{ kg}} \times \frac{1 \text{ mg}}{1 \times 10^{3} \text{ } \mu\text{g}} = 1.452 \text{ mg} = 1.5 \text{ mg}$

Temperature

1.80 $^{o}F = (\frac{9}{5} \times {}^{o}C) + 32$

$^{o}F = (\frac{9}{5} \times 39.9^{o}C) + 32 = 103.8^{o} F$ (goat)

$^{o}F = (\frac{9}{5} \times 22.2^{o}C) + 32 = 72.0^{o} F$ (Australian spiny anteater)

1.81 For Hg: mp is $\left[\frac{9}{5} \times (\_ 38.87)\right] + 32 = \_ 37.97^{o} F$

For Br_2: mp is $\left[\frac{9}{5} \times (\_ 7.2)\right] + 32 = 19.0^{o} F$

For Cs: mp is $\left[\frac{9}{5} \times (28.40)\right] + 32 = 83.12^{o} F$

For Ga: mp is $\left[\frac{9}{5} \times (29.78)\right] + 32 = 85.60^{o} F$

1.82 $^{o}C = \frac{5}{9} \times (^{o}F \_ 32) = \frac{5}{9} \times (6192 \_ 32) = 3422^{o} C$

K = ^{o}C + 273.15 = 3422 + 273.15 = 3695.15 K or 3695 K

1.83 $^{o}F = (\frac{9}{5} \times {}^{o}C) + 32 = (\frac{9}{5} \times 175) + 32 = 347^{o} F$

1.84 Ethanol boiling point 78.5^{o}C 173.3^{o}F 200°E

Ethanol melting point S117.3^{o}C S179.1^{o}F 0°E

(a) $\frac{200^{o} E}{[78.5^{o} C \_ (\_ 117.3^{o} C)]} = \frac{200^{o} E}{195.8^{o} C} = 1.021 \text{ } ^{o}E / {}^{o}C$

(b) $\dfrac{200^{o}\,E}{[173.3^{o}\,F - (-179.1^{o}\,F)]} = \dfrac{200^{o}\,E}{352.4^{o}\,F} = 0.5675\ {}^{o}E/{}^{o}F$

(c) ${}^{o}E = \dfrac{200}{195.8} \times ({}^{o}C + 117.3)$

H_2O melting point = $0^{o}C$; ${}^{o}E = \dfrac{200}{195.8} \times (0 + 117.3) = 119.8^{o}\,E$

H_2O boiling point = $100^{o}C$; ${}^{o}E = \dfrac{200}{195.8} \times (100 + 117.3) = 222.0^{o}\,E$

(d) ${}^{o}E = \dfrac{200}{352.4} \times ({}^{o}F + 179.1) = \dfrac{200}{352.4} \times (98.6 + 179.1) = 157.6^{o}\,E$

(e) ${}^{o}F = \left({}^{o}E \times \dfrac{352.4}{200} \right) - 179.1 = \left(130 \times \dfrac{352.4}{200} \right) - 179.1 = 50.0^{o}\,F$

Since the outside temperature is $50.0^{o}F$, I would wear a sweater or light jacket.

1.85 NH_3 boiling point S$33.4^{o}C$ S$28.1^{o}F$ $100^{o}A$
NH_3 melting point S$77.7^{o}C$ S$107.9^{o}F$ $0^{o}A$

(a) $\dfrac{100^{o}\,A}{[-33.4 - (-77.7^{o}\,C)]} = \dfrac{100^{o}\,A}{44.3^{o}\,C} = 2.26\ {}^{o}A/{}^{o}C$

(b) $\dfrac{100^{o}\,A}{[-28.1 - (-107.9^{o}\,F)]} = \dfrac{100^{o}\,A}{79.8^{o}\,F} = 1.25\ {}^{o}A/{}^{o}F$

(c) ${}^{o}A = \dfrac{100}{44.3} \times ({}^{o}C + 77.7)$

H_2O melting point = $0^{o}C$; ${}^{o}A = \dfrac{100}{44.3} \times (0 + 77.7) = 175^{o}\,A$

H_2O boiling point = $100^{o}C$; ${}^{o}A = \dfrac{100}{44.3} \times (100 + 77.7) = 401^{o}\,A$

(d) ${}^{o}A = \dfrac{100}{79.8} \times ({}^{o}F + 107.9) = \dfrac{100}{79.8} \times (98.6 + 107.9) = 259^{o}\,A$

Density

1.86 $250\ mg \times \dfrac{1 \times 10^{-3}\ g}{1\ mg} = 0.25\ g; \quad V = 0.25\ g \times \dfrac{1\ cm^3}{1.40\ g} = 0.18\ cm^3$

$500\ lb \times \dfrac{453.59\ g}{1\ lb} = 226,795\ g;\ V = 226,795\ g \times \dfrac{1\ cm^3}{1.40\ g} = 161,996\ cm^3 = 162,000\ cm^3$

1.87 For H_2: $V = 1.0078\ g \times \dfrac{1\ L}{0.0899\ g} = 11.2\ L$

For Cl_2: $V = 35.45\ g \times \dfrac{1\ L}{3.214\ g} = 11.03\ L$

1.88 $d = \frac{m}{V} = \frac{220.9\ g}{(0.50 \times 1.55 \times 25.00)\ cm^3} = 11.4\ \frac{g}{cm^3} = 11\ \frac{g}{cm^3}$

1.89 d = 2.40 mm = 0.240 cm
r = d/2 = 0.120 cm and $V = \pi r^2 h$

$$d = \frac{m}{V} = \frac{0.3624\ g}{(3.1416)(0.120\ cm)^2(15.0\ cm)} = 0.534\ g/cm^3$$

1.90 $d = \frac{m}{V} = \frac{8.763\ g}{(28.76 \_ 25.00)\ mL} = \frac{8.763\ g}{3.76\ mL} = 2.331\ \frac{g}{cm^3} = 2.33\ \frac{g}{cm^3}$

1.91 The explosion was caused by a chemical property. Na reacts violently with H_2O.

General Problems

1.92 (a) selenium, Se (b) rhenium, Re (c) cobalt, Co (d) rhodium, Rh

1.93 (a) Element 117 is a halogen because it would be found directly below At in group 7A.
(b) Element 119
(c) Element 115 would be found directly below Bi and would be a metal. Element 117 might have the properties of a semimetal.
(d) Element 119, at the bottom of group 1A, would likely be a soft, shiny, very reactive metal forming a +1 cation.

1.94 NaCl melting point = 1074 K
$^oC = K \S 273.15 = 1074 \S 273.15 = 800.85^oC = 801^oC$

$$^oF = (\frac{9}{5} \times\ ^oC) + 32 = (\frac{9}{5} \times 800.85) + 32 = 1473.53^oF = 1474^oF$$

NaCl boiling point = 1686 K
$^oC = K \S 273.15 = 1686 \S 273.15 = 1412.85^oC = 1413^oC$

$$^oF = (\frac{9}{5} \times\ ^oC) + 32 = (\frac{9}{5} \times 1412.85) + 32 = 2575.13^oF = 2575^oF$$

1.95 $$^oF = \left[\frac{9}{5} \times\ ^oC\right] + 32 = \left[\frac{9}{5} \times (\_ 38.9)\right] + 32 = \_ 38.0^oF$$

1.96 $V = 112.5\ g \times \frac{1\ mL}{1.4832\ g} = 75.85\ mL$

1.97 $15.28\ \frac{lb}{gal} \times \frac{453.59\ g}{1\ lb} \times \frac{1\ gal}{3.7854\ L} \times \frac{1\ L}{1000\ mL} = 1.831\ g/mL$

1.98 $V = 8.728 \times 10^{10}\ \text{lb} \times \frac{453.59\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{mL}}{1.831\ \text{g}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 2.162 \times 10^{10}\ \text{L}$

1.99 $0.22\ \text{in} \times \frac{2.54\ \text{cm}}{1\ \text{in}} \times \frac{10\ \text{mm}}{1\ \text{cm}} = 5.6\ \text{mm}$

1.100 (a) $\text{density} = \frac{1\ \text{lb}}{1\ \text{pint}} \times \frac{8\ \text{pints}}{1\ \text{gal}} \times \frac{1\ \text{gal}}{3.7854\ \text{L}} \times \frac{453.59\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = 0.95861\ \text{g/mL}$

(b) area in m^2 =

$1\ \text{acre} \times \frac{1\ \text{mi}^2}{640\ \text{acres}} \times \left(\frac{5280\ \text{ft}}{1\ \text{mi}}\right)^2 \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^2 \times \left(\frac{2.54\ \text{cm}}{1\ \text{in}}\right)^2 \times \left(\frac{1\ \text{m}}{100\ \text{cm}}\right)^2 = 4047\ \text{m}^2$

(c) mass of wood =

$1\ \text{cord} \times \frac{128\ \text{ft}^3}{1\ \text{cord}} \times \left(\frac{12\ \text{in}}{1\ \text{ft}}\right)^3 \times \left(\frac{2.54\ \text{cm}}{1\ \text{in}}\right)^3 \times \frac{0.40\ \text{g}}{1\ \text{cm}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 1450\ \text{kg} = 1400\ \text{kg}$

(d) mass of oil =

$1\ \text{barrel} \times \frac{42\ \text{gal}}{1\ \text{barrel}} \times \frac{3.7854\ \text{L}}{1\ \text{gal}} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{0.85\ \text{g}}{1\ \text{mL}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 135.1\ \text{kg} = 140\ \text{kg}$

(e) fat Calories =

$0.5\ \text{gal} \times \frac{32\ \text{servings}}{1\ \text{gal}} \times \frac{165\ \text{Calories}}{1\ \text{serving}} \times \frac{30.0\ \text{Cal from fat}}{100\ \text{Cal total}} = 792\ \text{Cal from fat}$

1.101 amount of chocolate =

$2.0\ \text{cups coffee} \times \frac{105\ \text{mg caffeine}}{1\ \text{cup coffee}} \times \frac{1.0\ \text{ounce chocolate}}{15\ \text{mg caffeine}} = 14\ \text{ounces of chocolate}$

14 ounces of chocolate is just under 1 pound.

1.102 (a) number of Hershey=s Kisses =

$2.0\ \text{lb} \times \frac{453.59\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{serving}}{41\ \text{g}} \times \frac{9\ \text{kisses}}{1\ \text{serving}} = 199\ \text{kisses} = 200\ \text{kisses}$

(b) Hershey=s Kiss volume = $\frac{41\ \text{g}}{1\ \text{serving}} \times \frac{1\ \text{serving}}{9\ \text{kisses}} \times \frac{1\ \text{mL}}{1.4\ \text{g}} = 3.254\ \text{mL} = 3.3\ \text{mL}$

(c) Calories/Hershey=s Kiss = $\frac{230\ \text{Cal}}{1\ \text{serving}} \times \frac{1\ \text{serving}}{9\ \text{kisses}} = 25.55\ \text{Cal/kiss} = 26\ \text{Cal/kiss}$

(d) % fat Calories =

$\frac{13\ \text{g fat}}{1\ \text{serving}} \times \frac{9\ \text{Cal from fat}}{1\ \text{g fat}} \times \frac{1\ \text{serving}}{230\ \text{Cal total}} \times 100\% = 51\%\ \text{Calories from fat}$

1.103 Let Y equal volume of vinegar and ($422.8\ \text{cm}^3$ S Y) equal the volume of oil.
Mass = volume x density
$397.8\ \text{g} = (\text{Y} \times 1.006\ \text{g/cm}^3) + [(422.8\ \text{cm}^3 - \text{Y}) \times 0.918\ \text{g/cm}^3]$
$397.8\ \text{g} = (1.006\ \text{g/cm}^3)\text{Y} + 388.1\ \text{g} - (0.918\ \text{g/cm}^3)\text{Y}$

397.8 g S 388.1 g = (1.006 g/cm^3)Y S (0.918 g/cm^3)Y
9.7 g = (0.088 g/cm^3)Y

Y = vinegar volume = $\frac{9.7\ g}{0.088\ g/cm^3}$ = 110 cm^3

oil volume = (422.8 cm^3 S Y) = (422.8 cm^3 S 110 cm^3) = 313 cm^3

1.104 $^oC = \frac{5}{9}$ x (^oF _ 32); Set $^oC = {}^oF$: $^oC = \frac{5}{9}$ x (^oC _ 32)

Solve for ^oC: ^oC x $\frac{9}{5} = {}^oC$ _ 32

(^oC x $\frac{9}{5}$) _ ^oC = _ 32

^oC x $\frac{4}{5}$ = _ 32

$^oC = \frac{5}{4}$(_ 32) = _ 40^oC

The Celsius and Fahrenheit scales Across@ at _ 40^oC (_ 40^oF).

1.105 Cork: volume = 1.30 cm x 5.50 cm x 3.00 cm = 21.45 cm^3

mass = $21.45\,cm^3$ x $\frac{0.235\,g}{1\,cm^3} = 5.041\,g$

Lead: volume = (1.15 cm)^3 = 1.521 cm^3

mass = $1.521\,cm^3$ x $\frac{11.35\,g}{1\,cm^3} = 17.26\,g$

total mass = 5.041 g + 17.26 g = 22.30 g
total volume = 21.45 cm^3 + 1.521 cm^3 = 22.97 cm^3

average density = $\frac{22.30\,g}{22.97\,cm^3} = 0.971\,g/cm^3$ so the cork and lead will float.

1.106 Convert 8 min, 25 s to s. $8\,min$ x $\frac{60\,s}{1\,min}$ + 25 s = 505 s

Convert 293.2 K to ^oF 293.2 S 273.15 = 20.05^oC

$^oF = (\frac{9}{5}$ x 20.05) + 32 = 68.09^oF

Final temperature = 68.09^oF + $505\,s$ x $\frac{3.0^oF}{60\,s} = 93.34^oF$

$^oC = \frac{5}{9}$ x (93.34 _ 32) = 34.1^oC

1.107 Ethyl alcohol density = $\frac{19.7325\,g}{25.00\,mL}$ = 0.7893 g/mL

total mass = metal mass + ethyl alcohol mass = 38.4704 g

ethyl alcohol mass = total mass S metal mass = 38.4704 g S 25.0920 g = 13.3784 g

ethyl alcohol volume = 13.3784 g x $\frac{1\,\text{mL}}{0.7893\,\text{g}}$ = 16.95 mL

metal volume = total volume S ethyl alcohol volume = 25.00 mL S 16.95 mL = 8.05 mL

metal density = $\frac{25.0920\,\text{g}}{8.05\,\text{mL}}$ = 3.12 g/mL

1.108 Average brass density = (0.670)(8.92 g/cm^3) + (0.330)(7.14 g/cm^3) = 8.333 g/cm^3

length = 1.62 in x $\frac{2.54\,\text{cm}}{1\,\text{in}}$ = 4.115 cm

diameter = 0.514 in x $\frac{2.54\,\text{cm}}{1\,\text{in}}$ = 1.306 cm

volume = $\pi r^2 h$ = (3.1416)[(1.306 cm)/2]^2(4.115 cm) = 5.512 cm^3

mass = 5.512 cm^3 x $\frac{8.333\,\text{g}}{1\,\text{cm}^3}$ = 45.9 g

1.109 35 sv = 35 x 10^9 $\frac{\text{m}^3}{\text{s}}$

(a) gulf stream flow = $\left(35 \text{ x } 10^9 \frac{\text{m}^3}{\text{s}}\right)\left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3\left(\frac{1 \text{ mL}}{1 \text{ cm}^3}\right)\left(\frac{60 \text{ s}}{1 \text{ min}}\right)$ = 2.1 x 10^{18} mL/min

(b) mass of H_2O = $\left(2.1 \text{ x } 10^{18} \frac{\text{mL}}{\text{min}}\right)\left(\frac{60 \text{ min}}{1 \text{ h}}\right)(24 \text{ h})\left(\frac{1.025 \text{ g}}{1 \text{ mL}}\right)$ = 3.1 x 10^{21} g = 3.1 x 10^{18} kg

(c) time = $\left(1.0 \text{ x } 10^{15} \text{ L}\right)\left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)\left(\frac{1 \text{ min}}{2.1 \text{ x } 10^{18} \text{ mL}}\right)$ = 0.48 min

1.110 (a) Gallium is a metal.

(b) Indium, which is right under gallium in the periodic table, should have similar chemical properties.

(c) Ga density = $\frac{0.2133 \text{ lb}}{1 \text{ in.}^3}$ x $\frac{453.59 \text{ g}}{1 \text{ lb}}$ x $\frac{1 \text{ in.}^3}{(2.54 \text{ cm})^3}$ = 5.904 g/cm^3

(d)

Ga boiling point	2204°C	1000°G
Ga melting point	29.78^{o}C	0°G

$\frac{1000^o\text{G} - 0^o\text{G}}{2204^o\text{C} - 29.78^o\text{C}} = \frac{1000^o\text{G}}{2174.22^o\text{C}}$ = 0.4599 ^{o}G/^{o}C

^{o}G = 0.4599 x (^{o}C S 29.78)

^{o}G = 0.4599 x (801 S 29.78) = 355°G

The melting point of sodium chloride (NaCl) on the gallium scale is 355°G.

Chapter 2. Atoms, Molecules and Ions

2

2.1 First, find the S:O ratio in each compound.
Substance A: S:O mass ratio = (6.00 g S) / (5.99 g O) = 1.00
Substance B: S:O mass ratio = (8.60 g S) / (12.88 g O) = 0.668

$$\frac{\text{S : O mass ratio in substance A}}{\text{S : O mass ratio in substance B}} = \frac{1.00}{0.668} = 1.50 = \frac{3}{2}$$

2.2 $0.0002 \text{ in} \times \frac{2.54 \text{ cm}}{1 \text{ in}} \times \frac{1 \text{ Au atom}}{2.9 \times 10^{-8} \text{ cm}} = 2 \times 10^{4} \text{ Au atoms}$

2.3 $1 \times 10^{19} \text{ C atoms} \times \frac{1.5 \times 10^{-10} \text{ m}}{\text{C atom}} \times \frac{1 \text{ km}}{1000 \text{ m}} \times \frac{1 \text{ time}}{40,075 \text{ km}} = 37.4 \text{ times}$. 40 times

2.4 $^{75}_{34}\text{Se}$ has 34 protons, 34 electrons, and (75 − 34) = 41 neutrons.

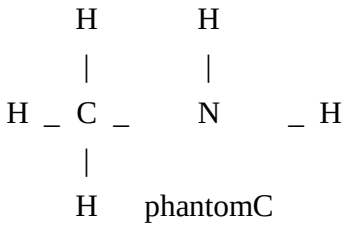
2.5 $^{35}_{17}\text{Cl}$ has (35 − 17) = 18 neutrons. $^{37}_{17}\text{Cl}$ has (37 − 17) = 20 neutrons.

2.6 The element with 47 protons is Ag. The mass number is the sum of the protons and the neutrons, 47 + 62 = 109. The isotope symbol is $^{109}_{47}\text{Ag}$.

2.7 atomic mass = (0.6917 x 62.94 amu) + (0.3083 x 64.93 amu) = 63.55 amu

2.8 $2.15 \text{ g} \times \frac{1 \text{ amu}}{1.6605 \times 10^{-24} \text{ g}} \times \frac{1 \text{ Cu}}{63.55 \text{ amu}} = 2.04 \times 10^{22} \text{ Cu atoms}$

2.9



phantomC

2.10 Figure (b) represents a collection of hydrogen peroxide (H_2O_2) molecules.

2.11 adrenaline, $C_9H_{13}NO_3$

2.12 (a) LiBr is composed of a metal (Li) and nonmetal (Br) and is ionic.

(b) $SiCl_4$ is composed of only nonmetals and is molecular.
(c) BF_3 is composed of only nonmetals and is molecular.
(d) CaO is composed of a metal (Ca) and nonmetal (O) and is ionic.

2.13 Figure (a) most likely represents an ionic compound because there are no discrete molecules, only a regular array of two different chemical species (ions). Figure (b) most likely represents a molecular compound because discrete molecules are present.

2.14 (a) HF is an acid. In water, HF dissociates to produce $H^+(aq)$.
(b) $Ca(OH)_2$ is a base. In water, $Ca(OH)_2$ dissociates to produce $OH^-(aq)$.
(c) LiOH is a base. In water, LiOH dissociates to produce $OH^-(aq)$.
(d) HCN is an acid. In water, HCN dissociates to produce $H^+(aq)$.

2.15 (a) CsF, cesium fluoride (b) K_2O, potassium oxide (c) CuO, copper(II) oxide (d) BaS, bariu

2.16 (a) vanadium(III) chloride, VCl_3 (b) manganese(IV) oxide, MnO_2
(c) copper(II) sulfide, CuS (d) aluminum oxide, Al_2O_3

2.17 red B potassium sulfide, K_2S; green B strontium iodide, SrI_2; blue B gallium oxide, Ga_2O_3

2.18 (a) NCl_3, nitrogen trichloride (b) P_4O_6, tetraphosphorus hexoxide
(c) S_2F_2, disulfur difluoride (d) SeO_2, selenium dioxide

2.19 (a) disulfur dichloride, S_2Cl_2 (b) iodine monochloride, ICl
(c) nitrogen triiodide, NI_3

2.20 (a) $Ca(ClO)_2$, calcium hypochlorite
(b) $Ag_2S_2O_3$, silver(I) thiosulfate or silver thiosulfate
(c) NaH_2PO_4, sodium dihydrogen phosphate (d) $Sn(NO_3)_2$, tin(II) nitrate
(e) $Pb(CH_3CO_2)_4$, lead(IV) acetate (f) $(NH_4)_2SO_4$, ammonium sulfate

2.21 (a) lithium phosphate, Li_3PO_4 (b) magnesium hydrogen sulfate, $Mg(HSO_4)_2$
(c) manganese(II) nitrate, $Mn(NO_3)_2$ (d) chromium(III) sulfate, $Cr_2(SO_4)_3$

2.22 Drawing 1 represents ionic compounds with one cation and two anions. Only (c) $CaCl_2$ is consistent with drawing 1.
Drawing 2 represents ionic compounds with one cation and one anion. Both (a) LiBr and (b) $NaNO_2$ are consistent with drawing 2.

2.23 (a) HIO_4, periodic acid (b) $HBrO_2$, bromous acid (c) H_2CrO_4, chromic acid

2.24 A normal visual image results when light from the sun or other source reflects off an object, strikes the retina in our eye, and is converted into electrical signals that are processed by the brain. The image obtained with a scanning tunneling microscope, by contrast, is a three-dimensional, computer-generated data plot that uses tunneling current to mimic depth perception. The nature of the computer-generated image depends on the identity of the molecules or atoms on the surface, on the precision with which the probe

tip is made, on how the data are manipulated, and on other experimental variables.

Understanding Key Concepts

2.25 Drawing (a) represents a collection of SO_2 molecules. Drawing (d) represents a mixture of S atoms and O_2 molecules.

2.26 To obey the law of mass conservation, the correct drawing must have the same number of red and yellow spheres as in drawing (a). The correct drawing is (d).

2.27 Figures (b) and (d) illustrate the law of multiple proportions. The mass ratio is 2.

2.28. (a) alanine, $C_3H_7NO_2$ (b) ethylene glycol, $C_2H_6O_2$ (c) acetic acid, $C_2H_4O_2$

2.29 A Na atom has 11 protons and 11 electrons [drawing (b)].
A Ca^{2+} ion has 20 protons and 18 electrons [drawing (c)].
A F^{s} ion has 9 protons and 10 electrons [drawing (a)].

2.30

2.31 (a) $MgSO_4$ (b) Li_2CO_3 (c) $FeCl_2$ (d) $Ca_3(PO_4)_2$

Additional Problems
Atomic Theory

2.32 The law of mass conservation in terms of Dalton=s atomic theory states that chemical reactions only rearrange the way that atoms are combined; the atoms themselves are not changed.
The law of definite proportions in terms of Dalton=s atomic theory states that the chemical combination of elements to make different substances occurs when atoms join together in small, whole-number ratios.

2.33 The law of multiple proportions states that if two elements combine in different ways to form different substances, the mass ratios are small, whole-number multiples of each other. This is very similar to Dalton=s statement that the chemical combination of elements to make different substances occurs when atoms join together in small, whole-number ratios.

2.34 First, find the C:H ratio in each compound.
Benzene: C:H mass ratio = (4.61 g C) / (0.39 g H) = 12
Ethane: C:H mass ratio (4.00 g C) / (1.00 g H) = 4.00
Ethylene: C:H mass ratio = (4.29 g C) / (0.71 g H) = 6.0

$$\frac{\text{C : H mass ratio in benzene}}{\text{C : H mass ratio in ethane}} = \frac{12}{4.00} = \frac{3}{1}$$

$$\frac{\text{C : H mass ratio in benzene}}{\text{C : H mass ratio in ethylene}} = \frac{12}{6.0} = \frac{2}{1}$$

$$\frac{\text{C : H mass ratio in ethylene}}{\text{C : H mass ratio in ethane}} = \frac{6.0}{4.00} = \frac{3}{2}$$

2.35 First, find the C:O ratio in each compound.
Carbon suboxide: C:O mass ratio = (1.32 g C) / (1.18 g O) = 1.12
Carbon dioxide: C:O mass ratio = (12.00 g C) / (32.00 g O) = 0.375

$$\frac{\text{C : O mass ratio in carbon suboxide}}{\text{C : O mass ratio in carbon dioxide}} = \frac{1.12}{0.375} = \frac{3}{1}$$

2.36 (a) For benzene:

$$4.61\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ C atom}}{12.011\text{ amu}} = 2.31 \times 10^{23}\text{ C atoms}$$

$$0.39\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ H atom}}{1.008\text{ amu}} = 2.3 \times 10^{23}\text{ H atoms}$$

$$\frac{\text{C}}{\text{H}} = \frac{2.31 \times 10^{23}\text{ C atoms}}{2.3 \times 10^{23}\text{ H atoms}} = \frac{1\text{ C}}{1\text{ H}}$$

A possible formula for benzene is CH.

For ethane:

$$4.00\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ C atom}}{12.011\text{ amu}} = 2.01 \times 10^{23}\text{ C atoms}$$

$$1.00\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ H atom}}{1.008\text{ amu}} = 5.97 \times 10^{23}\text{ H atoms}$$

$$\frac{\text{C}}{\text{H}} = \frac{2.01 \times 10^{23}\text{ C atoms}}{5.97 \times 10^{23}\text{ H atoms}} = \frac{1\text{ C}}{3\text{ H}}$$

A possible formula for ethane is CH_3.

For ethylene:

$$4.29\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ C atom}}{12.011\text{ amu}} = 2.15 \times 10^{23}\text{ C atoms}$$

$$0.71\text{ g} \times \frac{1\text{ amu}}{1.6605 \times 10^{-24}\text{ g}} \times \frac{1\text{ H atom}}{1.008\text{ amu}} = 4.2 \times 10^{23}\text{ H atoms}$$

$$\frac{\text{C}}{\text{H}} = \frac{2.15 \times 10^{23}\text{ C atoms}}{4.2 \times 10^{23}\text{ H atoms}} = \frac{1\text{ C}}{2\text{ H}}$$

A possible formula for ethylene is CH_2.

(b) The results in part (a) give the smallest whole-number ratio of C to H for benzene, ethane, and ethylene, and these ratios are consistent with their modern formulas.

2.37 $1.32\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{C atom}}{12.011\ \text{amu}} = 6.62 \times 10^{22}\ \text{C atoms}$

$1.18\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{O atom}}{15.9994\ \text{amu}} = 4.44 \times 10^{22}\ \text{O atoms}$

$\frac{\text{C}}{\text{O}} = \frac{6.62 \times 10^{22}\ \text{C atoms}}{4.44 \times 10^{22}\ \text{O atoms}} = \frac{1.5\ \text{C}}{1\ \text{O}}$;

therefore the formula for carbon suboxide is $C_{1.5}O$, or C_3O_2.

2.38 (a) $(1.67 \times 10^{-24}\ \frac{\text{g}}{\text{H atom}})(6.02 \times 10^{23}\ \text{H atoms}) = 1.01\ \text{g}$

This result is numerically equal to the atomic mass of H in grams.

(b) $(26.558 \times 10^{-24}\ \frac{\text{g}}{\text{O atom}})(6.02 \times 10^{23}\ \text{O atoms}) = 16.0\ \text{g}$

This result is numerically equal to the atomic mass of O in grams.

2.39 The mass of 6.02×10^{23} atoms is its atomic mass expressed in grams.
(a) If the atomic mass of an element is X, then 6.02×10^{23} atoms of this element weighs X grams.
(b) If the mass of 6.02×10^{23} atoms of element Y is 83.80 g, then the atomic mass of Y is 83.80. Y is Kr.

2.40 Assume a 1.00 g sample of the binary compound of zinc and sulfur.
$0.671 \times 1.00\ \text{g} = 0.671\ \text{g Zn}$; $0.329 \times 1.00\ \text{g} = 0.329\ \text{g S}$

$0.671\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{Zn atom}}{65.39\ \text{amu}} = 6.18 \times 10^{21}\ \text{Zn atoms}$

$0.329\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{S atom}}{32.066\ \text{amu}} = 6.18 \times 10^{21}\ \text{S atoms}$

$\frac{\text{Zn}}{\text{S}} = \frac{6.18 \times 10^{21}\ \text{Zn atoms}}{6.18 \times 10^{21}\ \text{S atoms}} = \frac{1\ \text{Zn}}{1\ \text{S}}$; therefore the formula is ZnS.

2.41 Assume a 1.000 g sample of one of the binary compounds.
$0.3104 \times 1.000\ \text{g} = 0.3104\ \text{g Ti}$; $0.6896 \times 1.000\ \text{g} = 0.6896\ \text{g Cl}$

$0.3104\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{Ti atom}}{47.88\ \text{amu}} = 3.90 \times 10^{21}\ \text{Ti atoms}$

$0.6896\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{Cl atom}}{35.453\ \text{amu}} = 1.17 \times 10^{22}\ \text{Cl atoms}$

$$\frac{\text{Cl}}{\text{Ti}} = \frac{1.17 \text{ x } 10^{22}}{3.90 \text{ x } 10^{21}} = \frac{3}{1}$$

Assume a 1.000 g sample of the other binary compound.

0.2524 x 1.000 g = 0.2524 g Ti; 0.7476 x 1.000 g = 0.7476 g Cl

$$0.2524 \text{ g x } \frac{1 \text{ amu}}{1.6605 \text{ x } 10^{-24} \text{ g}} \text{ x } \frac{1 \text{ Ti atom}}{47.88 \text{ amu}} = 3.17 \text{ x } 10^{21} \text{ Ti atoms}$$

$$0.7476 \text{ g x } \frac{1 \text{ amu}}{1.6605 \text{ x } 10^{-24} \text{ g}} \text{ x } \frac{1 \text{ Cl atom}}{35.453 \text{ amu}} = 1.27 \text{ x } 10^{22} \text{ Cl atoms}$$

$$\frac{\text{Cl}}{\text{Ti}} = \frac{1.27 \text{ x } 10^{22}}{3.17 \text{ x } 10^{21}} = \frac{4}{1}$$

Elements and Atoms

2.42 The atomic number is equal to the number of protons.
The mass number is equal to the sum of the number of protons and the number of neutrons.

2.43 The atomic number is equal to the number of protons.
The atomic mass is the weighted average mass (in amu) of the various isotopes for a particular element.

2.44 Atoms of the same element that have different numbers of neutrons are called isotopes.

2.45 The mass number is equal to the sum of the number of protons and the number of neutrons for a particular isotope.
For $^{14}_{6}$ C , mass number = 6 protons + 8 neutrons = 14.
For $^{14}_{7}$ N , mass number = 7 protons + 7 neutrons = 14.

2.46 The subscript giving the atomic number of an atom is often left off of an isotope symbol because one can readily look up the atomic number in the periodic table.

2.47 Te has isotopes with more neutrons than the isotopes of I.

2.48 (a) carbon, C (b) argon, Ar (c) vanadium, V

2.49 $^{137}_{55}$ Cs

2.50 (a) $^{220}_{86}$Rn (b) $^{210}_{84}$Po (c) $^{197}_{79}$Au

2.51 (a) $^{140}_{58}$ Ce (b) $^{60}_{27}$ Co

2.52 (a) $^{15}_{7}$N , 7 protons, 7 electrons, (15 S 7) = 8 neutrons

(b) $^{60}_{27}$Co, 27 protons, 27 electrons, (60 S 27) = 33 neutrons

(c) $^{131}_{53}$I, 53 protons, 53 electrons, (131 S 53) = 78 neutrons

(d) $^{142}_{58}$Ce, 58 protons, 58 electrons, (142 S 58) = 84 neutrons

2.53 (a) ^{27}Al, 13 protons and (27 S 13) = 14 neutrons
(b) ^{32}S, 16 protons and (32 S 16) = 16 neutrons
(c) ^{64}Zn, 30 protons and (64 S 30) = 34 neutrons
(d) ^{207}Pb, 82 protons and (207 S 82) = 125 neutrons

2.54 (a) $^{24}_{12}$Mg, magnesium (b) $^{58}_{28}$Ni, nickel
(c) $^{104}_{46}$Pd, palladium (d) $^{183}_{74}$W, tungsten

2.55 (a) $^{202}_{80}$Hg, mercury (b) $^{195}_{78}$Pt, platinum
(c) $^{184}_{76}$Os, osmium (d) $^{209}_{83}$Bi, bismuth

2.56 (0.199 x 10.0129 amu) + (0.801 x 11.009 31 amu) = 10.8 amu for B

2.57 (0.5184 x 106.9051 amu) + (0.4816 x 108.9048 amu) = 107.9 amu for Ag

2.58 24.305 amu = (0.7899 x 23.985 amu) + (0.1000 x 24.986 amu) + (0.1101 x Z)
Solve for Z. Z = 25.982 amu for ^{26}Mg.

2.59 The total abundance of all three isotopes must be 100.00%. The natural abundance of ^{29}Si is 4.67%. The natural abundance of ^{28}Si and ^{30}Si together must be 100.00% S 4.67% = 95.33%. Let Y be the natural abundance of ^{28}Si and [95.33 S Y] the natural abundance of ^{30}Si.
28.0855 amu = (0.0467 x 28.9765 amu) + (Y x 27.9769 amu)
+ ([0.9533 S Y] x 29.9738 amu)

Solve for Y. $Y = \frac{-1.842}{-1.997} = 0.922$

^{28}Si natural abundance = 92.2% ^{30}Si natural abundance = 95.33 S 92.2 = 3.1%

Compounds and Mixtures, Molecules and Ions

2.60 (a) muddy water, heterogeneous mixture
(b) concrete, heterogeneous mixture
(c) house paint, homogeneous mixture
(d) a soft drink, homogeneous mixture (heterogeneous mixture if it contains CO_2 bubbles)

2.61 (a) 18 karat gold, (b) window glass, and (d) liquefied air are homogeneous mixtures.
(c) Tomato juice is a heterogeneous mixture because the liquid contains solid pulp.

2.62 An atom is the smallest particle that retains the chemical properties of an element. A molecule is matter that results when two or more atoms are joined by covalent bonds. H and O are atoms, H_2O is a water molecule.

2.63 A molecule is the unit of matter that results when two or more atoms are joined by covalent bonds. An ion results when an atom gains or loses electrons. CH_4 is a methane molecule. Na^+ is the sodium cation.

2.64 A covalent bond results when two atoms share several (usually two) of their electrons. An ionic bond results from a complete transfer of one or more electrons from one atom to another. The CBH bonds in methane (CH_4) are covalent bonds. The bond in NaCl (Na^+Cl^S) is an ionic bond.

2.65 Covalent bonds typically form between nonmetals. (a) BBBr, (c) BrBCl, and (d) OBBr are covalent bonds.
Ionic bonds typically form between a metal and a nonmetal. (b) NaBBr is an ionic bond.

2.66 Element symbols are composed of one or two letters. If the element symbol is two letters, the first letter is uppercase and the second is lowercase. CO stands for carbon and oxygen in carbon monoxide.

2.67 (a) The formula of ammonia is NH_3.
(b) The ionic solid potassium chloride has the formula KCl.
(c) Cl^S is an anion.
(d) CH_4 is a neutral molecule.

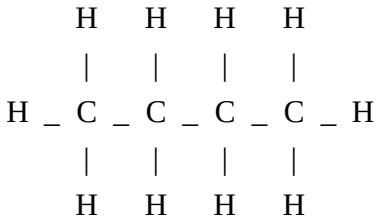
2.68 (a) Be^{2+}, 4 protons and 2 electrons
(b) Rb^+, 37 protons and 36 electrons
(c) Se^{2S}, 34 protons and 36 electrons
(d) Au^{3+}, 79 protons and 76 electrons

2.69 (a) A +2 cation that has 36 electrons must have 38 protons. X = Sr.
(b) A S1 anion that has 36 electrons must have 35 protons. X = Br.

2.70 C_3H_8O

2.71 $C_3H_6O_3$

2.72



2.73

Acids and Bases

2.74 (a) HI, acid (b) CsOH, base (c) H_3PO_4, acid
(d) $Ba(OH)_2$, base (e) H_2CO_3, acid

2.75 (a) HI, one H^+ ion (b) H_3PO_4, three H^+ ions (c) H_2CO_3, two H^+ ions

2.76 $HI(aq) \rightarrow H^+(aq) + I^-(aq)$; the anion is I^-
$H_3PO_4(aq) \rightarrow H^+(aq) + H_2PO_4^-(aq)$; the predominant anion is $H_2PO_4^-$
$H_2CO_3(aq) \rightarrow H^+(aq) + HCO_3^-(aq)$; the predominant anion is HCO_3^-

2.77 (b) $CsOH(aq) \rightarrow Cs^+(aq) + OH^-(aq)$; the cation is Cs^+
(d) $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$; the cation is Ba^{2+}

Naming Compounds

2.78 (a) KCl (b) $SnBr_2$ (c) CaO (d) $BaCl_2$ (e) AlH_3

2.79 (a) $Ca(CH_3CO_2)_2$ (b) $Fe(CN)_2$ (c) $Na_2Cr_2O_7$ (d) $Cr_2(SO_4)_3$ (e) $Hg(ClO_4)_2$

2.80 (a) barium ion (b) cesium ion (c) vanadium(III) ion
(d) hydrogen carbonate ion (e) ammonium ion (f) nickel(II) ion
(g) nitrite ion (h) chlorite ion (i) manganese(II) ion (j) perchlorate ion

2.81 (a) carbon tetrachloride (b) chlorine dioxide
(c) dinitrogen monoxide (d) dinitrogen trioxide

2.82 (a) SO_3^{2-} (b) PO_4^{3-} (c) Zr^{4+} (d) CrO_4^{2-} (e) $CH_3CO_2^-$ (f) $S_2O_3^{2-}$

2.83 (a) Zn^{2+} (b) Fe^{3+} (c) Ti^{4+} (d) Sn^{2+} (e) Hg_2^{2+} (f) Mn^{4+} (g) K^+ (h) Cu^{2+}

2.84 (a) zinc(II) cyanide (b) iron(III) nitrite (c) titanium(IV) sulfate
(d) tin(II) phosphate (e) mercury(I) sulfide (f) manganese(IV) oxide
(g) potassium periodate (h) copper(II) acetate

2.85 (a) magnesium sulfite (b) cobalt(II) nitrite (c) manganese(II) hydrogen carbonate (d) zinc(II) chr
(g) aluminum sulfate (h) lithium chlorate

2.86 (a) Na^+ and SO_4^{2S}; therefore the formula is Na_2SO_4
(b) Ba^{2+} and PO_4^{3S}; therefore the formula is $Ba_3(PO_4)_2$
(c) Ga^{3+} and SO_4^{2S}; therefore the formula is $Ga_2(SO_4)_3$

2.87 (a) Na_2O_2 (b) $AlBr_3$ (c) $Cr_2(SO_4)_3$

General Problems

2.88 atomic mass = (0.205 x 69.924 amu) + (0.274 x 71.922 amu)
+ (0.078 x 72.923 amu) + (0.365 x 73.921 amu)
+ (0.078 x 75.921 amu) = 72.6 amu

2.89 $$\text{mass of 1 C atom} = \frac{12.011\ \text{amu}}{1\ \text{C atoms}} \times \frac{1.6605 \times 10^{-24}\ \text{g}}{1\ \text{amu}} = 2.00 \times 10^{-23}\ \text{g / C atom}$$

$$\text{number of C atoms} = \frac{1 \times 10^{-5}\ \text{g}}{2.00 \times 10^{-23}\ \text{g / C atom}} = 5 \times 10^{17}\ \text{C atoms}$$

$$\text{time} = \frac{5 \times 10^{17}\ \text{C atoms}}{2\ \text{C atoms / s}} = 2.5 \times 10^{17}\ \text{s}$$

2.90 (a) sodium bromate (b) phosphoric acid
(c) phosphorous acid (d) vanadium(V) oxide

2.91 (a) $Ca(HSO_4)_2$ (b) SnO (c) $Ru(NO_3)_3$ (d) $(NH_4)_2CO_3$ (e) HI (f) $Be_3(PO_4)_2$

2.92 For NH_3, $$(2.34\ \text{g N})\left(\frac{3 \times 1.0079\ \text{amu H}}{14.0067\ \text{amu N}}\right) = 0.505\ \text{g H}$$

For N_2H_4, $$(2.34\ \text{g N})\left(\frac{4 \times 1.0079\ \text{amu H}}{2 \times 14.0067\ \text{amu N}}\right) = 0.337\ \text{g H}$$

2.93 $$\text{g N} = (1.575\ \text{g H})\left(\frac{3.670\ \text{g N}}{0.5275\ \text{g H}}\right) = 10.96\ \text{g N}$$

From Problem 2.92:

for NH_3, $$\frac{\text{g N}}{\text{g H}} = \frac{2.34\ \text{g N}}{0.505\ \text{g H}} = 4.63$$

for N_2H_4, $$\frac{\text{g N}}{\text{g H}} = \frac{2.34\ \text{g N}}{0.337\ \text{g H}} = 6.94$$

for compound X, $\frac{\text{g N}}{\text{g H}} = \frac{10.96 \text{ g N}}{1.575 \text{ g H}} = 6.96$; X is N_2H_4

2.94 TeO_4^{2s}, tellurate; TeO_3^{2s}, tellurite.
TeO_4^{2s} and TeO_3^{2s} are analogous to SO_4^{2s} and SO_3^{2s}.

2.95 H_2TeO_4, telluric acid; H_2TeO_3, tellurous acid

2.96 (a) I^s (b) Au^{3+} (c) Kr

2.97 $\frac{12.0000 \text{ amu}}{15.9994 \text{ amu}} = \frac{X}{16.0000 \text{ amu}}$; X = 12.0005 amu for ^{12}C prior to 1961.

2.98 $\frac{39.9626 \text{ amu}}{15.9994 \text{ amu}} = \frac{X}{16.0000 \text{ amu}}$; X = 39.9641 amu for ^{40}Ca prior to 1961.

2.99 (a) AsO_4^{3s}, arsenate (b) SeO_3^{2s}, selenite
(c) SeO_4^{2s}, selenate (d) $HAsO_4^{2s}$, hydrogen arsenate

2.100 (a) calcium-40, ^{40}Ca
(b) Not enough information, several different isotopes can have 63 neutrons.
(c) The neutral atom contains 26 electrons. The ion is iron-56, $^{56}Fe^{3+}$.
(d) Se^{2s}

2.101 Deuterium is ^2H and deuterium fluoride is ^2HF.
^2H has 1 proton, 1 neutron, and 1 electron.
F has 9 protons, 10 neutrons, and 9 electrons.
^2HF has 10 protons, 11 neutrons, and 10 electrons.
Chemically, ^2HF is like HF and is a weak acid.

2.102 $^1H^{35}Cl$ has 18 protons, 18 neutrons, and 18 electrons.
$^1H^{37}Cl$ has 18 protons, 20 neutrons, and 18 electrons.
$^2H^{35}Cl$ has 18 protons, 19 neutrons, and 18 electrons.
$^2H^{37}Cl$ has 18 protons, 21 neutrons, and 18 electrons.
$^3H^{35}Cl$ has 18 protons, 20 neutrons, and 18 electrons.
$^3H^{37}Cl$ has 18 protons, 22 neutrons, and 18 electrons.

2.103 (a) ^{40}Ar has 18 protons, 22 neutrons, and 18 electrons
(b) $^{40}Ca^{2+}$ has 20 protons, 20 neutrons, and 18 electrons
(c) $^{39}K^+$ has 19 protons, 20 neutrons, and 18 electrons
(d) $^{35}Cl^s$ has 17 protons, 18 neutrons, and 18 electrons

2.104 (a) Mg^{2+} and Cl^s, $MgCl_2$, magnesium chloride
(b) Ca^{2+} and O^{2s}, CaO, calcium oxide
(c) Li^+ and N^{3s}, Li_3N, lithium nitride
(d) Al^{3+} and O^{2s}, Al_2O_3, aluminum oxide

2.105

2.106

2.107 Mass of H_2SO_4 solution = 1.3028 g/mL x 40.00 mL = 52.112 g
Total mass of Zn and H_2SO_4 solution before reaction = 9.520 g + 52.112 g = 61.632 g
Total mass of solution after the reaction = 61.338 g
Because of the conservation of mass, the difference between the two masses is the mass of H_2 produced.
H_2 mass = 61.632 g S 61.338 g = 0.294 g

$$H_2 \text{ volume} = 0.294 \text{ g } H_2 \times \frac{1 \text{ L}}{0.0899 \text{ g } H_2} = 3.27 \text{ L } H_2$$

2.108 Molecular mass = (8 x 12.011 amu) + (9 x 1.0079 amu) + (1 x 14.0067 amu) + (2 x 15.9994 amu) = 151.165 amu

2.109

$$\text{mass \% C} = \frac{8 \times 12.011}{151.165} \times 100 = 63.565\%$$

$$\text{mass \% H} = \frac{9 \times 1.0079}{151.165} \times 100 = 6.0008\%$$

$$\text{mass \% N} = \frac{14.0067}{151.165} \times 100 = 9.2658\%$$

$$\text{mass \% O} = \frac{2 \times 15.9994}{151.165} \times 100 = 21.168\%$$

2.110 (a) Aspirin is likely a molecular compound because it is composed of only nonmetal elements.

(b) Assume a 100.0 g sample of aspirin. It would contain: 60.00 g C, 4.48 g H, and 35.52 g O.

$$60.00\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{C atom}}{12.011\ \text{amu}} = 3.008 \times 10^{24}\ \text{C atoms}$$

$$4.48\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{H atom}}{1.008\ \text{amu}} = 2.68 \times 10^{24}\ \text{H atoms}$$

$$35.52\ \text{g} \times \frac{1\ \text{amu}}{1.6605 \times 10^{-24}\ \text{g}} \times \frac{1\ \text{O atom}}{15.999\ \text{amu}} = 1.337 \times 10^{24}\ \text{O atoms}$$

The atom ratio in aspirin is:

$C_{3.008 \times 10^{24}}\ H_{2.68 \times 10^{24}}\ O_{1.337 \times 10^{24}}$, divide each subscript by 1×10^{24}

$C_{3.008}\ H_{2.68}\ O_{1.337}$, divide each subscript by the smallest, 1.337

$C_{3.008\ /\ 1.337}\ H_{2.68\ /\ 1.337}\ O_{1.337\ /\ 1.337}$

$C_{2.25}H_2\ O$, multiply each subscript by 4

$C_{(2.25 \times 4)}\ H_{(2 \times 4)}\ O_{(1 \times 4)}$

$C_9H_8O_4$

2.111 (a) Because X reacts by losing electrons, it is likely to be a metal.

(b) Because Y reacts by gaining electrons, it is likely to be a nonmetal.

(c) X_2Y_3

(d) X is likely to be in group 3A and Y is likely to be in group 6A.

2.112 65.39 amu = (0.4863 x 63.929 amu) + (0.2790 x Z) + (0.0410 x 66.927 amu) + (0.1875 x 67.925 amu) + (0.0062 x 69.925 amu)

Solve for Z.

65.39 amu = 47.00 amu + (0.2790 x Z)

65.39 amu S 47.00 amu = 18.39 amu = 0.2790 x Z

18.39 amu/0.2790 = Z

Z = 65.91 amu for ^{66}Zn

3 Formulas, Equations, and Moles

3.1 $2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2$

3.2 (a) $C_6H_{12}O_6 \rightarrow 2\ C_2H_6O + 2\ CO_2$
(b) $4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$
(c) $4\ NH_3 + Cl_2 \rightarrow N_2H_4 + 2\ NH_4Cl$

3.3 $3\ A_2 + 2\ B \rightarrow 2\ BA_3$

3.4 (a) Fe_2O_3: 2(55.85) + 3(16.00) = 159.7 amu
(b) H_2SO_4: 2(1.01) + 1(32.07) + 4(16.00) = 98.1 amu
(c) $C_6H_8O_7$: 6(12.01) + 8(1.01) + 7(16.00) = 192.1 amu
(d) $C_{16}H_{18}N_2O_4S$: 16(12.01) + 18(1.01) + 2(14.01) + 4(16.00) + 1(32.07) = 334.4 amu

3.5 $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

$$0.500\ mol\ Fe_2O_3 \times \frac{3\ mol\ CO}{1\ mol\ Fe_2O_3} = 1.50\ mol\ CO$$

3.6 $C_5H_{11}NO_2S$: 5(12.01) + 11(1.01) + 1(14.01) + 2(16.00) + 1(32.07) = 149.24 amu

3.7 $C_9H_8O_4$, 180.2 amu; 500 mg = 500 x 10^{-3} g = 0.500 g

$$0.500\ g \times \frac{1\ mol}{180.2\ g} = 2.77 \times 10^{-3}\ mol\ aspirin$$

$$2.77 \times 10^{-3}\ mol \times \frac{6.02 \times 10^{23}\ molecules}{1\ mol} = 1.67 \times 10^{21}\ aspirin\ molecules$$

3.8 salicylic acid, $C_7H_6O_3$, 138.1 amu; acetic anhydride, $C_4H_6O_3$, 102.1 amu
aspirin, $C_9H_8O_4$, 180.2 amu; acetic acid, $C_2H_4O_2$, 60.1 amu

$$4.50\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.1\ g\ C_7H_6O_3} \times \frac{1\ mol\ C_4H_6O_3}{1\ mol\ C_7H_6O_3} \times \frac{102.1\ g\ C_4H_6O_3}{1\ mol\ C_4H_6O_3} = 3.33\ g\ C_4H_6O_3$$

$$4.50\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.1\ g\ C_7H_6O_3} \times \frac{1\ mol\ C_9H_8O_4}{1\ mol\ C_7H_6O_3} \times \frac{180.2\ g\ C_9H_8O_4}{1\ mol\ C_9H_8O_4} = 5.87\ g\ C_9H_8O_4$$

$$4.50\ g\ C_7H_6O_3 \times \frac{1\ mol\ C_7H_6O_3}{138.1\ g\ C_7H_6O_3} \times \frac{1\ mol\ C_2H_4O_2}{1\ mol\ C_7H_6O_3} \times \frac{60.1\ g\ C_2H_4O_2}{1\ mol\ C_2H_4O_2} = 1.96\ g$$

$C_2H_4O_2$

3.9 C_2H_4, 28.1 amu; C_2H_6O, 46.1 amu

$$4.6\text{ g } C_2H_4 \times \frac{1\text{ mol } C_2H_4}{28.1\text{ g } C_2H_4} \times \frac{1\text{ mol } C_2H_6O}{1\text{ mol } C_2H_4} \times \frac{46.1\text{ g } C_2H_6O}{1\text{ mol } C_2H_6O} = 7.5\text{ g } C_2H_6O$$

(theoretical yield)

$$\text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\,\% = \frac{4.7\text{ g}}{7.5\text{ g}} \times 100\,\% = 63\,\%$$

3.10 CH_4, 16.04 amu; CH_2Cl_2, 84.93 amu; 1.85 kg = 1850 g

$$1850\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.04\text{ g } CH_4} \times \frac{1\text{ mol } CH_2Cl_2}{1\text{ mol } CH_4} \times \frac{84.93\text{ g } CH_2Cl_2}{1\text{ mol } CH_2Cl_2} = 9800\text{ g } CH_2Cl_2$$

(theoretical yield)

Actual yield = (9800 g)(0.431) = 4220 g CH_2Cl_2

3.11 Li_2O, 29.9 amu: 65 kg = 65,000 g; H_2O, 18.0 amu: 80.0 kg = 80,000 g

$$65{,}000\text{ g } Li_2O \times \frac{1\text{ mol } Li_2O}{29.9\text{ g } Li_2O} = 2.17 \times 10^3\text{ mol } Li_2O$$

$$80{,}000\text{ g } H_2O \times \frac{1\text{ mol } H_2O}{18.0\text{ g } H_2O} = 4.44 \times 10^3\text{ mol } H_2O$$

The reaction stoichiometry between Li_2O and H_2O is one to one. There are twice as many moles of H_2O as there are moles of Li_2O. Therefore, Li_2O is the limiting reactant.

$(4.44 \times 10^3\text{ mol} - 2.17 \times 10^3\text{ mol}) = 2.27 \times 10^3\text{ mol } H_2O$ remaining

$$2.27 \times 10^3\text{ mol } H_2O \times \frac{18.0\text{ g } H_2O}{1\text{ mol } H_2O} = 40{,}860\text{ g } H_2O = 40.9\text{ kg} = 41\text{ kg } H_2O$$

3.12 LiOH, 23.9 amu; CO_2, 44.0 amu

$$500.0\text{ g LiOH} \times \frac{1\text{ mol LiOH}}{23.9\text{ g LiOH}} \times \frac{1\text{ mol } CO_2}{1\text{ mol LiOH}} \times \frac{44.0\text{ g } CO_2}{1\text{ mol } CO_2} = 921\text{ g } CO_2$$

3.13 (a) $A + B_2 \rightarrow AB_2$

There is a 1:1 stoichiometry between the two reactants. A is the limiting reactant because there are fewer reactant A's than there are reactant B_2's.

(b) 1.0 mol of AB_2 can be made from 1.0 mol of A and 1.0 mol of B_2.

3.14 (a) 125 mL = 0.125 L; (0.20 mol/L)(0.125 L) = 0.025 mol $NaHCO_3$

(b) 650.0 mL = 0.6500 L; (2.50 mol/L)(0.6500 L) = 1.62 mol H_2SO_4

3.15 (a) NaOH, 40.0 amu; 500.0 mL = 0.5000 L

$$1.25\ \frac{\text{mol NaOH}}{\text{L}} \times 0.500\text{ L} \times \frac{40.0\text{ g NaOH}}{1\text{ mol NaOH}} = 25.0\text{ g NaOH}$$

(b) $C_6H_{12}O_6$, 180.2 amu

$$0.250\ \frac{\text{mol } C_6H_{12}O_6}{\text{L}} \times 1.50\text{ L} \times \frac{180.2\text{ g } C_6H_{12}O_6}{1\text{ mol } C_6H_{12}O_6} = 67.6\text{ g } C_6H_{12}O_6$$

3.16 $C_6H_{12}O_6$, 180.2 amu;

$$25.0\ g\ C_6H_{12}O_6 \times \frac{1\ mol\ C_6H_{12}O_6}{180.2\ g\ C_6H_{12}O_6} = 0.1387\ mol\ C_6H_{12}O_6$$

$$0.1387\ mol \times \frac{1\ L}{0.20\ mol} = 0.69\ L;\ 0.69\ L = 690\ mL$$

3.17 $C_{27}H_{46}O$, 386.7 amu; 750 mL = 0.750 L

$$0.005\ \frac{mol\ C_{27}H_{46}O}{L} \times 0.750\ L \times \frac{386.7\ g\ C_{27}H_{46}O}{1\ mol\ C_{27}H_{46}O} = 1\ g\ C_{27}H_{46}O$$

3.18 $M_i \times V_i = M_f \times V_f$; $M_f = \frac{M_i \times V_i}{V_f} = \frac{3.50\ M \times 75.0\ mL}{400.0\ mL} = 0.656\ M$

3.19 $M_i \times V_i = M_f \times V_f$; $V_i = \frac{M_f \times V_f}{M_i} = \frac{0.500\ M \times 250.0\ mL}{18.0\ M} = 6.94\ mL$

Dilute 6.94 mL of 18.0 M H_2SO_4 with enough water to make 250.0 mL of solution. The resulting solution will be 0.500 M H_2SO_4.

3.20 50.0 mL = 0.0500 L; (0.100 mol/L)(0.0500 L) = 5.00×10^{-3} mol NaOH

$$5.00 \times 10^{-3}\ mol\ NaOH \times \frac{1\ mol\ H_2SO_4}{2\ mol\ NaOH} = 2.50 \times 10^{-3}\ mol\ H_2SO_4$$

$$volume = 2.50 \times 10^{-3}\ mol \times \frac{1\ L}{0.250\ mol} = 0.0100\ L;\ 0.0100\ L = 10.0\ mL\ H_2SO_4$$

3.21 $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

25.0 mL = 0.0250 L and 68.5 mL = 0.0685 L

$$0.150\ \frac{mol\ KOH}{L} \times 0.0250\ L \times \frac{1\ mol\ HNO_3}{1\ mol\ KOH} = 3.75 \times 10^{-3}\ mol\ HNO_3$$

$$HNO_3\ molarity = \frac{3.75 \times 10^{-3}\ mol}{0.0685\ L} = 5.47 \times 10^{-2}\ M$$

3.22 From the reaction stoichiometry, moles NaOH = moles CH_3CO_2H

(0.200 mol/L)(0.0947 L) = 0.018 94 mol NaOH = 0.018 94 mol CH_3CO_2H

$$molarity = \frac{0.018\,94\ mol}{0.0250\ L} = 0.758\ M$$

3.23 For dimethylhydrazine, $C_2H_8N_2$, divide each subscript by 2 to obtain the empirical formula. The empirical formula is CH_4N. $C_2H_8N_2$, 60.1 amu or 60.1 g/mol

$$\%\ C = \frac{2 \times 12.0\ g}{60.1\ g} \times 100\,\% = 39.9\,\%$$

$$\%\ H = \frac{8 \times 1.01\ g}{60.1\ g} \times 100\,\% = 13.4\,\%$$

$$\% \ N = \frac{2 \times 14.0 \ g}{60.1 \ g} \times 100 \% = 46.6 \%$$

3.24 Assume a 100.0 g sample. From the percent composition data, a 100.0 g sample contains 14.25 g C, 56.93 g O, and 28.83 g Mg.

$$14.25 \text{ g C} \times \frac{1 \text{ mol C}}{12.0 \text{ g C}} = 1.19 \text{ mol C}$$

$$56.93 \text{ g O} \times \frac{1 \text{ mol O}}{16.0 \text{ g O}} = 3.56 \text{ mol O}$$

$$28.83 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.3 \text{ g Mg}} = 1.19 \text{ mol Mg}$$

$Mg_{1.19}C_{1.19}O_{3.56}$; divide each subscript by the smallest, 1.19.

$Mg_{1.19 / 1.19}C_{1.19 / 1.19}O_{3.56 / 1.19}$

The empirical formula is $MgCO_3$.

3.25 $$1.161 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.129 \text{ mol H}$$

$$2.818 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.0 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.0640 \text{ mol C}$$

$$0.129 \text{ mol H} \times \frac{1.01 \text{ g H}}{1 \text{ mol H}} = 0.130 \text{ g H}$$

$$0.0640 \text{ mol C} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} = 0.768 \text{ g C}$$

1.00 g total - (0.130 g H + 0.768 g C) = 0.102 g O

$$0.102 \text{ g O} \times \frac{1 \text{ mol O}}{16.0 \text{ g O}} = 0.006\,38 \text{ mol O}$$

$C_{0.0640}H_{0.129}O_{0.006\,38}$; divide each subscript by the smallest, 0.006 38.

$C_{0.0640 / 0.006\,38}H_{0.129 / 0.006\,38}O_{0.006\,38 / 0.006\,38}$

$C_{10.03}H_{20.22}O_1$ The empirical formula is $C_{10}H_{20}O$.

3.26 The empirical formula is CH_2O, 30 amu: molecular mass = 150 amu.

$$\frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{150 \text{ amu}}{30 \text{ amu}} = 5 \text{ ; therefore}$$

molecular formula = 5 x empirical formula = $C_{(5 \times 1)}H_{(5 \times 2)}O_{(5 \times 1)} = C_5H_{10}O_5$

3.27 (a) Assume a 100.0 g sample. From the percent composition data, a 100.0 g sample contains 21.86 g H and 78.14 g B.

$$21.86 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 21.6 \text{ mol H}$$

$$78.14 \text{ g B} \times \frac{1 \text{ mol B}}{10.8 \text{ g B}} = 7.24 \text{ mol B}$$

$B_{7.24}H_{21.6}$; divide each subscript by the smaller, 7.24.

$B_{7.24\,/\,7.24}\,H_{21.6\,/\,7.24}$ The empirical formula is BH_3, 13.8 amu.
27.7 amu / 13.8 amu = 2; molecular formula = $B_{(2\,x\,1)}H_{(2\,x\,3)} = B_2H_6$.
(b) Assume a 100.0 g sample. From the percent composition data, a 100.0 g sample contains 6.71 g H, 40.00 g C, and 53.28 g O.

$$6.71\ g\ H\ x\ \frac{1\ mol\ H}{1.01\ g\ H} = 6.64\ mol\ H$$

$$40.00\ g\ C\ x\ \frac{1\ mol\ C}{12.0\ g\ C} = 3.33\ mol\ C$$

$$53.28\ g\ O\ x\ \frac{1\ mol\ O}{16.0\ g\ O} = 3.33\ mol\ O$$

$C_{3.33}\,H_{6.64}\,O_{3.33}$; divide each subscript by the smallest, 3.33.
$C_{3.33\,/\,3.33}\,H_{6.64\,/\,3.33}\,O_{3.33\,/\,3.33}$ The empirical formula is CH_2O, 30.0 amu.
90.08 amu / 30.0 amu = 3; molecular formula = $C_{(3\,x\,1)}H_{(3\ x\,2)}O_{(3\,x\,1)} = C_3H_6O_3$

3.28 Main sources of error in calculating Avogadro's number by spreading oil on a pond are:
(i) the assumption that the oil molecules are tiny cubes
(ii) the assumption that the oil layer is one molecule thick
(iii) the assumption of a molecular mass of 200 for the oil

3.29 area of oil = $2.0 \times 10^7\ cm^2$
volume of oil = $4.9\ cm^3$ = area x 4 l = $(2.0 \times 10^7\ cm^2) \times 4\ l$

$$l = \frac{4.9\ cm^3}{(2.0\ x\ 10^7\ cm^2)(4)} = 6.125 \times 10^{-8}\ cm$$

area of oil = $2.0 \times 10^7\ cm^2 = l^2 \times N = (6.125 \times 10^{-8}\ cm)^2 \times N$

$$N = \frac{2.0\ x\ 10^7\ cm^2}{(6.125\ x\ 10^{-8}\ cm)^2} = 5.33 \times 10^{21}\ \text{oil molecules}$$

$$\text{moles of oil} = (4.9\ cm^3) \times (0.95\ g/cm^3) \times \frac{1\ mol\ oil}{200\ g\ oil} = 0.0233\ \text{mol oil}$$

$$\text{Avogadro's number} = \frac{5.33\ x\ 10^{21}\ \text{molecules}}{0.0233\ mol} = 2.3 \times 10^{23}\ \text{molecules/mole}$$

Understanding Key Concepts

3.30 The concentration of a solution is cut in half when the volume is doubled. This is best represented by box (b).

3.31 (c) $2\ A + B_2 \rightarrow A_2B_2$

3.32 The molecular formula for cytosine is $C_4H_5N_3O$.

$$\text{mol } CO_2 = 0.001\ \text{mol cyt} \times \frac{4\ C}{cyt} \times \frac{1\ CO_2}{C} = 0.004\ \text{mol } CO_2$$

$$\text{mol } H_2O = 0.001 \text{ mol cyt} \times \frac{5 \text{ H}}{\text{cyt}} \times \frac{1 \text{ } H_2O}{2 \text{ H}} = 0.0025 \text{ mol } H_2O$$

3.33 reactants, box (d), and products, box (c)

3.34 $C_{17}H_{18}F_3NO$ 17(12.01) + 18(1.01) + 3(19.00) + 1(14.01) + 1(16.00) = 309.36 amu

3.35 Because the two volumes are equal (let the volume = y L), the concentrations are proportional to the number of solute ions.

$$OH^- \text{ concentration} = 1.00 \text{ M} \times \frac{\text{y L}}{12 \text{ } H^+} \times \frac{8 \text{ } OH^-}{\text{y L}} = 0.67 \text{ M}$$

3.36 (a) $A_2 + 3 B_2 \rightarrow 2 AB_3$; B_2 is the limiting reactant because it is completely consumed.
(b) For 1.0 mol of A_2, 3.0 mol of B_2 are required. Because only 1.0 mol of B_2 is available, B_2 is the limiting reactant.

$$1 \text{ mol } B_2 \times \frac{2 \text{ mol } AB_3}{3 \text{ mol } B_2} = 2/3 \text{ mol } AB_3$$

3.37 $C_xH_y \xrightarrow{O_2} 3 CO_2 + 4 H_2O$; x is equal to the coefficient for CO_2 and y is equal to 2 times the coefficient for H_2O. The empirical formula for the hydrocarbon is C_3H_8.

Additional Problems
Balancing Equations

3.38 Equation (b) is balanced, (a) is not balanced .

3.39 (a) and (c) are not balanced, (b) is balanced.
(a) $2 Al + Fe_2O_3 \rightarrow Al_2O_3 + 2 Fe$ (balanced)
(c) $4 Au + 8 NaCN + O_2 + 2 H_2O \rightarrow 4 NaAu(CN)_2 + 4 NaOH$ (balanced)

3.40 (a) $Mg + 2 HNO_3 \rightarrow H_2 + Mg(NO_3)_2$
(b) $CaC_2 + 2 H_2O \rightarrow Ca(OH)_2 + C_2H_2$
(c) $2 S + 3 O_2 \rightarrow 2 SO_3$
(d) $UO_2 + 4 HF \rightarrow UF_4 + 2 H_2O$

3.41 (a) $2 NH_4NO_3 \rightarrow 2 N_2 + O_2 + 4 H_2O$
(b) $C_2H_6O + O_2 \rightarrow C_2H_4O_2 + H_2O$
(c) $C_2H_8N_2 + 2 N_2O_4 \rightarrow 3 N_2 + 2 CO_2 + 4 H_2O$

Molecular Masses and Moles

3.42 Hg_2Cl_2: 2(200.59) + 2(35.45) = 472.1 amu

$C_4H_8O_2$: 4(12.01) + 8(1.01) + 2(16.00) = 88.1 amu
CF_2Cl_2: 1(12.01) + 2(19.00) + 2(35.45) = 120.9 amu

3.43 (a) (1 x 30.97 amu) + (Y x 35.45 amu) = 137.3 amu; Solve for Y; Y = 3.
The formula is PCl_3.
(b) (10 x 12.01 amu) + (14 x 1.008 amu) + (Z x 14.01 amu) = 162.2 amu.
Solve for Z; Z = 2. The formula is $C_{10}H_{14}N_2$.

3.44 One mole equals the atomic mass or molecular mass in grams.
(a) Ti, 47.88 g (b) Br_2, 159.81 g (c) Hg, 200.59 g (d) H_2O, 18.02 g

3.45 (a) $1.00\ g\ Cr \times \frac{1\ mol\ Cr}{52.0\ g\ Cr} = 0.0192\ mol\ Cr$

(b) $1.00\ g\ Cl_2 \times \frac{1\ mol\ Cl_2}{70.9\ g\ Cl_2} = 0.0141\ mol\ Cl_2$

(c) $1.00\ g\ Au \times \frac{1\ mol\ Au}{197.0\ g\ Au} = 0.005\,08\ mol\ Au$

(d) $1.00\ g\ NH_3 \times \frac{1\ mol\ NH_3}{17.0\ g\ NH_3} = 0.0588\ mol\ NH_3$

3.46 There are 2 ions per each formula unit of NaCl. (2.5 mol)(2 mol ions/mol) = 5.0 mol ions

3.47 There are 2 K^+ ions per each formula unit of K_2SO_4.
$1.45\ mol\ K_2SO_4 \times \frac{2\ mol\ K^+}{1\ mol\ K_2SO_4} = 2.90\ mol\ K^+$

3.48 There are 3 ions (one Mg^{2+} and 2 Cl^-) per each formula unit of $MgCl_2$.
$MgCl_2$, 95.2 amu
$27.5\ g\ MgCl_2 \times \frac{1\,mol\,MgCl_2}{95.2\,g\,MgCl_2} \times \frac{3\,mol\,ions}{1\,mol\,MgCl_2} = 0.867\ mol\ ions$

3.49 There are 3 F^- anions per each formula unit of AlF_3.
AlF_3, 84.0 amu
$35.6\ g\ AlF_3 \times \frac{1\ mol\ AlF_3}{84.0\ g\ AlF_3} \times \frac{3\ mol\ anions}{1\ mol\ AlF_3} = 1.27\ mol\ F^-$

3.50 Molar mass = $\frac{3.28\ g}{0.0275\ mol} = 119\ g/mol$; molecular mass = 119 amu.

3.51 Molar mass = $\frac{221.6\ g}{0.5731\ mol} = 386.7\ g/mol$; molecular mass = 386.7 amu.

3.52 $FeSO_4$, 151.9 amu; 300 mg = 0.300 g

$$0.300\ \text{g}\ FeSO_4 \times \frac{1\ \text{mol}\ FeSO_4}{151.9\ \text{g}\ FeSO_4} = 1.97 \times 10^{-3}\ \text{mol}\ FeSO_4$$

$$1.97 \times 10^{-3}\ \text{mol}\ FeSO_4 \times \frac{6.02 \times 10^{23}\ \text{Fe(II) atoms}}{1\ \text{mol}\ FeSO_4} = 1.19 \times 10^{21}\ \text{Fe(II) atoms}$$

3.53 $0.0001\ \text{g C} \times \frac{1\ \text{mol C}}{12.0\ \text{g C}} \times \frac{6.02 \times 10^{23}\ \text{C atoms}}{1\ \text{mol C}} = 5 \times 10^{18}\ \text{C atoms}$

3.54 $C_8H_{10}N_4O_2$, 194.2 amu; 125 mg = 0.125 g

$0.125\ \text{g caffeine} \times \frac{1\ \text{mol caffeine}}{194.2\ \text{g caffeine}} = 6.44 \times 10^{-4}\ \text{mol caffeine}$

$0.125\ \text{g caffeine} \times \frac{1\ \text{mol caffeine}}{194.2\ \text{g caffeine}} \times \frac{6.022 \times 10^{23}\ \text{molecules}}{1\ \text{mol}} = 3.88 \times 10^{20}\ \text{caffeine molecules}$

3.55 $45\ \frac{\text{g}}{\text{egg}} \times \frac{6.02 \times 10^{23}\ \text{eggs}}{1\ \text{mol eggs}} = 2.7 \times 10^{25}\ \text{g / mol of eggs}$

3.56 (a) $1.0\ \text{g Li} \times \frac{1\ \text{mol Li}}{6.94\ \text{g Li}} = 0.14\ \text{mol Li}$

(b) $1.0\ \text{g Au} \times \frac{1\ \text{mol Au}}{197.0\ \text{g Au}} = 0.0051\ \text{mol Au}$

(c) penicillin G: $C_{16}H_{17}N_2O_4SK$, 372.5 amu

$1.0\ \text{g} \times \frac{1\ \text{mol penicillin G}}{372.5\ \text{g penicillin G}} = 2.7 \times 10^{-3}\ \text{mol penicillin G}$

3.57 (a) $0.0015\ \text{mol Na} \times \frac{23.0\ \text{g Na}}{1\ \text{mol Na}} = 0.034\ \text{g Na}$

(b) $0.0015\ \text{mol Pb} \times \frac{207.2\ \text{g Pb}}{1\ \text{mol Pb}} = 0.31\ \text{g Pb}$

(c) $C_{16}H_{13}ClN_2O$, 284.7 amu

$$0.0015\ \text{mol diazepam} \times \frac{284.7\ \text{g diazepam}}{1\ \text{mol diazepam}} = 0.43\ \text{g diazepam}$$

Stoichiometry Calculations

3.58 TiO_2, 79.88 amu; $100.0\ \text{kg Ti} \times \frac{79.88\ \text{kg}\ TiO_2}{47.88\ \text{kg Ti}} = 166.8\ \text{kg}\ TiO_2$

3.59 Fe_2O_3, 159.7 amu; $\%\ \text{Fe} = \frac{2(55.85\ \text{g})\ \text{Fe}}{159.7\ \text{g}\ Fe_2O_3} \times 100\,\% = 69.94\,\%$

mass Fe = (0.6994)(105 kg) = 73.4 kg

3.60 (a) $2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$

(b) Fe_2O_3, 159.7 amu; $525\ g\ Fe_2O_3 \times \frac{1\ mol\ Fe_2O_3}{159.7\ g\ Fe_2O_3} \times \frac{3\ mol\ C}{2\ mol\ Fe_2O_3} = 4.93\ mol\ C$

(c) $4.93\ mol\ C \times \frac{12.01\ g\ C}{1\ mol\ C} = 59.2\ g\ C$

3.61 (a) $Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$

(b) Fe_2O_3, 159.7 amu; CO, 28.01 amu

$3.02\ g\ Fe_2O_3 \times \frac{1\ mol\ Fe_2O_3}{159.7\ g\ Fe_2O_3} \times \frac{3\ mol\ CO}{1\ mol\ Fe_2O_3} \times \frac{28.01\ g\ CO}{1\ mol\ CO} = 1.59\ g\ CO$

(c) $1.68\ mol\ Fe_2O_3 \times \frac{3\ mol\ CO}{1\ mol\ Fe_2O_3} \times \frac{28.01\ g\ CO}{1\ mol\ CO} = 141\ g\ CO$

3.62 (a) $2\ Mg + O_2 \rightarrow 2\ MgO$

(b) Mg, 24.30 amu; O_2, 32.00 amu; MgO, 40.30 amu

$25.0\ g\ Mg \times \frac{1\ mol\ Mg}{24.30\ g\ Mg} \times \frac{1\ mol\ O_2}{2\ mol\ Mg} \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 16.5\ g\ O_2$

$25.0\ g\ Mg \times \frac{1\ mol\ Mg}{24.30\ g\ Mg} \times \frac{2\ mol\ MgO}{2\ mol\ Mg} \times \frac{40.30\ g\ MgO}{1\ mol\ MgO} = 41.5\ g\ MgO$

(c) $25.0\ g\ O_2 \times \frac{1\ mol\ O_2}{32.00\ g\ O_2} \times \frac{2\ mol\ Mg}{1\ mol\ O_2} \times \frac{24.30\ g\ Mg}{1\ mol\ Mg} = 38.0\ g\ Mg$

$25.0\ g\ O_2 \times \frac{1\ mol\ O_2}{32.00\ g\ O_2} \times \frac{2\ mol\ MgO}{1\ mol\ O_2} \times \frac{40.30\ g\ MgO}{1\ mol\ MgO} = 63.0\ g\ MgO$

3.63 $C_2H_4 + H_2O \rightarrow C_2H_6O$; C_2H_4, 28.05 amu; H_2O, 18.02 amu; C_2H_6O, 46.07 amu

(a) $0.133\ mol\ H_2O \times \frac{1\ mol\ C_2H_4}{1\ mol\ H_2O} \times \frac{28.05\ g\ C_2H_4}{1\ mol\ C_2H_4} = 3.73\ g\ C_2H_4$

$0.133\ mol\ H_2O \times \frac{1\ mol\ C_2H_6O}{1\ mol\ H_2O} \times \frac{46.07\ g\ C_2H_6O}{1\ mol\ C_2H_6O} = 6.13\ g\ C_2H_6O$

(b) $0.371\ mol\ C_2H_4 \times \frac{1\ mol\ H_2O}{1\ mol\ C_2H_4} \times \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} = 6.69\ g\ H_2O$

$0.371\ mol\ C_2H_4 \times \frac{1\ mol\ C_2H_6O}{1\ mol\ C_2H_4} \times \frac{46.07\ g\ C_2H_6O}{1\ mol\ C_2H_6O} = 17.1\ g\ C_2H_6O$

3.64 (a) $2\ HgO \rightarrow 2\ Hg + O_2$

(b) HgO, 216.6 amu; Hg, 200.6 amu; O_2, 32.0 amu

$45.5\ g\ HgO \times \frac{1\ mol\ HgO}{216.6\ g\ HgO} \times \frac{2\ mol\ Hg}{2\ mol\ HgO} \times \frac{200.6\ g\ Hg}{1\ mol\ Hg} = 42.1\ g\ Hg$

$$45.5\ g\ HgO\ x\ \frac{1\ mol\ HgO}{216.6\ g\ HgO}\ x\ \frac{1\ mol\ O_2}{2\ mol\ HgO}\ x\ \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 3.36\ g\ O_2$$

(c) $$33.3\ g\ O_2\ x\ \frac{1\ mol\ O_2}{32.00\ g\ O_2}\ x\ \frac{2\ mol\ HgO}{1\ mol\ O_2}\ x\ \frac{216.6\ g\ HgO}{1\ mol\ HgO} = 451\ g\ HgO$$

3.65 5.60 kg = 5600 g; $TiCl_4$, 189.7 amu; TiO_2, 79.88 amu

$$5600\ g\ TiCl_4\ x\ \frac{1\ mol\ TiCl_4}{189.7\ g\ TiCl_4}\ x\ \frac{1\ mol\ TiO_2}{1\ mol\ TiCl_4}\ x\ \frac{79.88\ g\ TiO_2}{1\ mol\ TiO_2} = 2358\ g\ TiO_2 = 2.36\ kg\ TiO_2$$

3.66 $$2.00\ g\ Ag\ x\ \frac{1\ mol\ Ag}{107.9\ g\ Ag} = 0.0185\ mol\ Ag$$

$$0.657\ g\ Cl\ x\ \frac{1\ mol\ Cl}{35.45\ g\ Cl} = 0.0185\ mol\ Cl$$

$Ag_{0.0185}Cl_{0.0185}$ Divide both subscripts by 0.0185. The empirical formula is AgCl.

3.67 $$5.0\ g\ Al\ x\ \frac{1\ mol\ Al}{27.0\ g\ Al} = 0.19\ mol\ Al;\ 4.45\ g\ O\ x\ \frac{1\ mol\ O}{16.0\ g\ O} = 0.28\ mol\ O$$

$Al_{0.19}O_{0.28}$; divide both subscripts by the smaller, 0.19.

$Al_{0.19\ /\ 0.19}O_{0.28\ /\ 0.19}$

$Al_1O_{1.5}$; multiply both subscripts by 2 to obtain integers. The empirical formula is Al_2O_3.

Limiting Reactants and Reaction Yield

3.68 $$3.44\ mol\ N_2\ x\ \frac{3\ mol\ H_2}{1\ mol\ N_2} = 10.3\ mol\ H_2\ required.$$

Because there is only 1.39 mol H_2, H_2 is the limiting reactant.

$$1.39\ mol\ H_2\ x\ \frac{2\ mol\ NH_3}{3\ mol\ H_2}\ x\ \frac{17.03\ g\ NH_3}{1\ mol\ NH_3} = 15.8\ g\ NH_3$$

$$1.39\ mol\ H_2\ x\ \frac{1\ mol\ N_2}{3\ mol\ H_2}\ x\ \frac{28.01\ g\ N_2}{1\ mol\ N_2} = 13.0\ g\ N_2\ reacted$$

$$3.44\ mol\ N_2\ x\ \frac{28.01\ g\ N_2}{1\ mol\ N_2} = 96.3\ g\ N_2\ initially$$

(96.3 g - 13.0 g) = 83.3 g N_2 left over

3.69 H_2, 2.016 amu; Cl_2, 70.91 amu; HCl 36.46 amu

$$3.56\ g\ H_2\ x\ \frac{1\ mol\ H_2}{2.016\ g\ H_2} = 1.77\ mol\ H_2$$

$$8.94\ g\ Cl_2\ x\ \frac{1\ mol\ Cl_2}{70.91\ g\ Cl_2} = 0.126\ mol\ Cl_2$$

Because the reaction stoichiometry between H_2 and Cl_2 is one to one, Cl_2 is the limiting reactant.

$$0.126 \text{ mol } Cl_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Cl_2} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 9.19 \text{ g HCl}$$

3.70 C_2H_4, 28.05 amu; Cl_2, 70.91 amu; $C_2H_4Cl_2$, 98.96 amu

$$15.4 \text{ g } C_2H_4 \times \frac{1 \text{ mol } C_2H_4}{28.05 \text{ g } C_2H_4} = 0.549 \text{ mol } C_2H_4$$

$$3.74 \text{ g } Cl_2 \times \frac{1 \text{ mol } Cl_2}{70.91 \text{ g } Cl_2} = 0.0527 \text{ mol } Cl_2$$

Because the reaction stoichiometry between C_2H_4 and Cl_2 is one to one, Cl_2 is the limiting reactant.

$$0.0527 \text{ mol } Cl_2 \times \frac{1 \text{ mol } C_2H_4Cl_2}{1 \text{ mol } Cl_2} \times \frac{98.96 \text{ g } C_2H_4Cl_2}{1 \text{ mol } C_2H_4Cl_2} = 5.22 \text{ g } C_2H_4Cl_2$$

3.71 (a) NaCl, 58.44 amu; $AgNO_3$, 169.9 amu; AgCl, 143.3 amu; $NaNO_3$, 85.00 amu

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

$$1.3 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 0.022 \text{ mol NaCl}$$

$$3.5 \text{ g } AgNO_3 \times \frac{1 \text{ mol } AgNO_3}{169.9 \text{ g } AgNO_3} = 0.021 \text{ mol } AgNO_3$$

Because the reaction stoichiometry between NaCl and $AgNO_3$ is one to one, $AgNO_3$ is the limiting reactant.

$$0.021 \text{ mol } AgNO_3 \times \frac{1 \text{ mol AgCl}}{1 \text{ mol } AgNO_3} \times \frac{143.3 \text{ g AgCl}}{1 \text{ mol AgCl}} = 3.0 \text{ g AgCl}$$

$$0.021 \text{ mol } AgNO_3 \times \frac{1 \text{ mol } NaNO_3}{1 \text{ mol } AgNO_3} \times \frac{85.00 \text{ g } NaNO_3}{1 \text{ mol } NaNO_3} = 1.8 \text{ g } NaNO_3$$

$$0.021 \text{ mol } AgNO_3 \times \frac{1 \text{ mol NaCl}}{1 \text{ mol } AgNO_3} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} = 1.2 \text{ g NaCl reacted}$$

(1.3 g - 1.2 g) = 0.1 g NaCl left over

(b) $BaCl_2$, 208.2 amu; H_2SO_4, 98.08 amu; $BaSO_4$, 233.4 amu; HCl, 36.46 amu

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ HCl$

$$2.65 \text{ g } BaCl_2 \times \frac{1 \text{ mol } BaCl_2}{208.2 \text{ g } BaCl_2} = 0.0127 \text{ mol } BaCl_2$$

$$6.78 \text{ g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.08 \text{ g } H_2SO_4} = 0.0691 \text{ mol } H_2SO_4$$

Because the reaction stoichiometry between $BaCl_2$ and H_2SO_4 is one to one, $BaCl_2$ is the limiting reactant.

$$0.0127 \text{ mol } BaCl_2 \times \frac{1 \text{ mol } BaSO_4}{1 \text{ mol } BaCl_2} \times \frac{233.4 \text{ g } BaSO_4}{1 \text{ mol } BaSO_4} = 2.96 \text{ g } BaSO_4$$

$$0.0127 \text{ mol } BaCl_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } BaCl_2} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 0.926 \text{ g HCl}$$

$$0.0127 \text{ mol } BaCl_2 \times \frac{1 \text{ mol } H_2SO_4}{1 \text{ mol } BaCl_2} \times \frac{98.1 \text{ g } H_2SO_4}{1 \text{ mol } H_2SO_4} = 1.25 \text{ g } H_2SO_4 \text{ reacted}$$

(6.78 g - 1.25 g) = 5.53 g H_2SO_4 left over

3.72 $CaCO_3$, 100.1 amu; HCl, 36.46 amu

$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2$

$$2.35 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g } CaCO_3} = 0.0235 \text{ mol } CaCO_3$$

$$2.35 \text{ g } HCl \times \frac{1 \text{ mol } HCl}{36.46 \text{ g } HCl} = 0.0645 \text{ mol } HCl$$

The reaction stoichiometry is 1 mole of $CaCO_3$ for every 2 moles of HCl. For 0.0235 mol $CaCO_3$, we only need 2(0.0235 mol) = 0.0470 mol HCl. We have 0.0645 mol HCl; therefore $CaCO_3$ is the limiting reactant.

$$0.0235 \text{ mol } CaCO_3 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3} \times \frac{22.4 \text{ L}}{1 \text{ mol } CO_2} = 0.526 \text{ L } CO_2$$

3.73 $2\,NaN_3 \rightarrow 3\,N_2 + 2\,Na$; NaN_3, 65.01 amu; N_2, 28.01 amu

$$38.5 \text{ g } NaN_3 \times \frac{1 \text{ mol } NaN_3}{65.01 \text{ g } NaN_3} \times \frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3} \times \frac{47.0 \text{ L}}{1.00 \text{ mol } N_2} = 41.8 \text{ L}$$

3.74 $CH_3CO_2H + C_5H_{12}O \rightarrow C_7H_{14}O_2 + H_2O$

CH_3CO_2H, 60.05 amu; $C_5H_{12}O$, 88.15 amu; $C_7H_{14}O_2$, 130.19 amu

$$3.58 \text{ g } CH_3CO_2H \times \frac{1 \text{ mol } CH_3CO_2H}{60.05 \text{ g } CH_3CO_2H} = 0.0596 \text{ mol } CH_3CO_2H$$

$$4.75 \text{ g } C_5H_{12}O \times \frac{1 \text{ mol } C_5H_{12}O}{88.15 \text{ g } C_5H_{12}O} = 0.0539 \text{ mol } C_5H_{12}O$$

Because the reaction stoichiometry between CH_3CO_2H and $C_5H_{12}O$ is one to one, isopentyl alcohol ($C_5H_{12}O$) is the limiting reactant.

$$0.0539 \text{ mol } C_5H_{12}O \times \frac{1 \text{ mol } C_7H_{14}O_2}{1 \text{ mol } C_5H_{12}O} \times \frac{130.19 \text{ g } C_7H_{14}O_2}{1 \text{ mol } C_7H_{14}O_2} = 7.02 \text{ g } C_7H_{14}O_2$$

7.02 g $C_7H_{14}O_2$ is the theoretical yield. Actual yield = (7.02 g)(0.45) = 3.2 g.

3.75 $K_2PtCl_4 + 2\,NH_3 \rightarrow 2\,KCl + Pt(NH_3)_2Cl_2$

K_2PtCl_4, 415.1 amu; NH_3, 17.03 amu; $Pt(NH_3)_2Cl_2$, 300.0 amu

$$55.8 \text{ g } K_2PtCl_4 \times \frac{1 \text{ mol } K_2PtCl_4}{415.1 \text{ g } K_2PtCl_4} = 0.134 \text{ mol } K_2PtCl_4$$

$$35.6 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} = 2.09 \text{ mol } NH_3$$

Only 2(0.134) = 0.268 mol NH_3 are needed to react with 0.134 mol K_2PtCl_4. Therefore, the NH_3 is in excess and K_2PtCl_4 is the limiting reactant.

$$0.134 \text{ mol } K_2PtCl_4 \times \frac{1 \text{ mol } Pt(NH_3)_2Cl_2}{1 \text{ mol } K_2PtCl_4} \times \frac{300.0 \text{ g } Pt(NH_3)_2Cl_2}{1 \text{ mol } Pt(NH_3)_2Cl_2} = 40.2 \text{ g } Pt(NH_3)_2Cl_2$$

40.2 g $Pt(NH_3)_2Cl_2$ is the theoretical yield.
Actual yield = (40.2 g)(0.95) = 38 g $Pt(NH_3)_2Cl_2$.

3.76 $CH_3CO_2H + C_5H_{12}O \rightarrow C_7H_{14}O_2 + H_2O$
CH_3CO_2H, 60.05 amu; $C_5H_{12}O$, 88.15 amu; $C_7H_{14}O_2$, 130.19 amu

$$1.87 \text{ g } CH_3CO_2H \times \frac{1 \text{ mol } CH_3CO_2H}{60.05 \text{ g } CH_3CO_2H} = 0.0311 \text{ mol } CH_3CO_2H$$

$$2.31 \text{ g } C_5H_{12}O \times \frac{1 \text{ mol } C_5H_{12}O}{88.15 \text{ g } C_5H_{12}O} = 0.0262 \text{ mol } C_5H_{12}O$$

Because the reaction stoichiometry between CH_3CO_2H and $C_5H_{12}O$ is one to one, isopentyl alcohol ($C_5H_{12}O$) is the limiting reactant.

$$0.0262 \text{ mol } C_5H_{12}O \times \frac{1 \text{ mol } C_7H_{14}O_2}{1 \text{ mol } C_5H_{12}O} \times \frac{130.19 \text{ g } C_7H_{14}O_2}{1 \text{ mol } C_7H_{14}O_2} = 3.41 \text{ g } C_7H_{14}O_2$$

3.41 g $C_7H_{14}O_2$ is the theoretical yield.

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% = \frac{2.96 \text{ g}}{3.41 \text{ g}} \times 100\% = 86.8\%$$

3.77 $K_2PtCl_4 + 2\,NH_3 \rightarrow 2\,KCl + Pt(NH_3)_2Cl_2$
K_2PtCl_4, 415.1 amu; NH_3, 17.03 amu; $Pt(NH_3)_2Cl_2$, 300.0 amu

$$3.42 \text{ g } K_2PtCl_4 \times \frac{1 \text{ mol } K_2PtCl_4}{415.1 \text{ g } K_2PtCl_4} = 0.008\,24 \text{ mol } K_2PtCl_4$$

$$1.61 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.03 \text{ g } NH_3} = 0.0945 \text{ mol } NH_3$$

Only 2 x (0.008 24) = 0.0165 mol of NH_3 are needed to react with 0.008 24 mol K_2PtCl_4. Therefore, the NH_3 is in excess and K_2PtCl_4 is the limiting reactant.

$$0.008\,24 \text{ mol } K_2PtCl_4 \times \frac{1 \text{ mol } Pt(NH_3)_2Cl_2}{1 \text{ mol } K_2PtCl_4} \times \frac{300.0 \text{ g } Pt(NH_3)_2Cl_2}{1 \text{ mol } Pt(NH_3)_2Cl_2} = 2.47 \text{ g } Pt(NH_3)_2Cl_2$$

2.47 g $Pt(NH_3)_2Cl_2$ is the theoretical yield. 2.08 g $Pt(NH_3)_2Cl_2$ is the actual yield.

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% = \frac{2.08 \text{ g}}{2.47 \text{ g}} \times 100\% = 84.2\%$$

Molarity, Solution Stoichiometry, Dilution, and Titration

3.78 (a) 35.0 mL = 0.0350 L; $\frac{1.200 \text{ mol } HNO_3}{\text{L}} \times 0.0350 \text{ L} = 0.0420 \text{ mol } HNO_3$

(b) 175 mL = 0.175 L; $\frac{0.67 \text{ mol } C_6H_{12}O_6}{\text{L}} \times 0.175 \text{ L} = 0.12 \text{ mol } C_6H_{12}O_6$

3.79 (a) C_2H_6O, 46.07 amu; 250.0 mL = 0.2500 L

$$\frac{0.600\ \text{mol}\ C_2H_6O}{\text{L}} \times 0.2500\ \text{L} = 0.150\ \text{mol}\ C_2H_6O$$

$(0.150\ \text{mol})(46.07\ \text{g/mol}) = 6.91\ \text{g}\ C_2H_6O$

(b) H_3BO_3, 61.83 amu; 167 mL = 0.167 L

$$\frac{0.200\ \text{mol}\ H_3BO_3}{\text{L}} \times 0.167\ \text{L} = 0.0334\ \text{mol}\ H_3BO_3$$

$(0.0334\ \text{mol})(61.83\ \text{g/mol}) = 2.07\ \text{g}\ H_3BO_3$

3.80 $BaCl_2$, 208.2 amu

$$15.0\ \text{g}\ BaCl_2 \times \frac{1\ \text{mol}\ BaCl_2}{208.2\ \text{g}\ BaCl_2} = 0.0720\ \text{mol}\ BaCl_2$$

$$0.0720\ \text{mol} \times \frac{1.0\ \text{L}}{0.45\ \text{mol}} = 0.16\ \text{L};\ 0.16\ \text{L} = 160\ \text{mL}$$

3.81 $$0.0171\ \text{mol KOH} \times \frac{1.00\ \text{L}}{0.350\ \text{mol KOH}} = 0.0489\ \text{L};\ 0.0489\ \text{L} = 48.9\ \text{mL}$$

3.82 NaCl, 58.4 amu; 400 mg = 0.400 g; 100 mL = 0.100 L

$$0.400\ \text{g NaCl} \times \frac{1\ \text{mol NaCl}}{58.4\ \text{g NaCl}} = 0.006\,85\ \text{mol NaCl}$$

$$\text{molarity} = \frac{0.006\,85\ \text{mol}}{0.100\ \text{L}} = 0.0685\ \text{M}$$

3.83 $C_6H_{12}O_6$, 180.2 amu; 90 mg = 0.090 g; 100 mL = 0.100 L

$$0.090\ \text{g}\ C_6H_{12}O_6 \times \frac{1\ \text{mol}\ C_6H_{12}O_6}{180.2\ \text{g}\ C_6H_{12}O_6} = 0.000\,50\ \text{mol}\ C_6H_{12}O_6$$

$$\text{molarity} = \frac{0.000\,50\ \text{mol}}{0.100\ \text{L}} = 0.0050\ \text{M} = 5.0 \times 10^{-3}\ \text{M}$$

3.84 NaCl, 58.4 amu; KCl, 74.6 amu; $CaCl_2$, 111.0 amu; 500 mL = 0.500 L

$$4.30\ \text{g NaCl} \times \frac{1\ \text{mol NaCl}}{58.4\ \text{g NaCl}} = 0.0736\ \text{mol NaCl}$$

$$0.150\ \text{g KCl} \times \frac{1\ \text{mol KCl}}{74.6\ \text{g KCl}} = 0.002\,01\ \text{mol KCl}$$

$$0.165\ \text{g}\ CaCl_2 \times \frac{1\ \text{mol}\ CaCl_2}{111.0\ \text{g}\ CaCl_2} = 0.001\,49\ \text{mol}\ CaCl_2$$

$0.0736\ \text{mol} + 0.002\,01\ \text{mol} + 2(0.001\,49\ \text{mol}) = 0.0786\ \text{mol}\ Cl^-$

Na^+ molarity = $\frac{0.0736\ mol}{0.500\ L}$ = 0.147 M

Ca^{2+} molarity = $\frac{0.001\,49\ mol}{0.500\ L}$ = 0.002 98 M

K^+ molarity = $\frac{0.002\,01\ mol}{0.500\ L}$ = 0.004 02 M

Cl^- molarity = $\frac{0.0786\ mol}{0.500\ L}$ = 0.157 M

3.85 3.045 g Cu x $\frac{1\ mol\ Cu}{63.546\ g\ Cu}$ = 0.047 92 mol Cu; 50.0 mL = 0.0500 L

$Cu(NO_3)_2$ molarity = $\frac{0.047\,92\ mol}{0.0500\ L}$ = 0.958 M

3.86 $M_f \times V_f = M_i \times V_i$; $M_f = \frac{M_i \times V_i}{V_f} = \frac{12.0\ M \times 35.7\ mL}{250.0\ mL} = 1.71\ M\ HCl$

3.87 $M_f \times V_f = M_i \times V_i$; $V_f = \frac{M_i \times V_i}{M_f} = \frac{0.0913\ M \times 70.00\ mL}{0.0150\ M} = 426\ mL$

3.88 $2\ HBr(aq) + K_2CO_3(aq) \rightarrow 2\ KBr(aq) + CO_2(g) + H_2O(l)$

K_2CO_3, 138.2 amu; 450 mL = 0.450 L

$\frac{0.500\ mol\ HBr}{L} \times 0.450\ L = 0.225\ mol\ HBr$

$0.225\ mol\ HBr \times \frac{1\ mol\ K_2CO_3}{2\ mol\ HBr} \times \frac{138.2\ g\ K_2CO_3}{1\ mol\ K_2CO_3} = 15.5\ g\ K_2CO_3$

3.89 $2\ C_4H_{10}S + NaOCl \rightarrow C_8H_{18}S_2 + NaCl + H_2O$

$C_4H_{10}S$, 90.19 amu; 5.00 mL = 0.005 00 L

$\frac{0.0985\ mol\ NaOCl}{L} \times 0.005\,00\ L = 4.925 \times 10^{-4}\ mol\ NaOCl$

$4.925 \times 10^{-4}\ mol\ NaOCl \times \frac{2\ mol\ C_4H_{10}S}{1\ mol\ NaOCl} \times \frac{90.19\ g\ C_4H_{10}S}{1\ mol\ C_4H_{10}S} = 0.0888\ g\ C_4H_{10}S$

3.90 $H_2C_2O_4$, 90.04 amu

$3.225\ g\ H_2C_2O_4 \times \frac{1\ mol\ H_2C_2O_4}{90.04\ g\ H_2C_2O_4} \times \frac{2\ mol\ KMnO_4}{5\ mol\ H_2C_2O_4} = 0.0143\ mol\ KMnO_4$

$0.0143\ mol \times \frac{1\ L}{0.250\ mol} = 0.0572\ L = 57.2\ mL$

3.91 $H_2C_2O_4$, 90.04 amu; 400.0 mL = 0.4000 L; 25.0 mL = 0.0250 L

$$12.0\ g\ H_2C_2O_4 \times \frac{1\ mol\ H_2C_2O_4}{90.04\ g\ H_2C_2O_4} = 0.133\ mol\ H_2C_2O_4$$

$$\text{molarity} = \frac{0.133\ mol}{0.4000\ L} = 0.333\ M\ H_2C_2O_4$$

$$H_2C_2O_4(aq) + 2\ KOH(aq) \rightarrow K_2C_2O_4(aq) + 2\ H_2O(l)$$

$$\frac{0.333\ mol\ C_2H_2O_4}{L} \times 0.0250\ L = 0.008\ 32\ mol\ H_2C_2O_4$$

$$0.008\ 32\ mol\ H_2C_2O_4 \times \frac{2\ mol\ KOH}{1\ mol\ H_2C_2O_4} = 0.0166\ mol\ KOH$$

$$0.0166\ mol \times \frac{1\ L}{0.100\ mol} = 0.166\ L;\ 0.166\ L = 166\ mL$$

Formulas and Elemental Analysis

3.92 CH_4N_2O, 60.1 amu

$$\%\ C = \frac{12.0\ g\ C}{60.1\ g} \times 100\,\% = 20.0\,\%$$

$$\%\ H = \frac{4 \times 1.01\ g\ H}{60.1\ g} \times 100\,\% = 6.72\,\%$$

$$\%\ N = \frac{2 \times 14.0\ g\ N}{60.1\ g} \times 100\,\% = 46.6\,\%$$

$$\%\ O = \frac{16.0\ g\ O}{60.1\ g} \times 100\,\% = 26.6\,\%$$

3.93 (a) $Cu_2(OH)_2CO_3$, 221.1 amu

$$\%\ Cu = \frac{2 \times 63.5\ g\ Cu}{221.1\ g} \times 100\% = 57.4\%$$

$$\%\ O = \frac{5 \times 16.0\ g\ O}{221.1\ g} \times 100\% = 36.2\%$$

$$\%\ C = \frac{12.0\ g\ C}{221.1\ g} \times 100\% = 5.43\%$$

$$\%\ H = \frac{2 \times 1.01\ g\ H}{221.1\ g} \times 100\% = 0.91\%$$

(b) $C_8H_9NO_2$, 151.2 amu

$$\%\ C = \frac{8 \times 12.0\ g\ C}{151.2\ g} \times 100\% = 63.5\%$$

$$\%\ H = \frac{9 \times 1.01\ g\ H}{151.2\ g} \times 100\% = 6.01\%$$

$$\% \text{ N} = \frac{14.0 \text{ g N}}{151.2 \text{ g}} \text{ x } 100\% = 9.26\%$$

$$\% \text{ O} = \frac{2 \text{ x } 16.0 \text{ g O}}{151.2 \text{ g}} \text{ x } 100\% = 21.2\%$$

(c) $Fe_4[Fe(CN)_6]_3$, 859.2 amu

$$\% \text{ Fe} = \frac{7 \text{ x } 55.85 \text{ g Fe}}{859.2 \text{ g}} \text{ x } 100\% = 45.50\%$$

$$\% \text{ C} = \frac{18 \text{ x } 12.01 \text{ g C}}{859.2 \text{ g}} \text{ x } 100\% = 25.16\%$$

$$\% \text{ N} = \frac{18 \text{ x } 14.01 \text{ g N}}{859.2 \text{ g}} \text{ x } 100\% = 29.35\%$$

3.94 Assume a 100.0 g sample. From the percent composition data, a 100.0 g sample contains 24.25 g F and 75.75 g Sn.

$$24.25 \text{ g F} \text{ x } \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 1.276 \text{ mol F}$$

$$75.75 \text{ g Sn} \text{ x } \frac{1 \text{ mol Sn}}{118.7 \text{ g Sn}} = 0.6382 \text{ mol Sn}$$

$Sn_{0.6382}F_{1.276}$; divide each subscript by the smaller, 0.6382.

$Sn_{0.6382 / 0.6382}F_{1.276 / 0.6382}$ The empirical formula is SnF_2.

3.95 (a) Assume a 100.0 g sample of ibuprofen. From the percent composition data, a 100.0 g sample contains 75.69 g C, 15.51 g O, and 8.80 g H.

$$75.69 \text{ g C} \text{ x } \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 6.302 \text{ mol C}$$

$$15.51 \text{ g O} \text{ x } \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.9694 \text{ mol O}$$

$$8.80 \text{ g H} \text{ x } \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 8.71 \text{ mol H}$$

$C_{6.302}H_{8.71}O_{0.9694}$, divide each subscript by the smallest, 0.9694.

$C_{6.302 / 0.9694}H_{8.71 / 0.9694}O_{0.9694 / 0.9694}$

$C_{6.5}H_9O$; multiply each subscript by 2 to obtain integers.

The empirical formula is $C_{13}H_{18}O_2$.

(b) Assume a 100.0 g sample of tetraethyllead. From the percent composition data, a 100.0 g sample contains 29.71 g C, 6.23 g H, and 64.06 g Pb.

$$29.71 \text{ g C} \text{ x } \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.474 \text{ mol C}$$

$$6.23 \text{ g H} \text{ x } \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 6.17 \text{ mol H}$$

$$64.06 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 0.3092 \text{ mol Pb}$$

$Pb_{0.3092}C_{2.474}H_{6.17}$; divide each subscript by the smallest, 0.3092.

$Pb_{0.3092 / 0.3092}C_{2.474 / 0.3092}H_{6.17 / 0.3092}$ The empirical formula is PbC_8H_{20}.

(c) Assume a 100.0 g sample of zircon. From the percent composition data, a 100.0 g sample contains 34.91 g O, 15.32 g Si, and 49.76 g Zr.

$$34.91 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.182 \text{ mol O}$$

$$15.32 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 0.5454 \text{ mol Si}$$

$$49.76 \text{ g Zr} \times \frac{1 \text{ mol Zr}}{91.22 \text{ g Zr}} = 0.5455 \text{ mol Zr}$$

$Zr_{0.5455}Si_{0.5454}O_{2.182}$; divide each subscript by the smallest, 0.5454.

$Zr_{0.5455 / 0.5454}Si_{0.5454 / 0.5454}O_{2.182 / 0.5454}$ The empirical formula is $ZrSiO_4$.

3.96 Mass of toluene sample = 45.62 mg = 0.045 62 g; mass of CO_2 = 152.5 mg = 0.1525 g; mass of H_2O = 35.67 mg = 0.035 67 g

$$0.1525 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.003\,465 \text{ mol C}$$

$$\text{mass C} = 0.003\,465 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.041\,62 \text{ g C}$$

$$0.035\,67 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.003\,959 \text{ mol H}$$

$$\text{mass H} = 0.003\,959 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.003\,991 \text{ g H}$$

The (mass C + mass H) = 0.041 62 g + 0.003 991 g = 0.045 61 g. The calculated mass of (C + H) essentially equals the mass of the toluene sample, this means that toluene contains only C and H and no other elements.

$C_{0.003\,465}H_{0.003\,959}$; divide each subscript by the smaller, 0.003 465.

$C_{0.003\,465 / 0.003\,465}H_{0.003\,959 / 0.003\,465}$

$CH_{1.14}$; multiply each subscript by 7 to obtain integers.

The empirical formula is C_7H_8.

3.97 5.024 mg = 0.005 024 g; 13.90 mg = 0.013 90 g; 6.048 mg = 0.006 048 g

$$0.013\,90 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 3.158 \times 10^{-4} \text{ mol C}$$

$$0.006\,048 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 6.713 \times 10^{-4} \text{ mol H}$$

3.158×10^{-4} mol C x $\frac{12.01\ g\ C}{1\ mol\ C}$ = 0.003 793 g C

6.713×10^{-4} mol H x $\frac{1.008\ g\ H}{1\ mol\ H}$ = 0.000 676 7 g H

mass N = 0.005 024 g - (0.003 793 g + 0.000 676 7 g) = 0.000 554 g N

0.000 554 g N x $\frac{1\ mol\ N}{14.01\ g\ N}$ = 3.95×10^{-5} mol N

Scale each mol quantity to eliminate exponents.

$C_{3.158}H_{6.713}N_{0.395}$; divide each subscript by the smallest, 0.395.

$C_{3.158\ /\ 0.395}H_{6.713\ /\ 0.395}N_{0.395\ /\ 0.395}$ The empirical formula is $C_8H_{17}N$.

3.98 Let X equal the molecular mass of cytochrome c.

$$0.0043 = \frac{55.847\ amu}{X}; \quad X = \frac{55.847\ amu}{0.0043} = 13{,}000\ amu$$

3.99 Let X equal the molecular mass of nitrogenase.

$$0.000\,872 = \frac{2\ x\ 95.94\ amu}{X}; \qquad X = \frac{2\ x\ 95.94\ amu}{0.000\,872} = 220{,}000\ amu$$

3.100 Let X equal the molecular mass of disilane.

$$0.9028 = \frac{2\ x\ 28.09\ amu}{X}; \quad X = \frac{2\ x\ 28.09\ amu}{0.9028} = 62.23\ amu$$

62.23 amu - 2(Si atomic mass) = 62.23 amu - 2(28.09 amu) = 6.05 amu

6.05 amu is the total mass of H atoms.

$$6.05\ amu\ x \frac{1\ H\ atom}{1.01\ amu} = 6\ H\ atoms$$; Disilane is Si_2H_6.

3.101 Let X equal the molecular mass of MS_2.

$$0.4006 = \frac{2\ x\ 32.07\ amu}{X}; \quad X = \frac{2\ x\ 32.07\ amu}{0.4006} = 160.1\ amu$$

Atomic mass of M = 160.1 amu - 2(S atomic mass)

= 160.1 amu - 2(32.07 amu) = 95.96 amu

M is Mo.

General Problems

3.102 (a) $C_6H_{12}O_6$, 180.2 amu

$$\%\ C = \frac{6\ x\ 12.01\ g\ C}{180.2\ g} x\ 100\ \% = 39.99\%$$

$$\% \text{ H} = \frac{12 \text{ x } 1.008 \text{ g H}}{180.2 \text{ g}} \text{ x } 100\,\% = 6.713\%$$

$$\% \text{ O} = \frac{6 \text{ x } 16.00 \text{ g O}}{180.2 \text{ g}} \text{ x } 100\,\% = 53.27\,\%$$

(b) H_2SO_4, 98.08 amu

$$\% \text{ H} = \frac{2 \text{ x } 1.008 \text{ g H}}{98.08 \text{ g}} \text{ x } 100\,\% = 2.055\,\%$$

$$\% \text{ S} = \frac{32.07 \text{ g S}}{98.08 \text{ g}} \text{ x } 100\,\% = 32.70\,\%$$

$$\% \text{ O} = \frac{4 \text{ x } 16.00 \text{ g O}}{98.08 \text{ g}} \text{ x } 100\,\% = 65.25\,\%$$

(c) $KMnO_4$, 158.0 amu

$$\% \text{ K} = \frac{39.10 \text{ g K}}{158.0 \text{ g}} \text{ x } 100\,\% = 24.75\,\%$$

$$\% \text{ Mn} = \frac{54.94 \text{ g Mn}}{158.0 \text{ g}} \text{ x } 100\,\% = 34.77\,\%$$

$$\% \text{ O} = \frac{4 \text{ x } 16.00 \text{ g O}}{158.0 \text{ g}} \text{ x } 100\,\% = 40.51\%$$

(d) $C_7H_5NO_3S$, 183.2 amu

$$\% \text{ C} = \frac{7 \text{ x } 12.01 \text{ g C}}{183.2 \text{ g}} \text{ x } 100\,\% = 45.89\,\%$$

$$\% \text{ H} = \frac{5 \text{ x } 1.008 \text{ g H}}{183.2 \text{ g}} \text{ x } 100\,\% = 2.751\%$$

$$\% \text{ N} = \frac{14.01 \text{ g N}}{183.2 \text{ g}} \text{ x } 100\,\% = 7.647\,\%$$

$$\% \text{ O} = \frac{3 \text{ x } 16.00 \text{ g O}}{183.2 \text{ g}} \text{ x } 100\,\% = 26.20\,\%$$

$$\% \text{ S} = \frac{32.07 \text{ g S}}{183.2 \text{ g}} \text{ x } 100\,\% = 17.51\%$$

3.103 (a) Assume a 100.0 g sample of aspirin. From the percent composition data, a 100.0 g sample contains 60.00 g C, 35.52 g O, and 4.48 g H.

$$60.00 \text{ g C} \text{ x } \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 4.996 \text{ mol C}$$

$$35.52 \text{ g O} \text{ x } \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.220 \text{ mol O}$$

$$4.48 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 4.44 \text{ mol H}$$

$C_{4.996}H_{4.44}O_{2.220}$; divide each subscript by the smallest, 2.220.
$C_{4.996 / 2.220}H_{4.44 / 2.220}O_{2.220 / 2.220}$
$C_{2.25}H_2O_1$; multiply each subscript by 4 to obtain integers.
The empirical formula is $C_9H_8O_4$.

(b) Assume a 100.0 g sample of ilmenite. From the percent composition data, a 100.0 g sample contains 31.63 g O, 31.56 g Ti, and 36.81 g Fe.

$$31.63 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.977 \text{ mol O}$$

$$31.56 \text{ g Ti} \times \frac{1 \text{ mol Ti}}{47.88 \text{ g Ti}} = 0.6591 \text{ mol Ti}$$

$$36.81 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 0.6591 \text{ mol Fe}$$

$Fe_{0.6591}Ti_{0.6591}O_{1.977}$; divide each subscript by the smallest, 0.6591.
$Fe_{0.6591 / 0.6591}Ti_{0.6591 / 0.6591}O_{1.977 / 0.6591}$ The empirical formula is $FeTiO_3$.

(c) Assume a 100.0 g sample of sodium thiosulfate. From the percent composition data, a 100.0 g sample contains 30.36 g O, 29.08 g Na, and 40.56 g S.

$$30.36 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.897 \text{ mol O}$$

$$29.08 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 1.265 \text{ mol Na}$$

$$40.56 \text{ g S} \times \frac{1 \text{ mol S}}{32.07 \text{ g S}} = 1.265 \text{ mol S}$$

$Na_{1.265}S_{1.265}O_{1.897}$; divide each subscript by the smallest, 1.265.
$Na_{1.265 / 1.265}S_{1.265 / 1.265}O_{1.897 / 1.265}$
$NaSO_{1.5}$; multiply each subscript by 2 to obtain integers.
The empirical formula is $Na_2S_2O_3$.

3.104 (a) $SiCl_4 + 2\ H_2O \rightarrow SiO_2 + 4\ HCl$
(b) $P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$
(c) $CaCN_2 + 3\ H_2O \rightarrow CaCO_3 + 2\ NH_3$
(d) $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

3.105 NaH, 24.00 amu; B_2H_6, 27.67 amu; $NaBH_4$, 37.83 amu
$2\ NaH + B_2H_6 \rightarrow 2\ NaBH_4$

$$8.55 \text{ g NaH} \times \frac{1 \text{ mol NaH}}{24.00 \text{ g NaH}} = 0.356 \text{ mol NaH}$$

$6.75\ g\ B_2H_6 \times \frac{1\ mol\ B_2H_6}{27.67\ g\ B_2H_6} = 0.244\ mol\ B_2H_6$

For 0.244 mol B_2H_6, 2 x (0.244) = 0.488 mol NaH are needed. Because only 0.356 mol of NaH is available, NaH is the limiting reactant.

$0.356\ mol\ NaH \times \frac{2\ mol\ NaBH_4}{2\ mol\ NaH} \times \frac{37.83\ g\ NaBH_4}{1\ mol\ NaBH_4} = 13.5\ g\ NaBH_4$ produced

$0.356\ mol\ NaH \times \frac{1\ mol\ B_2H_6}{2\ mol\ NaH} \times \frac{27.67\ g\ B_2H_6}{1\ mol\ B_2H_6} = 4.93\ g\ B_2H_6$ reacted

B_2H_6 left over = 6.75 g - 4.93 g = 1.82 g B_2H_6

3.106 Assume a 100.0 g sample of ferrocene. From the percent composition data, a 100.0 g sample contains 5.42 g H, 64.56 g C, and 30.02 g Fe.

$5.42\ g\ H \times \frac{1\ mol\ H}{1.01\ g\ H} = 5.37\ mol\ H$

$64.56\ g\ C \times \frac{1\ mol\ C}{12.01\ g\ C} = 5.376\ mol\ C$

$30.02\ g\ Fe \times \frac{1\ mol\ Fe}{55.85\ g\ Fe} = 0.5375\ mol\ Fe$

$C_{5.376}H_{5.37}Fe_{0.5375}$; divide each subscript by the smallest, 0.5375.

$C_{5.376\ /\ 0.5375}H_{5.37\ /\ 0.5375}Fe_{0.5375\ /\ 0.5375}$ The empirical formula is $C_{10}H_{10}Fe$.

3.107 Mass of 1 HCl molecule = $(36.5\ \frac{amu}{molecule})(1.6605 \times 10^{-24}\ \frac{g}{amu}) = 6.06 \times 10^{-23}$ g/molecule

Avogadro's number = $\left(\frac{36.5\ g/mol}{6.06\ \times\ 10^{-23}\ g/molecule}\right) = 6.02 \times 10^{23}$ molecules/mol

3.108 Na_2SO_4, 142.04 amu; Na_3PO_4, 163.94 amu; Li_2SO_4, 109.95 amu; 100.00 mL = 0.10000 L

$0.550\ g\ Na_2SO_4 \times \frac{1\ mol\ Na_2SO_4}{142.04\ g\ Na_2SO_4} = 0.003\ 872\ mol\ Na_2SO_4$

$1.188\ g\ Na_3PO_4 \times \frac{1\ mol\ Na_3PO_4}{163.94\ g\ Na_3PO_4} = 0.007\ 247\ mol\ Na_3PO_4$

$0.223\ g\ Li_2SO_4 \times \frac{1\ mol\ Li_2SO_4}{109.95\ g\ Li_2SO_4} = 0.002\ 028\ mol\ Li_2SO_4$

Na^+ molarity = $\frac{(2 \times 0.003\ 872\ mol) + (3 \times 0.007\ 247\ mol)}{0.100\ 00\ L} = 0.295\ M$

Li^+ molarity = $\frac{2 \times 0.002\ 028\ mol}{0.100\ 00\ L} = 0.0406\ M$

SO_4^{2-} molarity = $\frac{(1 \times 0.003\ 872\ mol) + (1 \times 0.002\ 028\ mol)}{0.100\ 00\ L} = 0.0590\ M$

PO_4^{3-} molarity = $\dfrac{1 \times 0.007\ 247\ \text{mol}}{0.100\ 00\ \text{L}} = 0.0725\ \text{M}$

3.109 23.46 mg = 0.023 46 g; 20.42 mg = 0.02042 g; 33.27 mg = 0.033 27 g

$0.033\,27\ \text{g}\ CO_2 \times \dfrac{1\ \text{mol}\ CO_2}{44.01\ \text{g}\ CO_2} \times \dfrac{1\ \text{mol C}}{1\ \text{mol}\ CO_2} = 7.560 \times 10^{-4}\ \text{mol C}$

$0.020\,42\ \text{g}\ H_2O \times \dfrac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} \times \dfrac{2\ \text{mol H}}{1\ \text{mol}\ H_2O} = 2.266 \times 10^{-3}\ \text{mol H}$

$7.560 \times 10^{-4}\ \text{mol C} \times \dfrac{12.01\ \text{g C}}{1\ \text{mol C}} = 0.009\,080\ \text{g C}$

$2.266 \times 10^{-3}\ \text{mol H} \times \dfrac{1.008\ \text{g H}}{1\ \text{mol H}} = 0.002\,284\ \text{g H}$

mass O = 0.023 46 g - (0.009 080 g + 0.002 284 g) = 0.012 10 g O

$0.012\,10\ \text{g O} \times \dfrac{1\ \text{mol O}}{16.00\ \text{g O}} = 7.563 \times 10^{-4}\ \text{mol O}$

Scale each mol quantity to eliminate exponents.

$C_{0.7560}H_{2.266}O_{0.7563}$; divide each subscript by the smallest, 0.7560.

$C_{0.7560\ /\ 0.7560}H_{2.266\ /\ 0.7560}O_{0.7563\ /\ 0.7560}$ The empirical formula is CH_3O, 31.0 amu.

62.0 amu / 31.0 amu = 2; molecular formula = $C_{(2 \times 1)}H_{(2 \times 3)}O_{(2 \times 1)} = C_2H_6O_2$

3.110 High resolution mass spectrometry is capable of measuring the mass of molecules with a particular isotopic composition.

3.111 (a) $CO(NH_2)_2(aq) + 6\ HOCl(aq) \rightarrow 2\ NCl_3(aq) + CO_2(aq) + 5\ H_2O(l)$

(b) $2\ Ca_3(PO_4)_2(s) + 6\ SiO_2(s) + 10\ C(s) \rightarrow P_4(g) + 6\ CaSiO_3(l) + 10\ CO(g)$

3.112 The combustion reaction is: $2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

C_8H_{18}, 114.23 amu; CO_2, 44.01 amu

pounds CO_2 = $1.00\ \text{gal} \times \dfrac{3.7854\ \text{L}}{1\ \text{gal}} \times \dfrac{1000\ \text{mL}}{1\ \text{L}} \times \dfrac{0.703\ \text{g}\ C_8H_{18}}{1\ \text{mL}} \times \dfrac{1\ \text{mol}\ C_8H_{18}}{114.23\ \text{g}\ C_8H_{18}} \times$

$\dfrac{16\ \text{mol}\ CO_2}{2\ \text{mol}\ C_8H_{18}} \times \dfrac{44.01\ \text{g}\ CO_2}{1\ \text{mol}\ CO_2} \times \dfrac{1\ \text{lb}}{453.59\ \text{g}} = 18.1\ \text{pounds}\ CO_2$

3.113 The reaction is: $CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O$

$CaCO_3$, 100.09 amu; CO_2, 44.01 amu

mol $CaCO_3$ = $6.35\ \text{g}\ CaCO_3 \times \dfrac{1\ \text{mol}\ CaCO_3}{100.09\ \text{g}\ CaCO_3} = 0.0634\ \text{mol}\ CaCO_3$

mol HCl = $500.0\ \text{mL HCl} \times \dfrac{1\ \text{L}}{1000\ \text{mL}} \times \dfrac{0.31\ \text{mol HCl}}{1\ \text{L}} = 0.155\ \text{mol HCl}$

Determine the limiting reactant.

mol HCl needed = $0.0634\ \text{mol}\ CaCO_3 \times \dfrac{2\ \text{mol HCl}}{1\ \text{mol}\ CaCO_3} = 0.127\ \text{mol HCl needed}$

Because we have excess HCl, $CaCO_3$ is the limiting reactant.

$$\text{mass } CO_2 = 0.0634 \text{ mol } CaCO_3 \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 2.79 \text{ g } CO_2$$

3.114 AgCl, 143.32 amu; CO_2, 44.01 amu; H_2O, 18.02 amu

$$\text{mol Cl in 1.00 g of X} = 1.95 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol Cl}}{1 \text{ mol AgCl}} = 0.0136 \text{ mol Cl}$$

$$\text{mass Cl} = 0.0136 \text{ mol Cl} \times \frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}} = 0.482 \text{ g Cl}$$

$$\text{mol C in 1.00 g of X} = 0.900 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.0204 \text{ mol C}$$

$$\text{mass C} = 0.0204 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.245 \text{ g C}$$

$$\text{mol H in 1.00 g of X} = 0.735 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.0816 \text{ mol H}$$

$$\text{mass H} = 0.0816 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.0823 \text{ g H}$$

mass N = 1.00 g - mass Cl - mass C - mass H = 1.00 - 0.482 g - 0.245 g - 0.0823 g = 0.19 g N

$$\text{mol N in 1.00 g of X} = 0.19 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 0.014 \text{ mol N}$$

Determine empirical formula.

$C_{0.0204}H_{0.0816}N_{0.014}Cl_{0.0136}$, divide each subscript by the smallest, 0.0136.

$C_{0.0204 / 0.0136}H_{0.0816 / 0.0136}N_{0.014 / 0.0136}Cl_{0.0136 / 0.0136}$

$C_{1.5}H_6NCl$, multiply each subscript by 2 to get integers.

The empirical formula is $C_3H_{12}N_2Cl_2$.

3.115 $CaCO_3$, 100.09 amu

$$\%\text{ Ca} = \frac{40.08 \text{ g Ca}}{100.09 \text{ g}} \times 100\% = 40.04\%$$

$$\%\text{ C} = \frac{12.01 \text{ g C}}{100.09 \text{ g}} \times 100\% = 12.00\%$$

$$\%\text{ O} = \frac{3 \times 16.00 \text{ g O}}{100.09 \text{ g}} \times 100\% = 47.96\%$$

Because the mass %'s for the pulverized rock are different from the mass %'s for pure $CaCO_3$ calculated here, the pulverized rock cannot be pure $CaCO_3$.

3.116 Let SA stand for salicylic acid.

$$\text{mol C in 1.00 g of SA} = 2.23 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.0507 \text{ mol C}$$

mass C = 0.0507 mol C x $\frac{12.011\ g\ C}{1\ mol\ C}$ = 0.609 g C

mol H in 1.00 g of SA = 0.39 g H_2O x $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$ x $\frac{2\ mol\ H}{1\ mol\ H_2O}$ = 0.043 mol H

mass H = 0.043 mol H x $\frac{1.008\ g\ H}{1\ mol\ H}$ = 0.043 g H

mass O = 1.00 g - mass C - mass H = 1.00 - 0.609 g - 0.043 g = 0.35 g O

mol O in 1.00 g of = 0.35 g N x $\frac{1\ mol\ O}{16.00\ g\ O}$ = 0.022 mol O

Determine empirical formula.

$C_{0.0507}H_{0.043}O_{0.022}$, divide each subscript by the smallest, 0.022.

$C_{0.0507\ /\ 0.022}H_{0.043\ /\ 0.022}O_{0.022\ /\ 0.022}$

$C_{2.3}H_2O$, multiply each subscript by 3 to get integers.

The empirical formula is $C_7H_6O_3$. The empirical formula mass = 138.12 g/mol

Because salicylic acid has only one acidic hydrogen, there is a 1 to 1 mol ratio between salicylic acid and NaOH in the acid-base titration.

mol SA in 1.00 g SA = 72.4 mL x $\frac{1\ L}{1000\ mL}$ x $\frac{0.100\ mol\ NaOH}{1\ L}$ x $\frac{1\ mol\ SA}{1\ mol\ NaOH}$ = 0.00724 mol SA

SA molar mass = $\frac{1.00\ g}{0.00724\ mol}$ = 138 g/mol

Because the empirical formula mass and the molar mass are the same, the empirical formula is the molecular formula for salicylic acid.

3.117 (a) mol C = 4.83 g CO_2 x $\frac{1\ mol\ CO_2}{44.01\ g\ CO_2}$ x $\frac{1\ mol\ C}{1\ mol\ CO_2}$ = 0.110 mol C

mass C = 0.110 mol C x $\frac{12.011\ g\ C}{1\ mol\ C}$ = 1.32 g C

mol H = 1.48 g H_2O x $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$ x $\frac{2\ mol\ H}{1\ mol\ H_2O}$ = 0.164 mol H

mass H = 0.164 mol H x $\frac{1.008\ g\ H}{1\ mol\ H}$ = 0.165 g H

109.8 mL = 0.1098 L

mol NaOH = (0.1098 L)(1.00 mol/L) = 0.110 mol NaOH

$H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$

mol H_2SO_4 = 0.110 mol NaOH x $\frac{1\ mol\ H_2SO_4}{2\ mol\ NaOH}$ = 0.0550 mol H_2SO_4

mol S = 0.0550 mol H_2SO_4 x $\frac{1\ mol\ S}{1\ mol\ H_2SO_4}$ = 0.0550 mol S

mass S = 0.0550 mol S x $\frac{32.06\ g\ S}{1\ mol\ S}$ = 1.76 g S

mass O = 5.00 g - mass C - mass H - mass S = 5.00 g -1.32 g - 0.165 g - 1.76 g = 1.75 g O

mol O = 1.75 g O x $\frac{1\ mol\ O}{16.00\ g\ O}$ = 0.109 mol O

$C_{0.110}H_{0.164}O_{0.109}S_{0.0550}$ Divide all subscripts by the smallest.

$C_{0.110\ /\ 0.0550}H_{0.164\ /\ 0.0550}O_{0.109\ /\ 0.0550}S_{0.0550\ /\ 0.0550}$

The empirical formula is $C_2H_3O_2S$. The empirical formula mass = 91.1 g/mol

(b) 54.9 mL = 0.0549 L

mol NaOH = (0.0549 L)(1.00 mol/L) = 0.0549 mol NaOH

Because X has two acidic hydrogens, two mol of NaOH are required to titrate 1 mol of X.

mol X = 0.0549 mol NaOH x $\frac{1\ mol\ X}{2\ mol\ NaOH}$ = 0.0274 mol X

X molar mass = $\frac{5.00\ g}{0.0274\ mol}$ = 182 g/mol

Because the molar mass is twice the empirical formula mass, the molecular formula is twice the empirical formula.

The molecular formula is $C_{(2\ x\ 2)}H_{(2\ x\ 3)}O_{(2\ x\ 2)}S_{(2\ x\ 1)} = C_4H_6O_4S_2$

3.118 Let X equal the mass of benzoic acid and Y the mass of gallic acid in the 1.00 g mixture. Therefore, X + Y = 1.00 g.

Because both acids contain only one acidic hydrogen, there is a 1 to 1 mol ratio between each acid and NaOH in the acid-base titration.

In the titration, mol benzoic acid + mol gallic acid = mol NaOH

Therefore, X x $\frac{1\ mol\ BA}{122\ g\ BA}$ + Y x $\frac{1\ mol\ GA}{170\ g\ GA}$ = mol NaOH

mol NaOH = 14.7 mL x $\frac{1\ L}{1000\ mL}$ x $\frac{0.500\ mol\ NaOH}{1\ L}$ = 0.00735 mol NaOH

We have two unknowns, X and Y, and two equations.

X + Y = 1.00 g

X x $\frac{1\ mol\ BA}{122\ g\ BA}$ + Y x $\frac{1\ mol\ GA}{170\ g\ GA}$ = 0.00735 mol NaOH

Rearrange to get X = 1.00 g - Y and then substitute it into the equation above to solve for Y.

(1.00 g _ Y) x $\frac{1\ mol\ BA}{122\ g\ BA}$ + Y x $\frac{1\ mol\ GA}{170\ g\ GA}$ = 0.00735 mol NaOH

$\frac{1\ mol}{122} - \frac{Y\ mol}{122\ g} + \frac{Y\ mol}{170\ g} = 0.00735\ mol$

$-\frac{Y\ mol}{122\ g} + \frac{Y\ mol}{170\ g} = 0.00735\ mol - \frac{1\ mol}{122} = -\ 8.47\ x\ 10^{-4}\ mol$

$\frac{(-\ Y\ mol)(170\ g) + (Y\ mol)(122\ g)}{(170\ g)(122\ g)} = -\ 8.47\ x\ 10^{-4}\ mol$

$$\frac{-48\ Y\ mol}{20740\ g} = -\ 8.47\ x\ 10^{-4}\ mol; \quad \frac{48\ Y}{20740\ g} = 8.47\ x\ 10^{-4}$$

$$Y = \frac{(20740\ g)(8.47\ x\ 10^{-4})}{48} = 0.366\ g$$

X = 1.00 g - 0.366 g = 0.634 g

In the 1.00 g mixture there is 0.63 g of benzoic acid and 0.37 g of gallic acid.

3.119 C_2H_6O, 46.07 amu; H_2O, 18.02 amu

Let X = mass of H_2O in the 10.00 g sample.

Let Y = mass of ethanol (C_2H_6O) in the 10.00 g sample.

X + Y = 10.00 g and Y = 10.00 g - X

mass of collected H_2O = 11.27 g

$$\text{mass of collected } H_2O = X + \left(Y\ x\ \frac{1\ mol\ C_2H_6O}{46.07\ g\ C_2H_6O}\ x\ \frac{3\ mol\ H_2O}{1\ mol\ C_2H_6O}\ x\ \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} \right)$$

Substitute for Y.

$$11.27\ g = X + \left((10.00\ g - X)\ x\ \frac{1\ mol\ C_2H_6O}{46.07\ g\ C_2H_6O}\ x\ \frac{3\ mol\ H_2O}{1\ mol\ C_2H_6O}\ x\ \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} \right)$$

11.27 g = X + (10.00 g - X)(1.173)

11.27 g = X + 11.73 g - 1.173 X

0.173 X = 11.73 g - 11.27 g = 0.46 g

$$X = \frac{0.46\ g}{0.173} = 2.7\ g\ H_2O$$

Y = 10.00 g - X = 10.00 g - 2.7 g = 7.3 g C_2H_6O

3.120 FeO, 71.85 amu; Fe_2O_3, 159.7 amu

Let X equal the mass of FeO and Y the mass of Fe_2O_3 in the 10.0 g mixture. Therefore, X + Y = 10.0 g.

$$\text{mol Fe} = 7.43\ g\ x\ \frac{1\ mol\ Fe}{55.85\ g\ Fe} = 0.133\ mol\ Fe$$

$$\text{mol FeO} + 2\ x\ \text{mol } Fe_2O_3 = 0.133\ mol\ Fe$$

$$X\ x\ \frac{1\ mol\ FeO}{71.85\ g\ FeO} + 2\ x \left(Y\ x\ \frac{1\ mol\ Fe_2O_3}{159.7\ g\ Fe_2O_3} \right) = 0.133\ mol\ Fe$$

Rearrange to get X = 10.0 g - Y and then substitute it into the equation above to solve for Y.

$$(10.0\ g - Y)\ x\ \frac{1\ mol\ FeO}{71.85\ g\ FeO} + 2\ x \left(Y\ x\ \frac{1\ mol\ Fe_2O_3}{159.7\ g\ Fe_2O_3} \right) = 0.133\ mol\ Fe$$

$$\frac{10.0\ mol}{71.85} - \frac{Y\ mol}{71.85\ g} + \frac{2\ Y\ mol}{159.7\ g} = 0.133\ mol$$

$$-\frac{Y\ mol}{71.85\ g} + \frac{2\ Y\ mol}{159.7\ g} = 0.133\ mol - \frac{10.0\ mol}{71.85} = -0.0062\ mol$$

$$\frac{(-Y\ mol)(159.7\ g) + (2\ Y\ mol)(71.85\ g)}{(71.85\ g)(159.7\ g)} = -0.0062\ mol$$

$$\frac{\_16.0\ \text{Y mol}}{11474\ \text{g}} = \_\ 0.0062\ \text{mol};\quad \frac{16.0\ \text{Y}}{11474\ \text{g}} = 0.0062$$

Y = (0.0062)(11474 g)/16.0 = 4.44 g = 4.4 g Fe_2O_3

X = 10.0 g - Y = 10.0 g - 4.4 g = 5.6 g FeO

3.121 AgCl, 143.32 amu;
Find the mass of Cl in 1.68 g of AgCl.

$$\text{mol Cl in 1.68 g of AgCl} = 1.68\ \text{g AgCl} \times \frac{1\ \text{mol AgCl}}{143.32\ \text{g AgCl}} \times \frac{1\ \text{mol Cl}}{1\ \text{mol AgCl}} = 0.0117\ \text{mol Cl}$$

$$\text{mass Cl} = 0.0117\ \text{mol Cl} \times \frac{35.453\ \text{g Cl}}{1\ \text{mol Cl}} = 0.415\ \text{g Cl}$$

All of the Cl in AgCl came from XCl_3.
Find the mass of X in 0.634 g of XCl_3. Mass of X = 0.634 g - 0.415 g = 0.219 g X

$$0.0117\ \text{mol Cl} \times \frac{1\,\text{mol X}}{3\,\text{mol Cl}} = 0.00390\ \text{mol X}$$

$$\text{molar mass of X} = \frac{0.219\,\text{g}}{0.00390\,\text{mol}} = 56.2\ \text{g/mol};\qquad \text{X = Fe}$$

3.122 $C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$; $C_6H_{12}O_6$, 180.16 amu; CO_2, 44.01 amu

$$66.3\ \text{g}\ C_6H_{12}O_6 \times \frac{1\,\text{mol}\ C_6H_{12}O_6}{180.16\,\text{g}\ C_6H_{12}O_6} \times \frac{6\,\text{mol}\ CO_2}{1\,\text{mol}\ C_6H_{12}O_6} \times \frac{44.01\,\text{g}\ CO_2}{1\,\text{mol}\ CO_2} = 97.2\ \text{g}\ CO_2$$

$$66.3\ \text{g}\ C_6H_{12}O_6 \times \frac{1\,\text{mol}\ C_6H_{12}O_6}{180.16\,\text{g}\ C_6H_{12}O_6} \times \frac{6\,\text{mol}\ CO_2}{1\,\text{mol}\ C_6H_{12}O_6} \times \frac{25.4\,\text{L}\ CO_2}{1\,\text{mol}\ CO_2} = 56.1\ \text{L}\ CO_2$$

3.123 $H_2C_2O_4$, 90.04 amu; 22.35 mL = 0.02235 L

$$0.5170\ \text{g}\ H_2C_2O_2 \times \frac{1\,\text{mol}\ H_2C_2O_4}{90.04\,\text{g}\ H_2C_2O_4} \times \frac{2\,\text{mol}\ KMnO_4}{5\,\text{mol}\ H_2C_2O_4} = 0.002\ 297\ \text{mol}\ KMnO_4$$

$$KMnO_4\ \text{molarity} = \frac{0.002\ 297\,\text{mol}\ KMnO_4}{0.022\ 35\,\text{L}} = 0.1028\ \text{M}$$

3.124 Mass of Cu = 2.196 g; mass of S = 2.748 g - 2.196 g = 0.552 g S

(a) $\%Cu = \frac{2.196\,\text{g}}{2.748\,\text{g}} \times 100\% = 79.91\%$

$\%S = \frac{0.552\,\text{g}}{2.748\,\text{g}} \times 100\% = 20.1\%$

(b) $2.196\ \text{g Cu} \times \frac{1\,\text{mol Cu}}{63.55\,\text{g Cu}} = 0.034\ 55\ \text{mol Cu}$

$0.552\ \text{g S} \times \frac{1\,\text{mol S}}{32.07\,\text{g S}} = 0.0172\ \text{mol S}$

$Cu_{0.03455}S_{0.0172}$; divide each subscript by the smaller, 0.0172.
$Cu_{0.03455\,/\,0.0172}S_{0.0172\,/\,0.0172}$ The empirical formula is Cu_2S.

(c) Cu_2S, 159.16 amu

$$\frac{5.6\text{ g } Cu_2S}{1\text{ cm}^3} \times \frac{1\text{ mol } Cu_2S}{159.16\text{ g } Cu_2S} \times \frac{2\text{ mol } Cu^+\text{ ions}}{1\text{ mol } Cu_2S} \times \frac{6.022\ \times\ 10^{23}\ Cu^+\text{ ions}}{1\text{ mol } Cu^+\text{ ions}}$$

$= 4.2 \times 10^{22}$ Cu^+ ions/cm^3

3.125 Mass of added Cl = mass of XCl_5 - mass of XCl_3 = 13.233 g - 8.729 g = 4.504 g

mass of Cl in XCl_5 = 5 Cl's $\times \frac{4.504\text{ g}}{2\text{ C'ls}}$ = 11.26 g Cl

mass of X in XCl_5 = 13.233 g - 11.26 g = 1.973 g X

11.26 g Cl $\times \frac{1\text{ mol Cl}}{35.45\text{ g Cl}}$ = 0.3176 mol Cl

0.3176 mol Cl $\times \frac{1\text{ mol X}}{5\text{ mol Cl}}$ = 0.063 52 mol X

molar mass of X = $\frac{1.973\text{ g X}}{0.063\ 52\text{ mol X}}$ = 31.1 g/mol; atomic mass =31.1 amu, X = P

3.126 PCl_3, 137.33 amu; PCl_5, 208.24 amu

Let Y = mass of PCl_3 in the mixture, and (10.00 - Y) = mass of PCl_5 in the mixture.

fraction Cl in PCl_3 = $\frac{(3)(35.453\text{ g/mol})}{137.33\text{ g/mol}}$ = 0.774 48

fraction Cl in PCl_5 = $\frac{(5)(35.453\text{ g/mol})}{208.24\text{ g/mol}}$ = 0.851 25

(mass of Cl in PCl_3) + (mass of Cl in PCl_5) = mass of Cl in the mixture

0.774 48Y + 0.851 25(10.00 g - Y) = (0.8104)(10.00 g)

Y = 5.32 g PCl_3 and 10.00 - Y = 4.68 g PCl_5

3.127 100.00 mL = 0.100 00 L; 71.02 mL = 0.071 02 L

mol H_2SO_4 = $\frac{0.1083\text{ mol } H_2SO_4}{\text{L}}$ x 0.100 00 L = 0.010 83 mol H_2SO_4

mol NaOH = $\frac{0.1241\text{ mol NaOH}}{\text{L}}$ x 0.071 02 L = 0.008 814 mol NaOH

$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$

mol H_2SO_4 reacted with NaOH = 0.008 814 mol NaOH x $\frac{1\text{ mol } H_2SO_4}{2\text{ mol NaOH}}$ = 0.004 407 mol H_2SO_4

mol H_2SO_4 reacted with MCO_3 = 0.010 83 mol - 0.004 407 mol = 0.006 423 mol H_2SO_4

mol H_2SO_4 reacted with MCO_3 = mol CO_3^{2-} in MCO_3 = mol CO_2 produced = 0.006 423 mol CO_2

(a) CO_3^{2-}, 60.01 amu; 0.006 423 mol CO_3^{2-} x $\frac{60.01\text{ g } CO_3^{2-}}{1\text{ mol } CO_3^{2-}}$ = 0.3854 g CO_3^{2-}

mass of M = 1.268 g - 0.3854 g = 0.8826 g M

molar mass of M = $\frac{0.8826\,\text{g}}{0.006\ \ 423\,\text{mol}}$ = 137.4 g/mol; M is Ba

(b) 0.006 423 mol CO_2 x $\frac{44.01\,\text{g}\ CO_2}{1\,\text{mol}\ CO_2}$ x $\frac{1\,\text{L}}{1.799\,\text{g}}$ = 0.1571 L CO_2

3.128 NH_4NO_3, 80.04 amu; $(NH_4)_2HPO_4$, 132.06 amu

Assume you have a 100.0 g sample of the mixture.

Let X = grams of NH_4NO_3 and (100.0 - X) = grams of $(NH_4)_2HPO_4$.

Both compounds contain 2 nitrogen atoms per formula unit.

Because the mass % N in the sample is 30.43%, the 100.0 g sample contains 30.43 g N.

$$\text{mol } NH_4NO_3 = (X)\ \text{x}\ \frac{1\ \text{mol}\ NH_4NO_3}{80.04\ \text{g}}$$

$$\text{mol } (NH_4)_2HPO_4 = (100.0\ \_\ X)\ \text{x}\ \frac{1\ \text{mol}\ (NH_4)_2HPO_4}{132.06\ \text{g}}$$

$$\text{mass N} = \left(\left((X)\ \text{x}\ \frac{1\ \text{mol}\ NH_4NO_3}{80.04\ \text{g}}\right) + \left((100.0\ \_\ X)\ \text{x}\ \frac{1\ \text{mol}\ (NH_4)_2HPO_4}{132.06\ \text{g}}\right)\right) \text{x}$$
$$\left(\frac{2\ \text{mol N}}{1\ \text{mol ammonium cmpds}}\right)\ \text{x}\ \left(\frac{14.0067\ \text{g N}}{1\ \text{mol N}}\right) = 30.43\ \text{g}$$

Solve for X.

$$\left(\frac{X}{80.04} + \frac{100.0\ \_\ X}{132.06}\right)(2)(14.0067) = 30.43$$

$$\left(\frac{X}{80.04} + \frac{100.0\ \_\ X}{132.06}\right) = 1.08627$$

$$\frac{(132.06)(X) + (100.0\ \_\ X)(80.04)}{(80.04)(132.06)} = 1.08627$$

(132.06)(X) + (100.0 - X)(80.04) = (1.08627)(80.04)(132.06)

132.06X + 8004 - 80.04X = 11481.96

132.06X - 80.04X = 11481.96 - 8004

52.02X = 3477.96

X = $\frac{3477.96}{52.02}$ = 66.86 g NH_4NO_3

(100.0 - X) = (100.0 - 66.86) = 33.14 g $(NH_4)_2HPO_4$

$$\frac{\text{mass}_{NH_4NO_3}}{\text{mass}_{(NH_4)_2HPO_4}} = \frac{66.86\ \text{g}}{33.14\ \text{g}} = 2.018$$

The mass ratio of NH_4NO_3 to $(NH_4)_2HPO_4$ in the mixture is 2 to 1.

3.129 $Na_2CO_3 \rightarrow Na_2O + CO_2$; Na_2CO_3, 106 amu; Na_2O, 62 amu

$CaCO_3 \rightarrow CaO + CO_2$; $CaCO_3$, 100 amu; CaO, 56 amu

In a 0.35 kg sample of glass there would be:

0.12 x 0.35 kg = 0.042 kg = 42 g of Na_2O

0.13 x 0.35 kg = 0.045 kg = 45 g of CaO

350 g - 42 g - 45 g = 263 g of SiO_2

mass Na_2CO_3 = 42 g Na_2O x $\frac{1\ mol\ Na_2O}{62\ g\ Na_2O}$ x $\frac{1\ mol\ Na_2CO_3}{1\ mol\ Na_2O}$ x $\frac{106\ g\ Na_2CO_3}{1\ mol\ Na_2CO_3}$ = 72 g Na_2CO_3

mass $CaCO_3$ = 45 g CaO x $\frac{1\ mol\ CaO}{56\ g\ CaO}$ x $\frac{1\ mol\ CaCO_3}{1\ mol\ CaO}$ x $\frac{100\ g\ CaCO_3}{1\ mol\ CaCO_3}$ = 80 g $CaCO_3$

To make 0.35 kg of glass, start with 72 g Na_2CO_3, 80 g $CaCO_3$, and 263 g SiO_2.

3.130 (a) 56.0 mL = 0.0560 L

mol X_2 = (0.0560 L X_2)$\left(\frac{1\ mol}{22.41\ L}\right)$ = 0.00250 mol X_2

mass X_2 = 1.12 g MX_2 - 0.720 g MX = 0.40 g X_2

molar mass X_2 = $\frac{0.40\ g}{0.00250\ mol}$ = 160 g/mol

atomic mass of X = 160/2 = 80 amu; X is Br.

(b) mol MX = 0.00250 mol X_2 x $\frac{2\ mol\ MX}{1\ mol\ X_2}$ = 0.00500 mol MX

mass of X in MX = 0.00500 mol MX x $\frac{1\ mol\ X}{1\ mol\ MX}$ x $\frac{80\ g\ X}{1\ mol\ X}$ = 0.40 g X

mass of M in MX = 0.720 g MX - 0.40 g X = 0.32 g M

molar mass M = $\frac{0.32\ g}{0.00500\ mol}$ = 64 g/mol

atomic mass of X = 64 amu; M is Cu.

4 Reactions in Aqueous Solution

4.1 (a) precipitation (b) redox (c) acid-base neutralization

4.2 $FeBr_3$ contains 3 Br^- ions. The molar concentration of Br^- ions = 3 x 0.225 M = 0.675 M

4.3 A_2Y is the strongest electrolyte because it is completely dissociated into ions.
A_2X is the weakest electrolyte because it is the least dissociated of the three substances.

4.4 (a) Ionic equation:
$2\ Ag^+(aq) + 2\ NO_3^-(aq) + 2\ Na^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) + 2\ Na^+(aq) + 2\ NO_3^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $2\ Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$
(b) Ionic equation:
$2\ H^+(aq) + SO_4^{2-}(aq) + MgCO_3(s) \rightarrow H_2O(l) + CO_2(g) + Mg^{2+}(aq) + SO_4^{2-}(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $2\ H^+(aq) + MgCO_3(s) \rightarrow H_2O(l) + CO_2(g) + Mg^{2+}(aq)$
(c) Ionic equation:
$Hg_2^{2+}(aq) + 2\ NO_3^-(aq) + 2\ NH_4^+(aq) + 2\ Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2\ NH_4^+(aq) + 2\ NO_3^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $Hg_2^{2+}(aq) + 2\ Cl^-(aq) \rightarrow Hg_2Cl_2(s)$

4.5 (a) $CdCO_3$, insoluble (b) MgO, insoluble (c) Na_2S, soluble
(d) $PbSO_4$, insoluble (e) $(NH_4)_3PO_4$, soluble (f) $HgCl_2$, soluble

4.6 (a) Ionic equation:
$Ni^{2+}(aq) + 2\ Cl^-(aq) + 2\ NH_4^+(aq) + S^{2-}(aq) \rightarrow NiS(s) + 2\ NH_4^+(aq) + 2\ Cl^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $Ni^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s)$
(b) Ionic equation:
$2\ Na^+(aq) + CrO_4^{2-}(aq) + Pb^{2+}(aq) + 2\ NO_3^-(aq) \rightarrow PbCrO_4(s) + 2\ Na^+(aq) + 2\ NO_3^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$
(c) Ionic equation:
$2\ Ag^+(aq) + 2\ ClO_4^-(aq) + Ca^{2+}(aq) + 2\ Br^-(aq) \rightarrow 2\ AgBr(s) + Ca^{2+}(aq) + 2\ ClO_4^-(aq)$
Delete spectator ions from the ionic equation, and reduce coefficients to get the net ionic equation.
Net ionic equation: $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
(d) Ionic equation:
$Zn^{2+}(aq) + 2\ Cl^-(aq) + 2\ K^+(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s) + 2\ K^+(aq) + 2\ Cl^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.

Net ionic equation: $Zn^{2+}(aq) + CO_3^{2-}(aq) \rightarrow ZnCO_3(s)$

4.7 $3\ CaCl_2(aq) + 2\ Na_3PO_4(aq) \rightarrow Ca_3(PO_4)_2(s) + 6\ NaCl(aq)$
Ionic equation:
$3\ Ca^{2+}(aq) + 6\ Cl^-(aq) + 6\ Na^+(aq) + 2\ PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s) + 6\ Na^+(aq) + 6\ Cl^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $3\ Ca^{2+}(aq) + 2\ PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$

4.8 A precipitate results from the reaction. The precipitate contains cations and anions in a 3:2 ratio. The precipitate is either $Mg_3(PO_4)_2$ or $Zn_3(PO_4)_2$.

4.9 (a) Ionic equation:
$2\ Cs^+(aq) + 2\ OH^-(aq) + 2\ H^+(aq) + SO_4^{2-}(aq) \rightarrow 2\ Cs^+(aq) + SO_4^{2-}(aq) + 2\ H_2O(l)$
Delete spectator ions from the ionic equation, and reduce coefficients to get the net ionic equation.
Net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

(b) Ionic equation:
$Ca^{2+}(aq) + 2\ OH^-(aq) + 2\ CH_3CO_2H(aq) \rightarrow Ca^{2+}(aq) + 2\ CH_3CO_2^-(aq) + 2\ H_2O(l)$
Delete spectator ions from the ionic equation, and reduce coefficients to get the net ionic equation.
Net ionic equation: $CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$

4.10 HY is the strongest acid because it is completely dissociated.
HX is the weakest acid because it is the least dissociated.

4.11

(a) $SnCl_4$:	Cl -1, Sn +4	(b) CrO_3:	O -2, Cr +6
(c) $VOCl_3$:	O -2, Cl -1, V +5	(d) V_2O_3:	O -2, V +3
(e) HNO_3:	O -2, H +1, N +5	(f) $FeSO_4$:	O -2, S +6, Fe +2

4.12 $2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightarrow 2\ CuI(s) + I_2(aq)$
oxidation numbers: Cu^{2+} +2; I^- -1; CuI: Cu +1, I -1; I_2: 0
oxidizing agent (oxidation number decreases), Cu^{2+}
reducing agent (oxidation number increases) , I^-

4.13 (a) $SnO_2(s) + 2\ C(s) \rightarrow Sn(s) + 2\ CO(g)$
C is oxidized (its oxidation number increases from 0 to +2). C is the reducing agent.
The Sn in SnO_2 is reduced (its oxidation number decreases from +4 to 0). SnO_2 is the oxidizing agent.
(b) $Sn^{2+}(aq) + 2\ Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2\ Fe^{2+}(aq)$
Sn^{2+} is oxidized (its oxidation number increases from +2 to +4). Sn^{2+} is the reducing agent.
Fe^{3+} is reduced (its oxidation number decreases from +3 to +2). Fe^{3+} is the oxidizing agent.
(c) $4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(l)$
The N in NH_3 is oxidized (its oxidation number increases from -3 to +2). NH_3 is the reducing agent.
Each O in O_2 is reduced (its oxidation number decreases from 0 to -2). O_2 is the oxidizing agent.

4.14 (a) Pt is below H in the activity series; therefore NO REACTION.
(b) Mg is below Ca in the activity series; therefore NO REACTION.

4.15 Because B will reduce A^+, B is above A in the activity series. Because B will not reduce C^+, C is above B in the activity series. Therefore C must be above A in the activity series and C will reduce A^+.

4.16

$$8\ H^+(aq) + Cr_2O_7^{2-}(aq) + I^-(aq) \rightarrow 2\ Cr^{3+}(aq) + IO_3^-(aq) + 4\ H_2O(l)$$

4.17

$$2\ MnO_4^-(aq) + Br^-(aq) \rightarrow 2\ MnO_2(s) + BrO_3^-(aq)$$
$$2\ H^+(aq) + 2\ MnO_4^-(aq) + Br^-(aq) \rightarrow 2\ MnO_2(s) + BrO_3^-(aq) + H_2O(l)$$
$$2\ H^+(aq) + 2\ OH^-(aq) + 2\ MnO_4^-(aq) + Br^-(aq) \rightarrow 2\ MnO_2(s) + BrO_3^-(aq) + H_2O(l) + 2\ OH^-(aq)$$
$$2\ H_2O(l) + 2\ MnO_4^-(aq) + Br^-(aq) \rightarrow 2\ MnO_2(s) + BrO_3^-(aq) + H_2O(l) + 2\ OH^-(aq)$$
$$H_2O(l) + 2\ MnO_4^-(aq) + Br^-(aq) \rightarrow 2\ MnO_2(s) + BrO_3^-(aq) + 2\ OH^-(aq)$$

4.18 (a) $MnO_4^-(aq) \rightarrow MnO_2(s)$ (reduction)
$IO_3^-(aq) \rightarrow IO_4^-(aq)$ (oxidation)

(b) $NO_3^-(aq) \rightarrow NO_2(g)$ (reduction)
$SO_2(aq) \rightarrow SO_4^{2-}(aq)$ (oxidation)

4.19 $NO_3^-(aq) + Cu(s) \rightarrow NO(g) + Cu^{2+}(aq)$
$[Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

$NO_3^-(aq) \rightarrow NO(g)$
$NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$[3\ e^- + 4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$2\ NO_3^-(aq) + 8\ H^+(aq) + 3\ Cu(s) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$

4.20 $Fe(OH)_2(s) + O_2(g) \rightarrow Fe(OH)_3(s)$
$[Fe(OH)_2(s) + OH^-(aq) \rightarrow Fe(OH)_3(s) + e^-] \times 4$ (oxidation half reaction)

$O_2(g) \rightarrow 2\ H_2O(l)$
$4\ H^+(aq) + O_2(g) \rightarrow 2\ H_2O(l)$
$4\ e^- + 4\ H^+(aq) + O_2(g) \rightarrow 2\ H_2O(l)$
$4\ e^- + 4\ H^+(aq) + 4\ OH^-(aq) + O_2(g) \rightarrow 2\ H_2O(l) + 4\ OH^-(aq)$
$4\ e^- + 4\ H_2O(l) + O_2(g) \rightarrow 2\ H_2O(l) + 4\ OH^-(aq)$
$4\ e^- + 2\ H_2O(l) + O_2(g) \rightarrow 4\ OH^-(aq)$ (reduction half reaction)

Combine the two half reactions.
$4\ Fe(OH)_2(s) + 4\ OH^-(aq) + 2\ H_2O(l) + O_2(g) \rightarrow 4\ Fe(OH)_3(s) + 4\ OH^-(aq)$
$4\ Fe(OH)_2(s) + 2\ H_2O(l) + O_2(g) \rightarrow 4\ Fe(OH)_3(s)$

4.21 31.50 mL = 0.031 50 L; 10.00 mL = 0.010 00 L

$$0.031\ 50\ L \times \frac{0.105\ mol\ BrO_3^-}{1\ L} \times \frac{6\ mol\ Fe^{2+}}{1\ mol\ BrO_3^-} = 1.98 \times 10^{-2}\ mol\ Fe^{2+}$$

$$\text{molarity} = \frac{1.98 \times 10^{-2}\ mol\ Fe^{2+}}{0.010\ 00\ L} = 1.98\ M\ Fe^{2+}\ \text{solution}$$

4.22 The $Na_2S_2O_3$, or hypo, is used to solubilize the remaining unreduced AgBr on the film so that it is no longer sensitive to light. The reaction is
$AgBr(s) + 2\ S_2O_3^{2-}(aq) \rightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$

4.23 To convert this negative image into the final printed photograph, the entire photographic procedure is repeated a second time. Light is passed through the negative image onto special photographic paper that is coated with the same kind of gelatin–AgBr emulsion used on the original film. Developing the photographic paper with hydroquinone and fixing the image with sodium thiosulfate reverses the negative image, and a final, positive image is produced.

Understanding Key Concepts

4.24 (a) $2\ Na^+(aq) + CO_3^{2-}(aq)$ does not form a precipitate. This is represented by box (1).
(b) $Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$. This is represented by box (2).
(c) $2\ Ag^+(aq) + SO_4^{2-}(aq) \rightarrow Ag_2SO_4(s)$. This is represented by box (3).

4.25 In the precipitate there are two cations (blue) for each anion (green). Looking at the ions in the list, the anion must have a -2 charge and the cation a +1 charge for charge neutrality of the precipitate. The cation must be Ag^+ because all Na^+ salts are soluble. Ag_2CrO_4 and Ag_2CO_3 are insoluble and consistent with the observed result.

4.26 One OH^- will react with each available H^+ on the acid forming H_2O. The acid is identified by how many of the 12 OH^- react with three molecules of each acid.
(a) Three HF's react with three OH^-, leaving nine OH^- unreacted (box 2).
(b) Three H_2SO_3's react with six OH^-, leaving six OH^- unreacted (box 3).
(c) Three H_3PO_4's react with nine OH^-, leaving three OH^- unreacted (box 1).

4.27 The concentration in the buret is three times that in the flask. The NaOCl concentration is 0.040 M. Because the I^- concentration in the buret is three times the OCl^- concentration in the flask and the reaction requires 2 I^- ions per OCl^- ion, 2/3 or 67% of the I^- solution from the buret must be added to the flask to react with all of the OCl^-.

4.28 (a) Ionic equation:
$K^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + K^+(aq) + NO_3^-(aq)$
(b) Ionic equation:
$HF(aq) + K^+(aq) + OH^-(aq) \rightarrow K^+(aq) + F^-(aq) + H_2O(l)$
(c) Ionic equation:
$Ba^{2+}(aq) + 2\ Cl^-(aq) + 2\ Na^+(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2\ Na^+(aq) + 2\ Cl^-(aq)$

Reaction (c) would have the highest initial conductivity because of the 3 net ions for each $BaCl_2$ (a strong electrolyte).
Reaction (b) would have have the lowest (almost zero) initial conductivity because HF is a very weak acid/electrolyte.
Reaction (a) would have an intermediate initial conductivity between that for reactions (b) and (c).
Figure (1) is for reaction (a); figure (2) is for reaction (b); and figure (3) is for reaction (c).

4.29 (a) $Sr^+ + At \rightarrow Sr + At^+$ No reaction.
(b) $Si + At^+ \rightarrow Si^+ + At$ Reaction would occur.
(c) $Sr + Si^+ \rightarrow Sr^+ + Si$ Reaction would occur.

Additional Problems
Aqueous Reactions and Net Ionic Equations

4.30 (a) precipitation (b) redox (c) acid-base neutralization

4.31 (a) redox (b) precipitation (c) acid-base neutralization

4.32 (a) Ionic equation:
$Hg^{2+}(aq) + 2\ NO_3^-(aq) + 2\ Na^+(aq) + 2\ I^-(aq) \rightarrow 2\ Na^+(aq) + 2\ NO_3^-(aq) + HgI_2(s)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $Hg^{2+}(aq) + 2\ I^-(aq) \rightarrow HgI_2(s)$

(b) $2\ HgO(s) \xrightarrow{Heat} 2\ Hg(l) + O_2(g)$
(c) Ionic equation:

$H_3PO_4(aq) + 3\ K^+(aq) + 3\ OH^-(aq) \rightarrow 3\ K^+(aq) + PO_4^{3-}(aq) + 3\ H_2O(l)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $H_3PO_4(aq) + 3\ OH^-(aq) \rightarrow PO_4^{3-}(aq) + 3\ H_2O(l)$

4.33 (a) $S_8(s) + 8\ O_2(g) \rightarrow 8\ SO_2(g)$
(b) Ionic equation:
$Ni^{2+}(aq) + 2\ Cl^-(aq) + 2\ Na^+(aq) + S^{2-}(aq) \rightarrow NiS(s) + 2\ Na^+(aq) + 2\ Cl^-(aq)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $Ni^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s)$
(c) Ionic equation:
$2\ CH_3CO_2H(aq) + Ba^{2+}(aq) + 2\ OH^-(aq) \rightarrow 2\ CH_3CO_2^-(aq) + Ba^{2+}(aq) + 2\ H_2O(l)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$

4.34 $Ba(OH)_2$ is soluble in aqueous solution, dissociates into $Ba^{2+}(aq)$ and $2\ OH^-(aq)$, and conducts electricity. In aqueous solution H_2SO_4 dissociates into $H^+(aq)$ and $HSO_4^-(aq)$. H_2SO_4 solutions conduct electricity. When equal molar solutions of $Ba(OH)_2$ and H_2SO_4 are mixed, the insoluble $BaSO_4$ is formed along with two H_2O. In water $BaSO_4$ does not produce any appreciable amount of ions and the mixture does not conduct electricity.

4.35 H_2O is polar and a good H^+ acceptor. It allows the polar HCl to dissociate into ions in aqueous solution: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$.
$CHCl_3$ is not very polar and not a H^+ acceptor and so does not allow the polar HCl to dissociate into ions.

4.36 (a) HBr, strong electrolyte
(b) HF, weak electrolyte
(c) $NaClO_4$, strong electrolyte
(d) $(NH_4)_2CO_3$, strong electrolyte
(e) NH_3, weak electrolyte
(f) C_2H_5OH, nonelectrolyte

4.37 It is possible for a molecular compound to be a strong electrolyte. For example, HCl is a molecular compound when pure but dissociates completely to give H^+ and Cl^- ions when it dissolves in water.

4.38 (a) K_2CO_3 contains 3 ions ($2\ K^+$ and $1\ CO_3^{2-}$).
The molar concentration of ions = 3 x 0.750 M = 2.25 M.
(b) $AlCl_3$ contains 4 ions ($1\ Al^{3+}$ and $3\ Cl^-$).
The molar concentration of ions = 4 x 0.355 M = 1.42 M.

4.39 (a) CH_3OH is a nonelectrolyte. The ion concentration from CH_3OH is zero.
(b) $HClO_4$ is a strong acid.
$HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-(aq)$
In solution, there are 2 moles of ions per mole of $HClO_4$.
The molar concentration of ions = 2×0.225 M = 0.450 M.

Precipitation Reactions and Solubility Rules

4.40 (a) Ag_2O, insoluble (b) $Ba(NO_3)_2$, soluble
(c) $SnCO_3$, insoluble (d) Fe_2O_3, insoluble

4.41 (a) ZnS, insoluble (b) $Au_2(CO_3)_3$, insoluble
(c) $PbCl_2$, insoluble (soluble in hot water) (d) MnO_2, insoluble

4.42 (a) No precipitate will form. (b) $FeCl_2(aq) + 2\ KOH(aq) \rightarrow Fe(OH)_2(s) + 2\ KCl(aq)$
(c) No precipitate will form. (d) No precipitate will form.

4.43 (a) $MnCl_2(aq) + Na_2S(aq) \rightarrow MnS(s) + 2\ NaCl(aq)$
(b) No precipitate will form.
(c) $3\ Hg(NO_3)_2(aq) + 2\ Na_3PO_4(aq) \rightarrow Hg_3(PO_4)_2(s) + 6\ NaNO_3(aq)$
(d) $Ba(NO_3)_2(aq) + 2\ KOH(aq) \rightarrow Ba(OH)_2(s) + 2\ KNO_3(aq)$

4.44 (a) $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2\ NaNO_3(aq)$
(b) $3\ MgCl_2(aq) + 2\ K_3PO_4(aq) \rightarrow Mg_3(PO_4)_2(s) + 6\ KCl(aq)$
(c) $ZnSO_4(aq) + Na_2CrO_4(aq) \rightarrow ZnCrO_4(s) + Na_2SO_4(aq)$

4.45 (a) $AlCl_3(aq) + 3\ NaOH(aq) \rightarrow Al(OH)_3(s) + 3\ NaCl(aq)$
(b) $Fe(NO_3)_2(aq) + Na_2S(aq) \rightarrow FeS(s) + 2\ NaNO_3(aq)$
(c) $CoSO_4(aq) + K_2CO_3(aq) \rightarrow CoCO_3(s) + K_2SO_4(aq)$

4.46 Add HCl(aq); it will selectively precipitate AgCl(s).

4.47 Add $Na_2SO_4(aq)$; it will selectively precipitate $BaSO_4(s)$.

4.48 Ag^+ is eliminated because it would have precipitated as AgCl(s); Ba^{2+} is eliminated because it would have precipitated as $BaSO_4(s)$. The solution might contain Cs^+ and/or NH_4^+. Neither of these will precipitate with OH^-, SO_4^{2-}, or Cl^-.

4.49 Cl^- is eliminated because it would have precipitated as AgCl(s). OH^- is eliminated because it would have precipitated as either AgOH(s) or $Cu(OH)_2(s)$. SO_4^{2-} is eliminated because it would have precipitated as $BaSO_4(s)$. The solution might contain NO_3^- because all nitrates are soluble.

Acids, Bases, and Neutralization Reactions

4.50 Add the solution to an active metal, such as magnesium. Bubbles of H_2 gas indicate the presence of an acid.

4.51 We use a double arrow to show the dissociation of a weak acid or weak base in aqueous solution to indicate the equilibrium between reactants and products.

4.52 (a) $2\ H^+(aq) + 2\ ClO_4^-(aq) + Ca^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ca^{2+}(aq) + 2\ ClO_4^-(aq) + 2\ H_2O(l)$

(b) $CH_3CO_2H(aq) + Na^+(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + Na^+(aq) + H_2O(l)$

4.53 (a) $2\ HF(aq) + Ca^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ca^{2+}(aq) + 2\ F^-(aq) + 2\ H_2O(l)$
(b) $Mg(OH)_2(s) + 2\ H^+(aq) + 2\ NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2\ NO_3^-(aq) + 2\ H_2O(l)$

4.54 (a) $LiOH(aq) + HI(aq) \rightarrow LiI(aq) + H_2O(l)$
Ionic equation: $Li^+(aq) + OH^-(aq) + H^+(aq) + I^-(aq) \rightarrow Li^+(aq) + I^-(aq) + H_2O(l)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

(b) $2\ HBr(aq) + Ca(OH)_2(aq) \rightarrow CaBr_2(aq) + 2\ H_2O(l)$
Ionic equation:
$2\ H^+(aq) + 2\ Br^-(aq) + Ca^{2+}(aq) + 2\ OH^-(aq) \rightarrow Ca^{2+}(aq) + 2\ Br^-(aq) + 2\ H_2O(l)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

4.55 (a) $2\ Fe(OH)_3(s) + 3\ H_2SO_4(aq) \rightarrow Fe_2(SO_4)_3(aq) + 6\ H_2O(l)$
Ionic equation and net ionic equation are the same.
$2\ Fe(OH)_3(s) + 3\ H^+(aq) + 3\ HSO_4^-(aq) \rightarrow 2\ Fe^{3+}(aq) + 3\ SO_4^{2-}(aq) + 6\ H_2O(l)$

(b) $HClO_3(aq) + NaOH(aq) \rightarrow NaClO_3(aq) + H_2O(l)$
Ionic equation $H^+(aq) + ClO_3^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + ClO_3^-(aq) + H_2O(l)$
Delete spectator ions from the ionic equation to get the net ionic equation.
Net ionic equation: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Redox Reactions and Oxidation Numbers

4.56 The best reducing agents are at the bottom left of the periodic table. The best oxidizing agents are at the top right of the periodic table (excluding the noble gases).

4.57 The most easily reduced elements in the periodic table are in the top-right corner, excluding group 8A.
The most easily oxidized elements in the periodic table are in the bottom-left corner.

4.58 (a) An oxidizing agent gains electrons.
(b) A reducing agent loses electrons.
(c) A substance undergoing oxidation loses electrons.
(d) A substance undergoing reduction gains electrons.

4.59 (a) In a redox reaction, the oxidation number decreases for an oxidizing agent.
(b) In a redox reaction, the oxidation number increases for a reducing agent.
(c) In a redox reaction, the oxidation number increases for a substance undergoing oxidation.
(d) In a redox reaction, the oxidation number decreases for a substance undergoing reduction.

4.60 (a) NO_2 O -2, N +4 (b) SO_3 O -2, S +6
(c) $COCl_2$ O -2, Cl -1, C +4 (d) CH_2Cl_2 Cl -1, H +1, C 0
(e) $KClO_3$ O -2, K +1, Cl +5 (f) HNO_3 O -2, H +1, N +5

4.61 (a) $VOCl_3$ O -2, Cl -1, V +5
(b) $CuSO_4$ O -2, S +6, Cu +2
(c) CH_2O O -2, H +1, C 0
(d) Mn_2O_7 O -2, Mn +7
(e) OsO_4 O -2, Os +8
(f) H_2PtCl_6 Cl -1, H +1, Pt +4

4.62 (a) ClO_3^- O -2, Cl +5 (b) SO_3^{2-} O -2, S +4
(c) $C_2O_4^{2-}$ O -2, C +3 (d) NO_2^- O -2, N +3
(e) BrO^- O -2, Br +1 (f) AsO_4^{3-} O -2, As +5

4.63 (a) $Cr(OH)_4^-$ O -2, H +1, Cr +3
(b) $S_2O_3^{2-}$ O -2, S +2
(c) NO_3^- O -2, N +5
(d) MnO_4^{2-} O -2, Mn +6
(e) HPO_4^{2-} O -2, H +1, P +5
(f) $V_2O_7^{4-}$ O -2, V +5

4.64 (a) $Ca(s) + Sn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Sn(s)$
Ca(s) is oxidized (oxidation number increases from 0 to +2).
$Sn^{2+}(aq)$ is reduced (oxidation number decreases from +2 to 0).
(b) $ICl(s) + H_2O(l) \rightarrow HCl(aq) + HOI(aq)$
No oxidation numbers change. The reaction is not a redox reaction.

4.65 (a) $Si(s) + 2\ Cl_2(g) \rightarrow SiCl_4(l)$
Si(s) is oxidized (oxidation number increases from 0 to +4).
$Cl_2(g)$ is reduced (oxidation number decreases from 0 to -1).
(b) $Cl_2(g) + 2\ NaBr(aq) \rightarrow Br_2(aq) + 2\ NaCl(aq)$
$Br^-(aq)$ is oxidized (oxidation number increases from -1 to 0).
$Cl_2(g)$ is reduced (oxidation number decreases from 0 to -1).

4.66 (a) Zn is below Na^+; therefore no reaction.
(b) Pt is below H^+; therefore no reaction.
(c) Au is below Ag^+; therefore no reaction.
(d) Ag is above Au^{3+}; the reaction is $Au^{3+}(aq) + 3\ Ag(s) \rightarrow 3\ Ag^+(aq) + Au(s)$.

4.67 Sr is more metallic than Sb because it is in the same period and to the left of Sb on the periodic table. Sr is the better reducing agent.
$2\ Sb^{3+}(aq) + 3\ Sr(s) \rightarrow 2\ Sb(s) + 3\ Sr^{2+}(aq)$ will occur, the reverse will not.

4.68 (a) "Any element higher in the activity series will react with the ion of any element lower

in the activity series."
$A + B^+ \rightarrow A^+ + B$; therefore A is higher than B.
$C^+ + D \rightarrow$ no reaction; therefore C is higher than D.
$B + D^+ \rightarrow B^+ + D$; therefore B is higher than D.
$B + C^+ \rightarrow B^+ + C$; therefore B is higher than C.
The net result is A > B > C > D.
(b) (1) C is below A^+; therefore no reaction.
(2) D is below A^+; therefore no reaction.

4.69 (a) "Any element higher in the activity series will react with the ion of any element lower in the activity series."
$2\ A + B^{2+} \rightarrow 2\ A^+ + B$; therefore A is higher than B.
$B + D^{2+} \rightarrow B^{2+} + D$; therefore B is higher than D.
$A^+ + C \rightarrow$ no reaction; therefore A is higher than C.
$2\ C + B^{2+} \rightarrow 2\ C^+ + B$; therefore C is higher than B.
The net result is A > C > B > D.
(b) (1) D is below A^+; therefore no reaction.
(2) C is above D^{2+}; therefore the reaction will occur.

Balancing Redox Reactions

4.70 (a) N oxidation number decreases from +5 to +2; reduction.
(b) Zn oxidation number increases from 0 to +2; oxidation.
(c) Ti oxidation number increases from +3 to +4; oxidation.
(d) Sn oxidation number decreases from +4 to +2; reduction.

4.71 (a) O oxidation number decreases from 0 to -2; reduction.
(b) O oxidation number increases from -1 to 0; oxidation.
(c) Mn oxidation number decreases from +7 to +6; reduction.
(d) C oxidation number increases from -2 to 0; oxidation.

4.72 (a) $NO_3^-(aq) \rightarrow NO(g)$
$NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$3\ e^- + 4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$

(b) $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

(c) $Ti^{3+}(aq) \rightarrow TiO_2(s)$
$Ti^{3+}(aq) + 2\ H_2O(l) \rightarrow TiO_2(s)$
$Ti^{3+}(aq) + 2\ H_2O(l) \rightarrow TiO_2(s) + 4\ H^+(aq)$
$Ti^{3+}(aq) + 2\ H_2O(l) \rightarrow TiO_2(s) + 4\ H^+(aq) + e^-$

(d) $Sn^{4+}(aq) + 2\ e^- \rightarrow Sn^{2+}(aq)$

4.73 (a) $O_2(g) \rightarrow OH^-(aq)$

$O_2(g) \rightarrow OH^-(aq) + H_2O(l)$
$3\ H^+(aq) + O_2(g) \rightarrow OH^-(aq) + H_2O(l)$
$3\ H^+(aq) + 3\ OH^-(aq) + O_2(g) \rightarrow 4\ OH^-(aq) + H_2O(l)$
$3\ H_2O(l) + O_2(g) \rightarrow 4\ OH^-(aq) + H_2O(l)$
$4\ e^- + 2\ H_2O(l) + O_2(g) \rightarrow 4\ OH^-(aq)$

(b) $H_2O_2(aq) \rightarrow O_2(g)$
$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq)$

$2\ OH^-(aq) + H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ OH^-(aq)$
$2\ OH^-(aq) + H_2O_2(aq) \rightarrow O_2(g) + 2\ H_2O(l) + 2\ e^-$

(c) $MnO_4^-(aq) \rightarrow MnO_4^{2-}(aq)$
$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$

(d) $CH_3OH(aq) \rightarrow CH_2O(aq)$
$CH_3OH(aq) \rightarrow CH_2O(aq) + 2\ H^+(aq)$
$CH_3OH(aq) + 2\ OH^-(aq) \rightarrow CH_2O(aq) + 2\ H^+(aq) + 2\ OH^-(aq)$
$CH_3OH(aq) + 2\ OH^-(aq) \rightarrow CH_2O(aq) + 2\ H_2O(l)$
$CH_3OH(aq) + 2\ OH^-(aq) \rightarrow CH_2O(aq) + 2\ H_2O(l) + 2\ e^-$

4.74 (a) $Te(s) + NO_3^-(aq) \rightarrow TeO_2(s) + NO(g)$
oxidation: $Te(s) \rightarrow TeO_2(s)$
reduction: $NO_3^-(aq) \rightarrow NO(g)$
(b) $H_2O_2(aq) + Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + H_2O(l)$
oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$
reduction: $H_2O_2(aq) \rightarrow H_2O(l)$

4.75 (a) $Mn(s) + NO_3^-(aq) \rightarrow Mn^{2+}(aq) + NO_2(g)$
oxidation: $Mn(s) \rightarrow Mn^{2+}(aq)$
reduction: $NO_3^-(aq) \rightarrow NO_2(g)$
(b) $Mn^{3+}(aq) \rightarrow MnO_2(s) + Mn^{2+}(aq)$
oxidation: $Mn^{3+}(aq) \rightarrow MnO_2(s)$
reduction: $Mn^{3+}(aq) \rightarrow Mn^{2+}(aq)$

4.76 (a) $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$
$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq)$
$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
$14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

(b) $CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq)$
$4\ H^+(aq) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq)$
$4\ H^+(aq) + 4\ OH^-(aq) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq) + 4\ OH^-(aq)$

$4\ H_2O(l) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq) + 4\ OH^-(aq)$
$4\ H_2O(l) + CrO_4^{2-}(aq) + 3\ e^- \rightarrow Cr(OH)_4^-(aq) + 4\ OH^-(aq)$

(c) $Bi^{3+}(aq) \rightarrow BiO_3^-(aq)$
$Bi^{3+}(aq) + 3\ H_2O(l) \rightarrow BiO_3^-(aq)$
$Bi^{3+}(aq) + 3\ H_2O(l) \rightarrow BiO_3^-(aq) + 6\ H^+(aq)$
$Bi^{3+}(aq) + 3\ H_2O(l) + 6\ OH^-(aq) \rightarrow BiO_3^-(aq) + 6\ H^+(aq) + 6\ OH^-(aq)$
$Bi^{3+}(aq) + 3\ H_2O(l) + 6\ OH^-(aq) \rightarrow BiO_3^-(aq) + 6\ H_2O(l)$
$Bi^{3+}(aq) + 6\ OH^-(aq) \rightarrow BiO_3^-(aq) + 3\ H_2O(l)$
$Bi^{3+}(aq) + 6\ OH^-(aq) \rightarrow BiO_3^-(aq) + 3\ H_2O(l) + 2\ e^-$

(d) $ClO^-(aq) \rightarrow Cl^-(aq)$
$ClO^-(aq) \rightarrow Cl^-(aq) + H_2O(l)$
$2\ H^+(aq) + ClO^-(aq) \rightarrow Cl^-(aq) + H_2O(l)$
$2\ H^+(aq) + 2\ OH^-(aq) + ClO^-(aq) \rightarrow Cl^-(aq) + H_2O(l) + 2\ OH^-(aq)$
$2\ H_2O(l) + ClO^-(aq) \rightarrow Cl^-(aq) + H_2O(l) + 2\ OH^-(aq)$
$H_2O(l) + ClO^-(aq) \rightarrow Cl^-(aq) + 2\ OH^-(aq)$
$H_2O(l) + ClO^-(aq) + 2\ e^- \rightarrow Cl^-(aq) + 2\ OH^-(aq)$

4.77 (a) $VO^{2+}(aq) \rightarrow V^{3+}(aq)$
$VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$
$2\ H^+(aq) + VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$
$2\ H^+(aq) + VO^{2+}(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$

(b) $Ni(OH)_2(s) \rightarrow Ni_2O_3(s)$
$2\ Ni(OH)_2(s) \rightarrow Ni_2O_3(s) + H_2O(l)$
$2\ Ni(OH)_2(s) \rightarrow Ni_2O_3(s) + H_2O(l) + 2\ H^+(aq)$
$2\ Ni(OH)_2(s) + 2\ OH^-(aq) \rightarrow Ni_2O_3(s) + H_2O(l) + 2\ H^+(aq) + 2\ OH^-(aq)$
$2\ Ni(OH)_2(s) + 2\ OH^-(aq) \rightarrow Ni_2O_3(s) + 3\ H_2O(l) + 2\ e^-$

(c) $NO_3^-(aq) \rightarrow NO_2(g)$
$NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$
$2\ H^+(aq) + NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$
$2\ H^+(aq) + NO_3^-(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$

(d) $Br_2(aq) \rightarrow BrO_3^-(aq)$
$Br_2(aq) \rightarrow 2\ BrO_3^-(aq)$
$Br_2(aq) + 6\ H_2O(l) \rightarrow 2\ BrO_3^-(aq)$
$Br_2(aq) + 6\ H_2O(l) \rightarrow 2\ BrO_3^-(aq) + 12\ H^+(aq)$
$Br_2(aq) + 6\ H_2O(l) + 12\ OH^-(aq) \rightarrow 2\ BrO_3^-(aq) + 12\ H^+(aq) + 12\ OH^-(aq)$
$Br_2(aq) + 6\ H_2O(l) + 12\ OH^-(aq) \rightarrow 2\ BrO_3^-(aq) + 12\ H_2O(l)$
$Br_2(aq) + 12\ OH^-(aq) \rightarrow 2\ BrO_3^-(aq) + 6\ H_2O(l) + 10\ e^-$

4.78 (a) $MnO_4^-(aq) \rightarrow MnO_2(s)$

$MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$4\ H^+(aq) + MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$[4\ H^+(aq) + MnO_4^-(aq) + 3\ e^- \rightarrow MnO_2(s) + 2\ H_2O(l)] \times 2$ (reduction half reaction)

$IO_3^-(aq) \rightarrow IO_4^-(aq)$
$H_2O(l) + IO_3^-(aq) \rightarrow IO_4^-(aq)$
$H_2O(l) + IO_3^-(aq) \rightarrow IO_4^-(aq) + 2\ H^+(aq)$
$[H_2O(l) + IO_3^-(aq) \rightarrow IO_4^-(aq) + 2\ H^+(aq) + 2\ e^-] \times 3$ (oxidation half reaction)
Combine the two half reactions.
$8\ H^+(aq) + 3\ H_2O(l) + 2\ MnO_4^-(aq) + 3\ IO_3^-(aq) \rightarrow$
$6\ H^+(aq) + 4\ H_2O(l) + 2\ MnO_2(s) + 3\ IO_4^-(aq)$
$2\ H^+(aq) + 2\ MnO_4^-(aq) + 3\ IO_3^-(aq) \rightarrow 2\ MnO_2(s) + 3\ IO_4^-(aq) + H_2O(l)$

$2\ H^+(aq) + 2\ OH^-(aq) + 2\ MnO_4^-(aq) + 3\ IO_3^-(aq) \rightarrow$
$2\ MnO_2(s) + 3\ IO_4^-(aq) + H_2O(l) + 2\ OH^-(aq)$
$2\ H_2O(l) + 2\ MnO_4^-(aq) + 3\ IO_3^-(aq) \rightarrow$
$2\ MnO_2(s) + 3\ IO_4^-(aq) + H_2O(l) + 2\ OH^-(aq)$
$H_2O(l) + 2\ MnO_4^-(aq) + 3\ IO_3^-(aq) \rightarrow 2\ MnO_2(s) + 3\ IO_4^-(aq) + 2\ OH^-(aq)$

(b) $Cu(OH)_2(s) \rightarrow Cu(s)$
$Cu(OH)_2(s) \rightarrow Cu(s) + 2\ H_2O(l)$
$2\ H^+(aq) + Cu(OH)_2(s) \rightarrow Cu(s) + 2\ H_2O(l)$
$[2\ H^+(aq) + Cu(OH)_2(s) + 2\ e^- \rightarrow Cu(s) + 2\ H_2O(l)] \times 2$ (reduction half reaction)

$N_2H_4(aq) \rightarrow N_2(g)$
$N_2H_4(aq) \rightarrow N_2(g) + 4\ H^+(aq)$
$N_2H_4(aq) \rightarrow N_2(g) + 4\ H^+(aq) + 4\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$4\ H^+(aq) + 2\ Cu(OH)_2(s) + N_2H_4(aq) \rightarrow 2\ Cu(s) + 4\ H_2O(l) + N_2(g) + 4\ H^+(aq)$
$2\ Cu(OH)_2(s) + N_2H_4(aq) \rightarrow 2\ Cu(s) + 4\ H_2O(l) + N_2(g)$

(c) $Fe(OH)_2(s) \rightarrow Fe(OH)_3(s)$
$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s)$
$Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq)$
$[Fe(OH)_2(s) + H_2O(l) \rightarrow Fe(OH)_3(s) + H^+(aq) + e^-] \times 3$ (oxidation half reaction)

$CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq)$
$4\ H^+(aq) + CrO_4^{2-}(aq) \rightarrow Cr(OH)_4^-(aq)$
$4\ H^+(aq) + CrO_4^{2-}(aq) + 3\ e^- \rightarrow Cr(OH)_4^-(aq)$ (reduction half reaction)

Combine the two half reactions.
$3\ Fe(OH)_2(s) + 3\ H_2O(l) + 4\ H^+(aq) + CrO_4^{2-}(aq) \rightarrow$
$3\ Fe(OH)_3(s) + 3\ H^+(aq) + Cr(OH)_4^-(aq)$

$3\ Fe(OH)_2(s) + 3\ H_2O(l) + H^+(aq) + CrO_4^{2-}(aq) \rightarrow 3\ Fe(OH)_3(s) + Cr(OH)_4^-(aq)$
$3\ Fe(OH)_2(s) + 3\ H_2O(l) + H^+(aq) + OH^-(aq) + CrO_4^{2-}(aq) \rightarrow$
$3\ Fe(OH)_3(s) + Cr(OH)_4^-(aq) + OH^-(aq)$
$3\ Fe(OH)_2(s) + 4\ H_2O(l) + CrO_4^{2-}(aq) \rightarrow 3\ Fe(OH)_3(s) + Cr(OH)_4^-(aq) + OH^-(aq)$

(d) $ClO_4^-(aq) \rightarrow ClO_2^-(aq)$
$ClO_4^-(aq) \rightarrow ClO_2^-(aq) + 2\ H_2O(l)$
$4\ H^+(aq) + ClO_4^-(aq) \rightarrow ClO_2^-(aq) + 2\ H_2O(l)$
$4\ H^+(aq) + ClO_4^-(aq) + 4\ e^- \rightarrow ClO_2^-(aq) + 2\ H_2O(l)$ (reduction half reaction)

$H_2O_2(aq) \rightarrow O_2(g)$
$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq)$
$[H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-] \times 2$ (oxidation half reaction)

Combine the two half reactions.
$4\ H^+(aq) + ClO_4^-(aq) + 2\ H_2O_2(aq) \rightarrow ClO_2^-(aq) + 2\ H_2O(l) + 2\ O_2(g) + 4\ H^+(aq)$
$ClO_4^-(aq) + 2\ H_2O_2(aq) \rightarrow ClO_2^-(aq) + 2\ H_2O(l) + 2\ O_2(g)$

4.79 (a) $S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ e^-$ (oxidation half reaction)

$I_2(aq) \rightarrow I^-(aq)$
$I_2(aq) \rightarrow 2\ I^-(aq)$
$I_2(aq) + 2\ e^- \rightarrow 2\ I^-(aq)$ (reduction half reaction)

Combine the two half reactions.
$2\ S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ I^-(aq)$

(b) $Mn^{2+}(aq) \rightarrow MnO_2(s)$
$Mn^{2+}(aq) + 2\ H_2O(l) \rightarrow MnO_2(s)$
$Mn^{2+}(aq) + 2\ H_2O(l) \rightarrow MnO_2(s) + 4\ H^+(aq)$
$Mn^{2+}(aq) + 2\ H_2O(l) \rightarrow MnO_2(s) + 4\ H^+(aq) + 2\ e^-$ (oxidation half reaction)

$H_2O_2(aq) \rightarrow 2\ H_2O(l)$
$2\ H^+(aq) + H_2O_2(aq) \rightarrow 2\ H_2O(l)$
$2\ H^+(aq) + H_2O_2(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.
$Mn^{2+}(aq) + 2\ H_2O(l) + 2\ H^+(aq) + H_2O_2(aq) \rightarrow MnO_2(s) + 4\ H^+(aq) + 2\ H_2O(l)$
$Mn^{2+}(aq) + H_2O_2(aq) \rightarrow MnO_2(s) + 2\ H^+(aq)$
$Mn^{2+}(aq) + H_2O_2(aq) + 2\ OH^-(aq) \rightarrow MnO_2(s) + 2\ H^+(aq) + 2\ OH^-(aq)$
$Mn^{2+}(aq) + H_2O_2(aq) + 2\ OH^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$

(c) $Zn(s) \rightarrow Zn(OH)_4^{2-}(aq)$

$4\ H_2O(l) + Zn(s) \rightarrow Zn(OH)_4^{2-}(aq)$

$4\ H_2O(l) + Zn(s) \rightarrow Zn(OH)_4^{2-}(aq) + 4\ H^+(aq)$

$[4\ H_2O(l) + Zn(s) \rightarrow Zn(OH)_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-] \times 4$ (oxidation half reaction)

$NO_3^-(aq) \rightarrow NH_3(aq)$

$NO_3^-(aq) \rightarrow NH_3(aq) + 3\ H_2O(l)$

$9\ H^+(aq) + NO_3^-(aq) \rightarrow NH_3(aq) + 3\ H_2O(l)$

$9\ H^+(aq) + NO_3^-(aq) + 8\ e^- \rightarrow NH_3(aq) + 3\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$16\ H_2O(l) + 4\ Zn(s) + 9\ H^+(aq) + NO_3^-(aq) \rightarrow$
$4\ Zn(OH)_4^{2-}(aq) + 16\ H^+(aq) + NH_3(aq) + 3\ H_2O(l)$

$13\ H_2O(l) + 4\ Zn(s) + NO_3^-(aq) \rightarrow 4\ Zn(OH)_4^{2-}(aq) + 7\ H^+(aq) + NH_3(aq)$

$13\ H_2O(l) + 4\ Zn(s) + NO_3^-(aq) + 7\ OH^-(aq) \rightarrow$
$4\ Zn(OH)_4^{2-}(aq) + 7\ H^+(aq) + 7\ OH^-(aq) + NH_3(aq)$

$13\ H_2O(l) + 4\ Zn(s) + NO_3^-(aq) + 7\ OH^-(aq) \rightarrow$
$4\ Zn(OH)_4^{2-}(aq) + 7\ H_2O(l) + NH_3(aq)$

$6\ H_2O(l) + 4\ Zn(s) + NO_3^-(aq) + 7\ OH^-(aq) \rightarrow 4\ Zn(OH)_4^{2-}(aq) + NH_3(aq)$

(d) $Bi(OH)_3(s) \rightarrow Bi(s)$

$Bi(OH)_3(s) \rightarrow Bi(s) + 3\ H_2O(l)$

$3\ H^+(aq) + Bi(OH)_3(s) \rightarrow Bi(s) + 3\ H_2O(l)$

$[3\ H^+(aq) + Bi(OH)_3(s) + 3\ e^- \rightarrow Bi(s) + 3\ H_2O(l)] \times 2$ (reduction half reaction)

$Sn(OH)_3^-(aq) \rightarrow Sn(OH)_6^{2-}(aq)$

$Sn(OH)_3^-(aq) + 3\ H_2O(l) \rightarrow Sn(OH)_6^{2-}(aq)$

$Sn(OH)_3^-(aq) + 3\ H_2O(l) \rightarrow Sn(OH)_6^{2-}(aq) + 3\ H^+(aq)$

$[Sn(OH)_3^-(aq) + 3\ H_2O(l) \rightarrow Sn(OH)_6^{2-}(aq) + 3\ H^+(aq) + 2\ e^-] \times 3$
(oxidation half reaction)

Combine the two half reactions.

$6\ H^+(aq) + 2\ Bi(OH)_3(s) + 3\ Sn(OH)_3^-(aq) + 9\ H_2O(l) \rightarrow$
$2\ Bi(s) + 6\ H_2O(l) + 3\ Sn(OH)_6^{2-}(aq) + 9\ H^+(aq)$

$2\ Bi(OH)_3(s) + 3\ Sn(OH)_3^-(aq) + 3\ H_2O(l) \rightarrow 2\ Bi(s) + 3\ Sn(OH)_6^{2-}(aq) + 3\ H^+(aq)$

$2\ Bi(OH)_3(s) + 3\ Sn(OH)_3^-(aq) + 3\ H_2O(l) + 3\ OH^-(aq) \rightarrow$
$2\ Bi(s) + 3\ Sn(OH)_6^{2-}(aq) + 3\ H^+(aq) + 3\ OH^-(aq)$

$2\ Bi(OH)_3(s) + 3\ Sn(OH)_3^-(aq) + 3\ H_2O(l) + 3\ OH^-(aq) \rightarrow$
$2\ Bi(s) + 3\ Sn(OH)_6^{2-}(aq) + 3\ H_2O(l)$

$2\ Bi(OH)_3(s) + 3\ Sn(OH)_3^-(aq) + 3\ OH^-(aq) \rightarrow 2\ Bi(s) + 3\ Sn(OH)_6^{2-}(aq)$

4.80 (a) $Zn(s) \rightarrow Zn^{2+}(aq)$

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$ (oxidation half reaction)

$VO^{2+}(aq) \rightarrow V^{3+}(aq)$
$VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$
$2\ H^+(aq) + VO^{2+}(aq) \rightarrow V^{3+}(aq) + H_2O(l)$
$[2\ H^+(aq) + VO^{2+}(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$Zn(s) + 2\ VO^{2+}(aq) + 4\ H^+(aq) \rightarrow Zn^{2+}(aq) + 2\ V^{3+}(aq) + 2\ H_2O(l)$

(b) $Ag(s) \rightarrow Ag^+(aq)$
$Ag(s) \rightarrow Ag^+(aq) + e^-$ (oxidation half reaction)

$NO_3^-(aq) \rightarrow NO_2(g)$
$NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$
$2\ H^+(aq) + NO_3^-(aq) \rightarrow NO_2(g) + H_2O(l)$
$2\ H^+(aq) + NO_3^-(aq) + e^- \rightarrow NO_2(g) + H_2O(l)$ (reduction half reaction)

Combine the two half reactions.
$2\ H^+(aq) + Ag(s) + NO_3^-(aq) \rightarrow Ag^+(aq) + NO_2(g) + H_2O(l)$

(c) $Mg(s) \rightarrow Mg^{2+}(aq)$
$[Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

$VO_4^{3-}(aq) \rightarrow V^{2+}(aq)$
$VO_4^{3-}(aq) \rightarrow V^{2+}(aq) + 4\ H_2O(l)$
$8\ H^+(aq) + VO_4^{3-}(aq) \rightarrow V^{2+}(aq) + 4\ H_2O(l)$
$[8\ H^+(aq) + VO_4^{3-}(aq) + 3\ e^- \rightarrow V^{2+}(aq) + 4\ H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$3\ Mg(s) + 16\ H^+(aq) + 2\ VO_4^{3-}(aq) \rightarrow 3\ Mg^{2+}(aq) + 2\ V^{2+}(aq) + 8\ H_2O(l)$

(d) $I^-(aq) \rightarrow I_3^-(aq)$
$3\ I^-(aq) \rightarrow I_3^-(aq)$
$[3\ I^-(aq) \rightarrow I_3^-(aq) + 2\ e^-] \times 8$ (oxidation half reaction)

$IO_3^-(aq) \rightarrow I_3^-(aq)$
$3\ IO_3^-(aq) \rightarrow I_3^-(aq)$
$3\ IO_3^-(aq) \rightarrow I_3^-(aq) + 9\ H_2O(l)$
$18\ H^+(aq) + 3\ IO_3^-(aq) \rightarrow I_3^-(aq) + 9\ H_2O(l)$
$18\ H^+(aq) + 3\ IO_3^-(aq) + 16\ e^- \rightarrow I_3^-(aq) + 9\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.
$18\ H^+(aq) + 3\ IO_3^-(aq) + 24\ I^-(aq) \rightarrow 9\ I_3^-(aq) + 9\ H_2O(l)$
Divide each coefficient by 3.
$6\ H^+(aq) + IO_3^-(aq) + 8\ I^-(aq) \rightarrow 3\ I_3^-(aq) + 3\ H_2O(l)$

4.81 (a) $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

$8\ H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

$[8\ H^+(aq) + MnO_4^-(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)] \times 4$ (reduction half reaction)

$C_2H_5OH(aq) \rightarrow CH_3CO_2H(aq)$

$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3CO_2H(aq)$

$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3CO_2H(aq) + 4\ H^+(aq)$

$[C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3CO_2H(aq) + 4\ H^+(aq) + 4\ e^-] \times 5$ (oxidation half reaction)

Combine the two half reactions.

$32\ H^+(aq) + 4\ MnO_4^-(aq) + 5\ C_2H_5OH(aq) + 5\ H_2O(l) \rightarrow 4\ Mn^{2+}(aq) + 16\ H_2O(l) + 5\ CH_3CO_2H(aq) + 20\ H^+(aq)$

$12\ H^+(aq) + 4\ MnO_4^-(aq) + 5\ C_2H_5OH(aq) \rightarrow 4\ Mn^{2+}(aq) + 11\ H_2O(l) + 5\ CH_3CO_2H(aq)$

(b) $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ (reduction half reaction)

$H_2O_2(aq) \rightarrow O_2(g)$

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq)$

$[H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

Combine the two half reactions.

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ O_2(g) + 6\ H^+(aq)$

$8\ H^+(aq) + Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l) + 3\ O_2(g)$

(c) $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq)$

$[Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ e^-] \times 4$ (oxidation half reaction)

$IO_4^-(aq) \rightarrow I^-(aq)$

$IO_4^-(aq) \rightarrow I^-(aq) + 4\ H_2O(l)$

$8\ H^+(aq) + IO_4^-(aq) \rightarrow I^-(aq) + 4\ H_2O(l)$

$8\ H^+(aq) + IO_4^-(aq) + 8\ e^- \rightarrow I^-(aq) + 4\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$4\ Sn^{2+}(aq) + 8\ H^+(aq) + IO_4^-(aq) \rightarrow 4\ Sn^{4+}(aq) + I^-(aq) + 4\ H_2O(l)$

(d) $PbO_2(s) + Cl^-(aq) \rightarrow PbCl_2(s)$

$PbO_2(s) + 2\ Cl^-(aq) \rightarrow PbCl_2(s)$

$PbO_2(s) + 2\ Cl^-(aq) \rightarrow PbCl_2(s) + 2\ H_2O(l)$

$PbO_2(s) + 4\ H^+(aq) + 2\ Cl^-(aq) \rightarrow PbCl_2(s) + 2\ H_2O(l)$

$[PbO_2(s) + 4\ H^+(aq) + 2\ Cl^-(aq) + 2\ e^- \rightarrow PbCl_2(s) + 2\ H_2O(l)] \times 2$ (reduction half reaction)

$H_2O(l) \rightarrow O_2(g)$

$2\ H_2O(l) \rightarrow O_2(g)$

$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq)$

$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$ (oxidation half reaction)

Combine the two half reactions.

$2\ PbO_2(s) + 8\ H^+(aq) + 4\ Cl^-(aq) + 2\ H_2O(l) \rightarrow 2\ PbCl_2(s) + 4\ H_2O(l) + O_2(g) + 4\ H^+(aq)$

$2\ PbO_2(s) + 4\ H^+(aq) + 4\ Cl^-(aq) \rightarrow 2\ PbCl_2(s) + 2\ H_2O(l) + O_2(g)$

Redox Titrations

4.82 $I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ I^-(aq)$; 35.20 mL = 0.032 50 L

$$0.035\ 20\ L \times \frac{0.150\ mol\ S_2O_3^{2-}}{L} \times \frac{1\ mol\ I_2}{2\ mol\ S_2O_3^{2-}} \times \frac{253.8\ g\ I_2}{1\ mol\ I_2} = 0.670\ g\ I_2$$

4.83 $$2.486\ g\ I_2 \times \frac{1\ mol\ I_2}{253.8\ g\ I_2} \times \frac{2\ mol\ S_2O_3^{2-}}{1\ mol\ I_2} = 1.959 \times 10^{-2}\ mol\ S_2O_3^{2-}$$

$$1.959 \times 10^{-2}\ mol \times \frac{1\ L}{0.250\ mol} = 0.0784\ L;\ 0.0784\ L = 78.4\ mL$$

4.84 $3\ H_3AsO_3(aq) + BrO_3^-(aq) \rightarrow Br^-(aq) + 3\ H_3AsO_4(aq)$

22.35 mL = 0.022 35 L and 50.00 mL = 0.050 00 L

$$0.022\ 35\ L \times \frac{0.100\ mol\ BrO_3^-}{L} \times \frac{3\ mol\ H_3AsO_3}{1\ mol\ BrO_3^-} = 6.70 \times 10^{-3}\ mol\ H_3AsO_3$$

$$\text{molarity} = \frac{6.70 \times 10^{-3}\ mol}{0.050\ 00\ L} = 0.134\ M\ As(III)$$

4.85 As_2O_3, 197.84 amu; 28.55 mL = 0.028 55 L

$$1.550\ g\ As_2O_3 \times \frac{1\ mol\ As_2O_3}{197.84\ g\ As_2O_3} \times \frac{2\ mol\ H_3AsO_3}{1\ mol\ As_2O_3} \times \frac{1\ mol\ BrO_3^-}{3\ mol\ H_3AsO_3}$$

$= 5.223 \times 10^{-3}$ mol BrO_3^-; $KBrO_3$ molarity $= \frac{5.223 \times 10^{-3}\ mol}{0.028\ 55\ L} = 0.1829\ M$

4.86 $2\ Fe^{3+}(aq) + Sn^{2+}(aq) \rightarrow 2\ Fe^{2+}(aq) + Sn^{4+}(aq)$; 13.28 mL = 0.013 28 L

$$0.013\,28\ \text{L} \times \frac{0.1015\ \text{mol}\ Sn^{2+}}{\text{L}} \times \frac{2\ \text{mol}\ Fe^{3+}}{1\ \text{mol}\ Sn^{2+}} \times \frac{55.847\ \text{g}\ Fe^{3+}}{1\ \text{mol}\ Fe^{3+}} = 0.1506\ \text{g}\ Fe^{3+}$$

$$\text{mass \% Fe} = \frac{0.1506\ \text{g}}{0.1875\ \text{g}} \times 100\% = 80.32\%$$

4.87 Fe_2O_3, 159.69 amu; 23.84 mL = 0.023 84 L

$$1.4855\ \text{g}\ Fe_2O_3 \times \frac{1\ \text{mol}\ Fe_2O_3}{159.69\ \text{g}\ Fe_2O_3} \times \frac{2\ \text{mol}\ Fe^{3+}}{1\ \text{mol}\ Fe_2O_3} \times \frac{1\ \text{mol}\ Sn^{2+}}{2\ \text{mol}\ Fe^{3+}} = 0.009\,302\ \text{mol}\ Sn^{2+}$$

$$Sn^{2+}\ \text{molarity} = \frac{0.009\,302\ \text{mol}}{0.023\,84\ \text{L}} = 0.3902\ \text{M}$$

4.88 $C_2H_5OH(aq) + 2\ Cr_2O_7^{2-}(aq) + 16\ H^+(aq) \rightarrow 2\ CO_2(g) + 4\ Cr^{3+}(aq) + 11\ H_2O(l)$

C_2H_5OH, 46.07 amu; 8.76 mL = 0.008 76 L

$$0.008\,76\ \text{L} \times \frac{0.049\,88\ \text{mol}\ Cr_2O_7^{2-}}{\text{L}} \times \frac{1\ \text{mol}\ C_2H_5OH}{2\ \text{mol}\ Cr_2O_7^{2-}} \times \frac{46.07\ \text{g}\ C_2H_5OH}{1\ \text{mol}\ C_2H_5OH}$$

$$= 0.010\,07\ \text{g}\ C_2H_5OH$$

$$\text{mass \% } C_2H_5OH = \frac{0.010\,07\ \text{g}}{10.002\ \text{g}} \times 100\% = 0.101\%$$

4.89 21.08 mL = 0.021 08 L

$$0.021\,08\ \text{L} \times 9.88 \times 10^{-4}\ \text{mol}\ MnO_4^-\text{overL} \times \frac{5\ \text{mol}\ H_2C_2O_4}{2\ \text{mol}\ MnO_4^-} \times \frac{1\ \text{mol}\ Ca^{2+}}{1\ \text{mol}\ H_2C_2O_4} \times \frac{40.08\ \text{g}\ Ca^{2+}}{1\ \text{mol}\ Ca^{2+}}$$

$$= 0.002\,09\ \text{g} = 2.09\ \text{mg}$$

General Problems

4.90 (a) $[Fe(CN)_6]^{3-}(aq) \rightarrow Fe(CN)_6]^{4-}(aq)$

$([Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq)) \times 4$ (reduction half reaction)

$N_2H_4(aq) \rightarrow N_2(g)$

$N_2H_4(aq) \rightarrow N_2(g) + 4\ H^+(aq)$

$N_2H_4(aq) \rightarrow N_2(g) + 4\ H^+(aq) + 4\ e^-$

$N_2H_4(aq) + 4\ OH^-(aq) \rightarrow N_2(g) + 4\ H^+(aq) + 4\ OH^-(aq) + 4\ e^-$

$N_2H_4(aq) + 4\ OH^-(aq) \rightarrow N_2(g) + 4\ H_2O(l) + 4\ e^-$ (oxidation half reaction)

Combine the two half reactions.

$4\ [Fe(CN)_6]^{3-}(aq) + N_2H_4(aq) + 4\ OH^-(aq) \rightarrow$

$4\ [Fe(CN)_6]^{4-}(aq) + N_2(g) + 4\ H_2O(l)$

(b) $Cl_2(g) \rightarrow Cl^-(aq)$
$Cl_2(g) \rightarrow 2\ Cl^-(aq)$
$Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ (reduction half reaction)

$SeO_3^{2-}(aq) \rightarrow SeO_4^{2-}(aq)$
$SeO_3^{2-}(aq) + H_2O(l) \rightarrow SeO_4^{2-}(aq)$
$SeO_3^{2-}(aq) + H_2O(l) \rightarrow SeO_4^{2-}(aq) + 2\ H^+(aq)$
$SeO_3^{2-}(aq) + H_2O(l) \rightarrow SeO_4^{2-}(aq) + 2\ H^+(aq) + 2\ e^-$
$SeO_3^{2-}(aq) + H_2O(l) + 2\ OH^-(aq) \rightarrow SeO_4^{2-}(aq) + 2\ H^+(aq) + 2\ OH^-(aq) + 2\ e^-$
$SeO_3^{2-}(aq) + H_2O(l) + 2\ OH^-(aq) \rightarrow SeO_4^{2-}(aq) + 2\ H_2O(l) + 2\ e^-$
$SeO_3^{2-}(aq) + 2\ OH^-(aq) \rightarrow SeO_4^{2-}(aq) + H_2O(l) + 2\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$SeO_3^{2-}(aq) + Cl_2(g) + 2\ OH^-(aq) \rightarrow SeO_4^{2-}(aq) + 2\ Cl^-(aq) + H_2O(l)$

(c) $CoCl_2(aq) \rightarrow Co(OH)_3(s) + Cl^-(aq)$
$CoCl_2(aq) \rightarrow Co(OH)_3(s) + 2\ Cl^-(aq)$
$CoCl_2(aq) + 3\ H_2O(l) \rightarrow Co(OH)_3(s) + 2\ Cl^-(aq)$
$CoCl_2(aq) + 3\ H_2O(l) \rightarrow Co(OH)_3(s) + 2\ Cl^-(aq) + 3\ H^+(aq)$
$[CoCl_2(aq) + 3\ H_2O(l) \rightarrow Co(OH)_3(s) + 2\ Cl^-(aq) + 3\ H^+(aq) + e^-] \times 2$
(oxidation half reaction)
$HO_2^-(aq) \rightarrow H_2O(l)$
$HO_2^-(aq) \rightarrow 2\ H_2O(l)$
$3\ H^+(aq) + HO_2^-(aq) \rightarrow 2\ H_2O(l)$
$3\ H^+(aq) + HO_2^-(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$ (reduction half reaction)
Combine the two half reactions.
$2\ CoCl_2(aq) + 6\ H_2O(l) + 3\ H^+(aq) + HO_2^-(aq) \rightarrow$
$2\ Co(OH)_3(s) + 4\ Cl^-(aq) + 6\ H^+(aq) + 2\ H_2O(l)$
$2\ CoCl_2(aq) + 4\ H_2O(l) + HO_2^-(aq) \rightarrow 2\ Co(OH)_3(s) + 4\ Cl^-(aq) + 3\ H^+(aq)$
$2\ CoCl_2(aq) + 4\ H_2O(l) + HO_2^-(aq) + 3\ OH^-(aq) \rightarrow$
$2\ Co(OH)_3(s) + 4\ Cl^-(aq) + 3\ H^+(aq) + 3\ OH^-(aq)$
$2\ CoCl_2(aq) + 4\ H_2O(l) + HO_2^-(aq) + 3\ OH^-(aq) \rightarrow$
$2\ Co(OH)_3(s) + 4\ Cl^-(aq) + 3\ H_2O(l)$
$2\ CoCl_2(aq) + H_2O(l) + HO_2^-(aq) + 3\ OH^-(aq) \rightarrow 2\ Co(OH)_3(s) + 4\ Cl^-(aq)$

4.91 57.91 mL = 0.057 91 L

$$0.057\ 91\ L \times 0.1018\ mol\ Ce^{4+}\text{overL} \times \frac{1\ mol\ Fe^{2+}}{1\ mol\ Ce^{4+}} \times \frac{55.85\ g\ Fe^{2+}}{1\ mol\ Fe^{2+}} = 0.3292\ g\ Fe^{2+}$$

$$\text{mass \% Fe} = \frac{0.3292\ g}{1.2284\ g} \times 100\% = 26.80\%$$

4.92 (a) C_2H_6 H +1, C -3
(b) $Na_2B_4O_7$ O -2, Na +1, B +3
(c) Mg_2SiO_4 O -2, Mg +2, Si +4

4.93 (a) $PbO_2(s) \rightarrow Pb^{2+}(aq)$

$PbO_2(s) \rightarrow Pb^{2+}(aq) + 2\ H_2O(l)$

$4\ H^+(aq) + PbO_2(s) \rightarrow Pb^{2+}(aq) + 2\ H_2O(l)$

$[4\ H^+(aq) + PbO_2(s) + 2\ e^- \rightarrow Pb^{2+}(aq) + 2\ H_2O(l)] \times 5$ (reduction half reaction)

$Mn^{2+}(aq) \rightarrow MnO_4^-(aq)$

$4\ H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq)$

$4\ H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq) + 8\ H^+(aq)$

$[4\ H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-] \times 2$

(oxidation half reaction)

Combine the two half reactions.

$20\ H^+(aq) + 5\ PbO_2(s) + 8\ H_2O(l) + 2\ Mn^{2+}(aq) \rightarrow$

$5\ Pb^{2+}(aq) + 10\ H_2O(l) + 2\ MnO_4^-(aq) + 16\ H^+(aq)$

$4\ H^+(aq) + 5\ PbO_2(s) + 2\ Mn^{2+}(aq) \rightarrow 5\ Pb^{2+}(aq) + 2\ H_2O(l) + 2\ MnO_4^-(aq)$

(b) $As_2O_3(s) \rightarrow H_3AsO_4(aq)$

$As_2O_3(s) \rightarrow 2\ H_3AsO_4(aq)$

$5\ H_2O(l) + As_2O_3(s) \rightarrow 2\ H_3AsO_4(aq)$

$5\ H_2O(l) + As_2O_3(s) \rightarrow 2\ H_3AsO_4(aq) + 4\ H^+(aq)$

$5\ H_2O(l) + As_2O_3(s) \rightarrow 2\ H_3AsO_4(aq) + 4\ H^+(aq) + 4\ e^-$ (oxidation half reaction)

$NO_3^-(aq) \rightarrow HNO_2(aq)$

$NO_3^-(aq) \rightarrow HNO_2(aq) + H_2O(l)$

$3\ H^+(aq) + NO_3^-(aq) \rightarrow HNO_2(aq) + H_2O(l)$

$[3\ H^+(aq) + NO_3^-(aq) + 2\ e^- \rightarrow HNO_2(aq) + H_2O(l)] \times 2$

(reduction half reaction)

Combine the two half reactions.

$5\ H_2O(l) + As_2O_3(s) + 6\ H^+(aq) + 2\ NO_3^-(aq) \rightarrow$

$2\ H_3AsO_4(aq) + 4\ H^+(aq) + 2\ HNO_2(aq) + 2\ H_2O(l)$

$3\ H_2O(l) + As_2O_3(s) + 2\ H^+(aq) + 2\ NO_3^-(aq) \rightarrow 2\ H_3AsO_4(aq) + 2\ HNO_2(aq)$

(c) $Br_2(aq) \rightarrow Br^-(aq)$

$Br_2(aq) \rightarrow 2\ Br^-(aq)$

$Br_2(aq) + 2\ e^- \rightarrow 2\ Br^-(aq)$ (reduction half reaction)

$SO_2(g) \rightarrow HSO_4^-(aq)$

$2\ H_2O(l) + SO_2(g) \rightarrow HSO_4^-(aq)$

$2\ H_2O(l) + SO_2(g) \rightarrow HSO_4^-(aq) + 3\ H^+(aq)$

$2\ H_2O(l) + SO_2(g) \rightarrow HSO_4^-(aq) + 3\ H^+(aq) + 2\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$2\ H_2O(l) + Br_2(aq) + SO_2(g) \rightarrow 2\ Br^-(aq) + HSO_4^-(aq) + 3\ H^+(aq)$

(d) $I^-(aq) \rightarrow I_2(s)$
$2\ I^-(aq) \rightarrow I_2(s)$
$2\ I^-(aq) \rightarrow I_2(s) + 2\ e^-$ (oxidation half reaction)

$NO_2^-(aq) \rightarrow NO(g)$
$NO_2^-(aq) \rightarrow NO(g) + H_2O(l)$
$2\ H^+(aq) + NO_2^-(aq) \rightarrow NO(g) + H_2O(l)$
$[2\ H^+(aq) + NO_2^-(aq) + e^- \rightarrow NO(g) + H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$4\ H^+(aq) + 2\ NO_2^-(aq) + 2\ I^-(aq) \rightarrow 2\ NO(g) + I_2(s) + 2\ H_2O(l)$

4.94 (a) "Any element higher in the activity series will react with the ion of any element lower in the activity series."
$C + B^+ \rightarrow C^+ + B$; therefore C is higher than B.
$A^+ + D \rightarrow$ no reaction; therefore A is higher than D.
$C^+ + A \rightarrow$ no reaction; therefore C is higher than A.
$D + B^+ \rightarrow D^+ + B$; therefore D is higher than B.
The net result is C > A > D > B.
(b) (1) The reaction, $A^+ + C \rightarrow A + C^+$, will occur because C is above A in the activity series.
(2) The reaction, $A^+ + B \rightarrow A + B^+$, will not occur because B is below A in the activity series.

4.95 (a) $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$
(b) $Ag_2CrO_4(s) \rightleftharpoons 2\ Ag^+(aq) + CrO_4^{2-}(aq)$
$2x \qquad x$
In a saturated solution $2x = [Ag^+]$ and $x = [CrO_4^{2-}]$.
$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 1.1 \times 10^{-12} = (2x)^2(x) = 4x^3$; Solve for x; $x = 6.5 \times 10^{-5}$ M
$[Ag^+] = 2x = 2(6.5 \times 10^{-5}\ M) = 1.3 \times 10^{-4}$ M; $[CrO_4^{2-}] = x = 6.5 \times 10^{-5}$ M

4.96 $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^-(aq)$
$x \qquad 2x$
$[Mg^{2+}] = x = 2.6 \times 10^{-4}$ M and $[F^-] = 2x = 2(2.6 \times 10^{-4}\ M) = 5.2 \times 10^{-4}$ M in a saturated solution.
$K_{sp} = [Mg^{2+}][F^-]^2 = (2.6 \times 10^{-4}\ M)(5.2 \times 10^{-4}\ M)^2 = 7.0 \times 10^{-11}$

4.97 65.20 mL = 0.065 20 L

$$1.926 \text{ g succinic acid} \times \frac{1 \text{ mol succinic acid}}{118.1 \text{ g succinic acid}} = 0.016\ 31 \text{ mol succinic acid}$$

$$0.5000 \frac{\text{mol NaOH}}{1 \text{ L}} \times 0.065\ 20 \text{ L} = 0.032\ 60 \text{ mol NaOH}$$

$$\frac{0.032\ 60 \text{ mol NaOH}}{0.016\ 31 \text{ mol succinic acid}} = 2;$$ therefore succinic acid has two acidic hydrogens.

4.98 (a) Add HCl to precipitate Hg_2Cl_2. $Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$
(b) Add H_2SO_4 to precipitate $PbSO_4$. $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$
(c) Add Na_2CO_3 to precipitate $CaCO_3$. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
(d) Add Na_2SO_4 to precipitate $BaSO_4$. $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

4.99 (a) Add $AgNO_3$ to precipitate AgCl. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
(b) Add $NiCl_2$ to precipitate NiS. $Ni^{2+}(aq) + S^{2-}(aq) \rightarrow NiS(s)$
(c) Add $CaCl_2$ to precipitate $CaCO_3$. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
(d) Add $MgCl_2$ to precipitate $Mg(OH)_2$. $Mg^{2+}(aq) + 2\ OH^-(aq) \rightarrow Mg(OH)_2(s)$

4.100 All four reactions are redox reactions.

(a) $Mn(OH)_2(s) \rightarrow Mn(OH)_3(s)$
$Mn(OH)_2(s) + OH^-(aq) \rightarrow Mn(OH)_3(s)$
$[Mn(OH)_2(s) + OH^-(aq) \rightarrow Mn(OH)_3(s) + e^-] \times 2$ (oxidation half reaction)

$H_2O_2(aq) \rightarrow 2\ H_2O(l)$
$2\ H^+(aq) + H_2O_2(aq) \rightarrow 2\ H_2O(l)$
$2\ e^- + 2\ H^+(aq) + H_2O_2(aq) \rightarrow 2\ H_2O(l)$
$2\ e^- + 2\ OH^-(aq) + 2\ H^+(aq) + H_2O_2(aq) \rightarrow 2\ H_2O(l) + 2\ OH^-(aq)$
$2\ e^- + 2\ H_2O(l) + H_2O_2(aq) \rightarrow 2\ H_2O(l) + 2\ OH^-(aq)$
$2\ e^- + H_2O_2(aq) \rightarrow 2\ OH^-(aq)$ (reduction half reaction)

Combine the two half reactions.
$2\ Mn(OH)_2(s) + 2\ OH^-(aq) + H_2O_2(aq) \rightarrow 2\ Mn(OH)_3(s) + 2\ OH^-(aq)$
$2\ Mn(OH)_2(s) + H_2O_2(aq) \rightarrow 2\ Mn(OH)_3(s)$

(b) $[MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + e^-] \times 2$ (oxidation half reaction)

$MnO_4^{2-}(aq) \rightarrow MnO_2(s)$
$MnO_4^{2-}(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$4\ H^+(aq) + MnO_4^{2-}(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$2\ e^- + 4\ H^+(aq) + MnO_4^{2-}(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.
$4\ H^+(aq) + 3\ MnO_4^{2-}(aq) \rightarrow MnO_2(s) + 2\ MnO_4^-(aq) + 2\ H_2O(l)$

(c) $I^-(aq) \rightarrow I_3^-(aq)$

$3\ I^-(aq) \rightarrow I_3^-(aq)$

$[3\ I^-(aq) \rightarrow I_3^-(aq) + 2\ e^-] \times 8$ (oxidation half reaction)

$IO_3^-(aq) \rightarrow I_3^-(aq)$

$3\ IO_3^-(aq) \rightarrow I_3^-(aq)$

$3\ IO_3^-(aq) \rightarrow I_3^-(aq) + 9\ H_2O(l)$

$18\ H^+(aq) + 3\ IO_3^-(aq) \rightarrow I_3^-(aq) + 9\ H_2O(l)$

$16\ e^- + 18\ H^+(aq) + 3\ IO_3^-(aq) \rightarrow I_3^-(aq) + 9\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$24\ I^-(aq) + 3\ IO_3^-(aq) + 18\ H^+(aq) \rightarrow 9\ I_3^-(aq) + 9\ H_2O(l)$

Divide all coefficients by 3.

$8\ I^-(aq) + IO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_3^-(aq) + 3\ H_2O(l)$

(d) $P(s) \rightarrow HPO_3^{2-}(aq)$

$3\ H_2O(l) + P(s) \rightarrow HPO_3^{2-}(aq)$

$3\ H_2O(l) + P(s) \rightarrow HPO_3^{2-}(aq) + 5\ H^+(aq)$

$[3\ H_2O(l) + P(s) \rightarrow HPO_3^{2-}(aq) + 5\ H^+(aq) + 3\ e^-] \times 2$

(oxidation half reaction)

$PO_4^{3-}(aq) \rightarrow HPO_3^{2-}(aq)$

$PO_4^{3-}(aq) \rightarrow HPO_3^{2-}(aq) + H_2O(l)$

$3\ H^+(aq) + PO_4^{3-}(aq) \rightarrow HPO_3^{2-}(aq) + H_2O(l)$

$[2\ e^- + 3\ H^+(aq) + PO_4^{3-}(aq) \rightarrow HPO_3^{2-}(aq) + H_2O(l)] \times 3$

(reduction half reaction)

Combine the two half reactions and add OH^-.

$6\ H_2O(l) + 2\ P(s) + 9\ H^+(aq) + 3\ PO_4^{3-}(aq) \rightarrow 5\ HPO_3^{2-}(aq) + 10\ H^+(aq) + 3\ H_2O(l)$

$3\ H_2O(l) + 2\ P(s) + 3\ PO_4^{3-}(aq) \rightarrow 5\ HPO_3^{2-}(aq) + H^+(aq)$

$3\ H_2O(l) + 2\ P(s) + 3\ PO_4^{3-}(aq) + OH^-(aq) \rightarrow 5\ HPO_3^{2-}(aq) + H^+(aq) + OH^-(aq)$

$3\ H_2O(l) + 2\ P(s) + 3\ PO_4^{3-}(aq) + OH^-(aq) \rightarrow 5\ HPO_3^{2-}(aq) + H_2O(l)$

$2\ H_2O(l) + 2\ P(s) + 3\ PO_4^{3-}(aq) + OH^-(aq) \rightarrow 5\ HPO_3^{2-}(aq)$

4.101 100.0 mL = 0.1000 L; 47.14 mL = 0.047 14 L

mol HCl and HBr = mol H^+ = $0.1235 \frac{\text{mol NaOH}}{1\text{ L}} \times 0.047\ 14\text{ L} = 5.8218 \times 10^{-3}$ mol

mass of AgCl and AgBr = 0.9974 g; mol Ag = mol H^+ = 5.8218×10^{-3} mol

mass of Ag = 5.8218×10^{-3} mol Ag $\times \frac{107.87\text{ g Ag}}{1\text{ mol Ag}}$ = 0.6280 g Ag

mass of Cl and Br = 0.9974 g - 0.6280 g = 0.3694 g of Cl and Br

Let Y = moles Cl and Z = moles Br in 0.3694 g of Cl and Br.

Let (Y + Z) = moles Ag in 0.6280 g Ag.

For Ag: $0.6280\ g = (Y + Z) \times 107.87\ g$
For Cl and Br: $0.3694\ g = (Y \times 35.453\ g) + (Z \times 79.904\ g)$
Solve the simultaneous equations for Y and Z.
Rearrange the Ag equation: $\left(\frac{0.6280\ g}{107.87\ g} - Z\right) = Y$
Substitute for Y in the Cl and Br equation above and solve for Z.

$$0.3694\ g = \left[\left(\frac{0.6280\ g}{107.87\ g} - Z\right) \times 35.453\ g\right] + (Z \times 79.904\ g)$$

$$Z = \frac{0.1630}{44.451} = 3.667 \times 10^{-3}$$

$$Y = \left(\frac{0.6280\ g}{107.87\ g} - Z\right) = \left(\frac{0.6280\ g}{107.87\ g} - 3.667 \times 10^{-3}\right) = 2.155 \times 10^{-3}$$

$$\text{HCl molarity} = \frac{2.155 \times 10^{-3}\ mol}{0.1000\ L} = 0.021\ 55\ M$$

$$\text{HBr molarity} = \frac{3.667 \times 10^{-3}\ mol}{0.1000\ L} = 0.036\ 67\ M$$

4.102 (a) $S_4O_6^{2-}(aq) \rightarrow H_2S(aq)$
$S_4O_6^{2-}(aq) \rightarrow 4\ H_2S(aq)$
$S_4O_6^{2-}(aq) \rightarrow 4\ H_2S(aq) + 6\ H_2O(l)$
$20\ H^+(aq) + S_4O_6^{2-}(aq) \rightarrow 4\ H_2S(aq) + 6\ H_2O(l)$
$18\ e^- + 20\ H^+(aq) + S_4O_6^{2-}(aq) \rightarrow 4\ H_2S(aq) + 6\ H_2O(l)$ (reduction half reaction)

$Al(s) \rightarrow Al^{3+}(aq)$
$[Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-] \times 6$ (oxidation half reaction)

Combine the two half reactions.
$20\ H^+(aq) + S_4O_6^{2-}(aq) + 6\ Al(s) \rightarrow 4\ H_2S(aq) + 6\ Al^{3+}(aq) + 6\ H_2O(l)$

(b) $S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$[2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$
$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq)$
$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
$14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$
$6\ e^- + 14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$14\ H^+(aq) + 6\ S_2O_3^{2-}(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3\ S_4O_6^{2-}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

(c) $ClO_3^-(aq) \rightarrow Cl^-(aq)$
$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$
$6\ H^+(aq) + ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$
$[6\ e^- + 6\ H^+(aq) + ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)] \times 14$ (reduction half reaction)

$As_2S_3(s) \rightarrow H_2AsO_4^-(aq) + HSO_4^-(aq)$
$As_2S_3(s) \rightarrow 2\ H_2AsO_4^-(aq) + 3\ HSO_4^-(aq)$
$20\ H_2O(l) + As_2S_3(s) \rightarrow 2\ H_2AsO_4^-(aq) + 3\ HSO_4^-(aq)$
$20\ H_2O(l) + As_2S_3(s) \rightarrow 2\ H_2AsO_4^-(aq) + 3\ HSO_4^-(aq) + 33\ H^+(aq)$

$[20\ H_2O(l) + As_2S_3(s) \rightarrow 2\ H_2AsO_4^-(aq) + 3\ HSO_4^-(aq) + 33\ H^+(aq) + 28\ e^-] \times 3$
(oxidation half reaction)

Combine the two half reactions.
$84\ H^+(aq) + 60\ H_2O(l) + 14\ ClO_3^-(aq) + 3\ As_2S_3(s) \rightarrow$
$14\ Cl^-(aq) + 6\ H_2AsO_4^-(aq) + 9\ HSO_4^-(aq) + 42\ H_2O(l) + 99\ H^+(aq)$
$18\ H_2O(l) + 14\ ClO_3^-(aq) + 3\ As_2S_3(s) \rightarrow$
$14\ Cl^-(aq) + 6\ H_2AsO_4^-(aq) + 9\ HSO_4^-(aq) + 15\ H^+(aq)$

(d) $IO_3^-(aq) \rightarrow I^-(aq)$
$IO_3^-(aq) \rightarrow I^-(aq) + 3\ H_2O(l)$
$6\ H^+(aq) + IO_3^-(aq) \rightarrow I^-(aq) + 3\ H_2O(l)$
$[6\ e^- + 6\ H^+(aq) + IO_3^-(aq) \rightarrow I^-(aq) + 3\ H_2O(l)] \times 7$ (reduction half reaction)

$Re(s) \rightarrow ReO_4^-(aq)$
$4\ H_2O(l) + Re(s) \rightarrow ReO_4^-(aq)$
$4\ H_2O(l) + Re(s) \rightarrow ReO_4^-(aq) + 8\ H^+(aq)$
$[4\ H_2O(l) + Re(s) \rightarrow ReO_4^-(aq) + 8\ H^+(aq) + 7\ e^-] \times 6$ (oxidation half reaction)

Combine the two half reactions.
$42\ H^+(aq) + 24\ H_2O(l) + 7\ IO_3^-(aq) + 6\ Re(s) \rightarrow$
$7\ I^-(aq) + 6\ ReO_4^-(aq) + 21\ H_2O(l) + 48\ H^+(aq)$
$3\ H_2O(l) + 7\ IO_3^-(aq) + 6\ Re(s) \rightarrow 7\ I^-(aq) + 6\ ReO_4^-(aq) + 6\ H^+(aq)$
(e) $HSO_4^-(aq) + Pb_3O_4(s) \rightarrow PbSO_4(s)$
$3\ HSO_4^-(aq) + Pb_3O_4(s) \rightarrow 3\ PbSO_4(s)$
$3\ HSO_4^-(aq) + Pb_3O_4(s) \rightarrow 3\ PbSO_4(s) + 4\ H_2O(l)$
$5\ H^+(aq) + 3\ HSO_4^-(aq) + Pb_3O_4(s) \rightarrow 3\ PbSO_4(s) + 4\ H_2O(l)$
$[2\ e^- + 5\ H^+(aq) + 3\ HSO_4^-(aq) + Pb_3O_4(s) \rightarrow 3\ PbSO_4(s) + 4\ H_2O(l)] \times 10$
(reduction half reaction)

$As_4(s) \rightarrow H_2AsO_4^-(aq)$
$As_4(s) \rightarrow 4\ H_2AsO_4^-(aq)$

$16\ H_2O(l) + As_4(s) \rightarrow 4\ H_2AsO_4^-(aq)$
$16\ H_2O(l) + As_4(s) \rightarrow 4\ H_2AsO_4^-(aq) + 24\ H^+(aq)$
$16\ H_2O(l) + As_4(s) \rightarrow 4\ H_2AsO_4^-(aq) + 24\ H^+(aq) + 20\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$26\ H^+(aq) + 30\ HSO_4^-(aq) + As_4(s) + 10\ Pb_3O_4(s) \rightarrow$
$4\ H_2AsO_4^-(aq) + 30\ PbSO_4(s) + 24\ H_2O(l)$

(f) $HNO_2(aq) \rightarrow NO_3^-(aq)$
$H_2O(l) + HNO_2(aq) \rightarrow NO_3^-(aq)$
$H_2O(l) + HNO_2(aq) \rightarrow NO_3^-(aq) + 3\ H^+(aq)$
$H_2O(l) + HNO_2(aq) \rightarrow NO_3^-(aq) + 3\ H^+(aq) + 2\ e^-$ (oxidation half reaction)

$HNO_2(aq) \rightarrow NO(g)$
$HNO_2(aq) \rightarrow NO(g) + H_2O(l)$
$H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)$
$[1\ e^- + H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$3\ HNO_2(aq) \rightarrow NO_3^-(aq) + 2\ NO(g) + H_2O(l) + H^+(aq)$

4.103 (a) $C_4H_4O_6^{2-}(aq) \rightarrow CO_3^{2-}(aq)$
$C_4H_4O_6^{2-}(aq) \rightarrow 4\ CO_3^{2-}(aq)$
$C_4H_4O_6^{2-}(aq) + 6\ H_2O(l) \rightarrow 4\ CO_3^{2-}(aq)$

$C_4H_4O_6^{2-}(aq) + 6\ H_2O(l) \rightarrow 4\ CO_3^{2-}(aq) + 16\ H^+(aq)$
$[C_4H_4O_6^{2-}(aq) + 6\ H_2O(l) \rightarrow 4\ CO_3^{2-}(aq) + 16\ H^+(aq) + 10\ e^-] \times 3$
(oxidation half reaction)

$ClO_3^-(aq) \rightarrow Cl^-(aq)$
$ClO_3^-(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$
$ClO_3^-(aq) + 6\ H^+(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)$
$[6\ e^- + ClO_3^-(aq) + 6\ H^+(aq) \rightarrow Cl^-(aq) + 3\ H_2O(l)] \times 5$ (reduction half reaction)

Combine the two half reactions.
$3\ C_4H_4O_6^{2-}(aq) + 18\ H_2O(l) + 5\ ClO_3^-(aq) + 30\ H^+(aq) \rightarrow$
$12\ CO_3^{2-}(aq) + 48\ H^+(aq) + 5\ Cl^-(aq) + 15\ H_2O(l)$
$3\ C_4H_4O_6^{2-}(aq) + 3\ H_2O(l) + 5\ ClO_3^-(aq) \rightarrow 12\ CO_3^{2-}(aq) + 18\ H^+(aq) + 5\ Cl^-(aq)$
$3\ C_4H_4O_6^{2-}(aq) + 3\ H_2O(l) + 5\ ClO_3^-(aq) + 18\ OH^-(aq) \rightarrow$
$12\ CO_3^{2-}(aq) + 18\ H^+(aq) + 18\ OH^-(aq) + 5\ Cl^-(aq)$
$3\ C_4H_4O_6^{2-}(aq) + 3\ H_2O(l) + 5\ ClO_3^-(aq) + 18\ OH^-(aq) \rightarrow$
$12\ CO_3^{2-}(aq) + 18\ H_2O(aq) + 5\ Cl^-(aq)$
$3\ C_4H_4O_6^{2-}(aq) + 5\ ClO_3^-(aq) + 18\ OH^-(aq) \rightarrow 12\ CO_3^{2-}(aq) + 15\ H_2O(l) + 5\ Cl^-(aq)$

(b) $Al(s) \rightarrow Al(OH)_4^-(aq)$

$Al(s) + 4\ OH^-(aq) \rightarrow Al(OH)_4^-(aq)$

$[Al(s) + 4\ OH^-(aq) \rightarrow Al(OH)_4^-(aq) + 3\ e^-] \times 11$ (oxidation half reaction)

$BiONO_3(s) \rightarrow Bi(s) + NH_3(aq)$

$BiONO_3(s) \rightarrow Bi(s) + NH_3(aq) + 4\ H_2O(l)$

$BiONO_3(s) + 11\ H^+(aq) \rightarrow Bi(s) + NH_3(aq) + 4\ H_2O(l)$

$[BiONO_3(s) + 11\ H^+(aq) + 11\ e^- \rightarrow Bi(s) + NH_3(aq) + 4\ H_2O(l)] \times 3$ (reduction half reaction)

Combine the two half reactions.

$11\ Al(s) + 44\ OH^-(aq) + 3\ BiONO_3(s) + 33\ H^+(aq) \rightarrow 11\ Al(OH)_4^-(aq) + 3\ Bi(s) + 3\ NH_3(aq) + 12\ H_2O(l)$

$11\ Al(s) + 11\ OH^-(aq) + 3\ BiONO_3(s) + 33\ H_2O(l) \rightarrow 11\ Al(OH)_4^-(aq) + 3\ Bi(s) + 3\ NH_3(aq) + 12\ H_2O(l)$

$11\ Al(s) + 11\ OH^-(aq) + 3\ BiONO_3(s) + 21\ H_2O(l) \rightarrow 11\ Al(OH)_4^-(aq) + 3\ Bi(s) + 3\ NH_3(aq)$

(c) $H_2O_2(aq) \rightarrow O_2(g)$

$H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq)$

$[H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-] \times 4$ (oxidation half reaction)

$Cl_2O_7(aq) \rightarrow ClO_2^-(aq)$

$Cl_2O_7(aq) \rightarrow 2\ ClO_2^-(aq)$

$Cl_2O_7(aq) \rightarrow 2\ ClO_2^-(aq) + 3\ H_2O(l)$

$Cl_2O_7(aq) + 6\ H^+(aq) \rightarrow 2\ ClO_2^-(aq) + 3\ H_2O(l)$

$Cl_2O_7(aq) + 6\ H^+(aq) + 8\ e^- \rightarrow 2\ ClO_2^-(aq) + 3\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$4\ H_2O_2(aq) + Cl_2O_7(aq) + 6\ H^+(aq) \rightarrow 4\ O_2(g) + 8\ H^+(aq) + 2\ ClO_2^-(aq) + 3\ H_2O(l)$

$4\ H_2O_2(aq) + Cl_2O_7(aq) \rightarrow 4\ O_2(g) + 2\ H^+(aq) + 2\ ClO_2^-(aq) + 3\ H_2O(l)$

$4\ H_2O_2(aq) + Cl_2O_7(aq) + 2\ OH^-(aq) \rightarrow 4\ O_2(g) + 2\ H^+(aq) + 2\ OH^-(aq) + 2\ ClO_2^-(aq) + 3\ H_2O(l)$

$4\ H_2O_2(aq) + Cl_2O_7(aq) + 2\ OH^-(aq) \rightarrow 4\ O_2(g) + 2\ ClO_2^-(aq) + 5\ H_2O(l)$

(d) $Tl_2O_3(s) \rightarrow TlOH(s)$

$Tl_2O_3(s) \rightarrow 2\ TlOH(s)$

$Tl_2O_3(s) \rightarrow 2\ TlOH(s) + H_2O(l)$

$Tl_2O_3(s) + 4\ H^+(aq) \rightarrow 2\ TlOH(s) + H_2O(l)$

$Tl_2O_3(s) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ TlOH(s) + H_2O(l)$ (reduction half reaction)

$NH_2OH(aq) \rightarrow N_2(g)$

$2\ NH_2OH(aq) \rightarrow N_2(g)$

$2\ NH_2OH(aq) \rightarrow N_2(g) + 2\ H_2O(l)$

$2\ NH_2OH(aq) \rightarrow N_2(g) + 2\ H_2O(l) + 2\ H^+(aq)$

$[2\ NH_2OH(aq) \rightarrow N_2(g) + 2\ H_2O(l) + 2\ H^+(aq) + 2\ e^-] \times 2$ (oxidation half reaction)

Combine the two half reactions.
$Tl_2O_3(s) + 4\ H^+(aq) + 4\ NH_2OH(aq) \rightarrow 2\ TlOH(s) + 2\ N_2(g) + 5\ H_2O(l) + 4\ H^+(aq)$
$Tl_2O_3(s) + 4\ NH_2OH(aq) \rightarrow 2\ TlOH(s) + 2\ N_2(g) + 5\ H_2O(l)$

(e) $Cu(NH_3)_4^{2+}(aq) \rightarrow Cu(s) + 4\ NH_3(aq)$
$Cu(NH_3)_4^{2+}(aq) + 2\ e^- \rightarrow Cu(s) + 4\ NH_3(aq)$ (reduction half reaction)

$S_2O_4^{2-}(aq) \rightarrow SO_3^{2-}(aq)$
$S_2O_4^{2-}(aq) \rightarrow 2\ SO_3^{2-}(aq)$
$S_2O_4^{2-}(aq) + 2\ H_2O(l) \rightarrow 2\ SO_3^{2-}(aq)$
$S_2O_4^{2-}(aq) + 2\ H_2O(l) \rightarrow 2\ SO_3^{2-}(aq) + 4\ H^+(aq)$
$S_2O_4^{2-}(aq) + 2\ H_2O(l) \rightarrow 2\ SO_3^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$Cu(NH_3)_4^{2+}(aq) + S_2O_4^{2-}(aq) + 2\ H_2O(l) \rightarrow Cu(s) + 4\ NH_3(aq) + 2\ SO_3^{2-}(aq) + 4\ H^+(aq)$
$Cu(NH_3)_4^{2+}(aq) + S_2O_4^{2-}(aq) + 2\ H_2O(l) + 4\ OH^-(aq) \rightarrow$
$Cu(s) + 4\ NH_3(aq) + 2\ SO_3^{2-}(aq) + 4\ H^+(aq) + 4\ OH^-(aq)$
$Cu(NH_3)_4^{2+}(aq) + S_2O_4^{2-}(aq) + 2\ H_2O(l) + 4\ OH^-(aq) \rightarrow$
$Cu(s) + 4\ NH_3(aq) + 2\ SO_3^{2-}(aq) + 4\ H_2O(l)$
$Cu(NH_3)_4^{2+}(aq) + S_2O_4^{2-}(aq) + 4\ OH^-(aq) \rightarrow$
$Cu(s) + 4\ NH_3(aq) + 2\ SO_3^{2-}(aq) + 2\ H_2O(l)$

(f) $Mn(OH)_2(s) \rightarrow MnO_2(s)$
$Mn(OH)_2(s) \rightarrow MnO_2(s) + 2\ H^+(aq)$
$[Mn(OH)_2(s) \rightarrow MnO_2(s) + 2\ H^+(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

$MnO_4^-(aq) \rightarrow MnO_2(s)$
$MnO_4^-(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$MnO_4^-(aq) + 4\ H^+(aq) \rightarrow MnO_2(s) + 2\ H_2O(l)$
$[MnO_4^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow MnO_2(s) + 2\ H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$3\ Mn(OH)_2(s) + 2\ MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ MnO_2(s) + 6\ H^+(aq) + 4\ H_2O(l)$
$3\ Mn(OH)_2(s) + 2\ MnO_4^-(aq) + 2\ H^+(aq) \rightarrow 5\ MnO_2(s) + 4\ H_2O(l)$
$3\ Mn(OH)_2(s) + 2\ MnO_4^-(aq) + 2\ H^+(aq) + 2\ OH^-(aq) \rightarrow$
$5\ MnO_2(s) + 4\ H_2O(l) + 2\ OH^-(aq)$
$3\ Mn(OH)_2(s) + 2\ MnO_4^-(aq) + 2\ H_2O(l) \rightarrow 5\ MnO_2(s) + 4\ H_2O(l) + 2\ OH^-(aq)$
$3\ Mn(OH)_2(s) + 2\ MnO_4^-(aq) \rightarrow 5\ MnO_2(s) + 2\ H_2O(l) + 2\ OH^-(aq)$

4.104 CuO, 79.55 amu; Cu_2O, 143.09 amu
Let X equal the mass of CuO and Y the mass of Cu_2O in the 10.50 g mixture. Therefore,

X + Y = 10.50 g.

$$\text{mol Cu} = 8.66\ \text{g} \times \frac{1\ \text{mol Cu}}{63.546\ \text{g Cu}} = 0.1363\ \text{mol Cu}$$

$$\text{mol CuO} + 2 \times \text{mol Cu}_2\text{O} = 0.1363\ \text{mol Cu}$$

$$X \times \frac{1\ \text{mol CuO}}{79.55\ \text{g CuO}} + 2 \times \left(Y \times \frac{1\ \text{mol Cu}_2\text{O}}{143.09\ \text{g Cu}_2\text{O}} \right) = 0.1363\ \text{mol Cu}$$

Rearrange to get X = 10.50 g - Y and then substitute it into the equation above to solve for Y.

$$(10.50\ \text{g} - Y) \times \frac{1\ \text{mol CuO}}{79.55\ \text{g CuO}} + 2 \times \left(Y \times \frac{1\ \text{mol Cu}_2\text{O}}{143.09\ \text{g Cu}_2\text{O}} \right) = 0.1363\ \text{mol Cu}$$

$$\frac{10.50\ \text{mol}}{79.55} - \frac{Y\ \text{mol}}{79.55\ \text{g}} + \frac{2\ Y\ \text{mol}}{143.09\ \text{g}} = 0.1363\ \text{mol}$$

$$-\frac{Y\ \text{mol}}{79.55\ \text{g}} + \frac{2\ Y\ \text{mol}}{143.09\ \text{g}} = 0.1363\ \text{mol} - \frac{10.50\ \text{mol}}{79.55} = 0.0043\ \text{mol}$$

$$\frac{(-Y\ \text{mol})(143.09\ \text{g}) + (2\ Y\ \text{mol})(79.55\ \text{g})}{(79.55\ \text{g})(143.09\ \text{g})} = 0.0043\ \text{mol}$$

$$\frac{16.01\ Y\ \text{mol}}{11383\ \text{g}} = 0.0043\ \text{mol}; \quad \frac{16.01\ Y}{11383\ \text{g}} = 0.0043$$

Y = (0.0043)(11383 g)/16.01 = 3.06 g Cu_2O

X = 10.50 g - Y = 10.50 g - 3.06 g = 7.44 g CuO

4.105 (a) PbI_2, 461.01 amu

$Pb(NO_3)_2(aq) + 2\ KI(aq) \rightarrow PbI_2(s) + 2\ KNO_3(aq)$

75.0 mL = 0.0750 L and 100.0 mL = 0.1000 L

mol $Pb(NO_3)_2$ = (0.0750 L)(0.100 mol/L) = 7.50×10^{-3} mol $Pb(NO_3)_2$

mol KI = (0.1000 L)(0.190 mol/L) = 1.90×10^{-2} mol KI

$$\text{mols KI needed} = 7.50 \times 10^{-3}\ \text{mol Pb(NO}_3\text{)}_2 \times \frac{2\ \text{mol KI}}{1\ \text{mol Pb(NO}_3\text{)}_2} = 1.50 \times 10^{-2}\ \text{mol KI}$$

There is an excess of KI, so $Pb(NO_3)_2$ is the limiting reactant.

$$\text{mass PbI}_2 = 7.50 \times 10^{-3}\ \text{mol Pb(NO}_3\text{)}_2 \times \frac{1\ \text{mol PbI}_2}{1\ \text{mol Pb(NO}_3\text{)}_2} \times \frac{461.01\ \text{g PbI}_2}{1\ \text{mol PbI}_2} = 3.46\ \text{g PbI}_2$$

(b) Because $Pb(NO_3)_2$ is the limiting reactant, Pb^{2+} is totally consumed and $[Pb^{2+}] = 0$.

mol K^+ = mol KI = 1.90×10^{-2} mol

$$\text{mol NO}_3^- = 7.50 \times 10^{-3}\ \text{mol Pb(NO}_3\text{)}_2 \times \frac{2\ \text{mol NO}_3^-}{1\ \text{mol Pb(NO}_3\text{)}_2} = 0.0150\ \text{mol NO}_3^-$$

mol I^- = (initial mol KI) - (mol KI needed) = 0.0190 mol - 0.0150 mol = 0.0040 mol I^-

total volume = 0.0750 L + 0.1000 L = 0.1750 L

$$[K^+] = \frac{0.0190\ mol}{0.1750\ L} = 0.109\ M$$

$$[NO_3^-] = \frac{0.0150\ mol}{0.1750\ L} = 0.0857\ M$$

$$[I^-] = \frac{0.0040\ mol}{0.1750\ L} = 0.023\ M$$

Multi-Concept Problems

4.106 NaOH, 40.00 amu; $Ba(OH)_2$, 171.34 amu

Let X equal the mass of NaOH and Y the mass of $Ba(OH)_2$ in the 10.0 g mixture.

Therefore, X + Y = 10.0 g.

$$\text{mol HCl} = 108.9\ mL \times \frac{1\ L}{1000\ mL} \times \frac{1.50\ mol\ HCl}{1\ L} = 0.163\ \text{mol HCl}$$

$$\text{mol NaOH} + 2 \times \text{mol } Ba(OH)_2 = 0.163\ \text{mol HCl}$$

$$X \times \frac{1\ mol\ NaOH}{40.00\ g\ NaOH} + 2 \times \left(Y \times \frac{1\ mol\ Ba(OH)_2}{171.34\ g\ Ba(OH)_2} \right) = 0.163\ \text{mol HCl}$$

Rearrange to get X = 10.0 g - Y and then substitute it into the equation above to solve for Y.

$$(10.0\ g - Y) \times \frac{1\ mol\ NaOH}{40.00\ g\ NaOH} + 2 \times \left(Y \times \frac{1\ mol\ Ba(OH)_2}{171.34\ g\ Ba(OH)_2} \right) = 0.163\ \text{mol HCl}$$

$$\frac{10.00\ mol}{40.00} - \frac{Y\ mol}{40.00\ g} + \frac{2\ Y\ mol}{171.34\ g} = 0.163\ \text{mol}$$

$$-\frac{Y\ mol}{40.00\ g} + \frac{2\ Y\ mol}{171.34\ g} = 0.163\ mol - \frac{10.00\ mol}{40.00} = -0.087\ \text{mol}$$

$$\frac{(-Y\ mol)(171.34\ g) + (2\ Y\ mol)(40.00\ g)}{(40.00\ g)(171.34\ g)} = -0.087\ \text{mol}$$

$$\frac{-91.34\ Y\ mol}{6853.6\ g} = -0.087\ mol; \quad \frac{91.34\ Y}{6853.6\ g} = 0.087$$

Y = (0.087)(6853.6 g)/91.34 = 6.5 g $Ba(OH)_2$

X = 10.0 g - Y = 10.0 g - 6.5 g = 3.5 g NaOH

4.107 100.0 mL = 0.1000 L and 50.0 mL = 0.0500 L

mol Na_2SO_4 = (0.1000 L)(0.100 mol/L) = 0.0100 mol Na_2SO_4

mol SO_4^{2-} = mol Na_2SO_4 = 0.0100 mol SO_4^{2-}

$$\text{mol } Na^+ = 0.0100\ \text{mol } Na_2SO_4 \times \frac{2\ mol\ Na^+}{1\ mol\ Na_2SO_4} = 0.0200\ \text{mol } Na^+$$

mol $ZnCl_2$ = (0.0500 L)(0.300 mol/L) = 0.0150 mol $ZnCl_2$

mol Zn^{2+} = mol $ZnCl_2$ = 0.0150 mol Zn^{2+}

$$\text{mol } Cl^- = 0.0150\ \text{mol } ZnCl_2 \times \frac{2\ mol\ Cl^-}{1\ mol\ ZnCl_2} = 0.0300\ \text{mol } Cl^-$$

mol $Ba(CN)_2$ = (0.1000 L)(0.200 mol/L) = 0.0200 mol $Ba(CN)_2$

mol Ba^{2+} = mol $Ba(CN)_2$ = 0.0200 mol Ba^{2+}

mol CN^- = 0.0200 mol $Ba(CN)_2$ x $\frac{2 \text{ mol } CN^-}{1 \text{ mol } Ba(CN)_2}$ = 0.0400 mol CN^-

The following two reactions will take place to form precipitates.

$Zn^{2+}(aq) + 2\ CN^-(aq) \rightarrow Zn(CN)_2(s)$

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

For Zn^{2+}, mol CN^- needed = 0.0150 mol Zn^{2+} x $\frac{2 \text{ mol } CN^-}{1 \text{ mol } Zn^{2+}}$ = 0.0300 mol CN^- needed

CN^- is in excess, so Zn^{2+} is the limiting reactant and is totally consumed.

mol CN^- remaining after reaction= 0.0400 mol - 0.0300 mol = 0.0100 mol CN^-

For Ba^{2+}, mol SO_4^{2-} needed = mol Ba^{2+} = 0.0200 mol SO_4^{2-} needed

Ba^{2+} is in excess, so SO_4^{2-} is the limiting reactant and is totally consumed.

mol Ba^{2+} remaining after reaction = 0.0200 mol - 0.0100 mol = 0.0100 mol Ba^{2+}

total volume = 0.1000 L + 0.0500 L + 0.1000 L = 0.2500 L

$[Zn^{2+}] = 0$

$[SO_4^{2-}] = 0$

$[Na^+] = \frac{0.0200 \text{ mol}}{0.2500 \text{ L}} = 0.0800 \text{ M}$

$[Cl^-] = \frac{0.0300 \text{ mol}}{0.2500 \text{ L}} = 0.120 \text{ M}$

$[CN^-] = \frac{0.0100 \text{ mol}}{0.2500 \text{ L}} = 0.0400 \text{ M}$

$[Ba^{2+}] = \frac{0.0100 \text{ mol}}{0.2500 \text{ L}} = 0.0400 \text{ M}$

4.108 KNO_3, 101.10 amu; $BaCl_2$, 208.24 amu; NaCl, 58.44 amu; $BaSO_4$, 233.40 amu; AgCl, 143.32 amu

(a) The two precipitates are $BaSO_4(s)$ and AgCl(s).

(b) H_2SO_4 only reacts with $BaCl_2$.

$H_2SO_4(aq) + BaCl_2(aq) \rightarrow BaSO_4(s) + 2\ HCl(aq)$

Calculate the number of moles of $BaCl_2$ in 100.0 g of the mixture.

mol $BaCl_2$ = 67.3 g $BaSO_4$ x $\frac{1 \text{ mol } BaSO_4}{233.40 \text{ g } BaSO_4}$ x $\frac{1 \text{ mol } BaCl_2}{1 \text{ mol } BaSO_4}$ = 0.288 mol $BaCl_2$

Calculate mass and moles of $BaCl_2$ in 250.0 g sample.

mass $BaCl_2$ = 0.288 mol $BaCl_2$ x $\frac{208.24 \text{ g } BaCl_2}{1 \text{ mol } BaCl_2}$ x $\frac{250.0 \text{ g}}{100.0 \text{ g}}$ = 150. g $BaCl_2$

mol $BaCl_2$ = 150. g $BaCl_2$ x $\frac{1 \text{ mol } BaCl_2}{208.24 \text{ g } BaCl_2}$ = 0.720 mol $BaCl_2$

$AgNO_3$ reacts with both NaCl and $BaCl_2$ in the remaining 150.0 g of the mixture.

$3\ AgNO_3(aq) + NaCl(aq) + BaCl_2(aq) \rightarrow 3\ AgCl(s) + NaNO_3(aq) + Ba(NO_3)_2(aq)$

Calculate the moles of AgCl that would have been produced from the 250.0 g mixture.

mol AgCl = 197.6 g AgCl x $\frac{1\ \text{mol AgCl}}{143.32\ \text{g AgCl}}$ x $\frac{250.0\ \text{g}}{150.0\ \text{g}}$ = 2.30 mol AgCl

mol AgCl = 2 x (mol $BaCl_2$) + mol NaCl

Calculate the moles and mass of NaCl in the 250.0 g mixture.

2.30 mol AgCl = 2 x 0.720 mol $BaCl_2$ + mol NaCl

mol NaCl = 2.30 mol - 2(0.720 mol) = 0.86 mol NaCl

mass NaCl = 0.86 mol NaCl x $\frac{58.44\ \text{g NaCl}}{1\ \text{mol NaCl}}$ = 50. g NaCl

Calculate the mass of KNO_3 in the 250.0 g mixture.

total mass = mass $BaCl_2$ + mass NaCl + mass KNO_3

250.0 g = 150. g $BaCl_2$ + 50. g NaCl + mass KNO_3

mass KNO_3 = 250.0 g - 150. g $BaCl_2$ - 50. g NaCl = 50. g KNO_3

4.109 100.0 mL = 0.1000 L; 50.0 mL = 0.0500 L; 250.0 mL = 0.2500 L

After step (2):

$BaCl_2(aq) + 2\ AgNO_3(aq) \rightarrow AgCl(s) + Ba(NO_3)_2(aq)$

mol $BaCl_2$ = (0.1000 L)(0.100 mol/L) = 0.0100 mol $BaCl_2$

mol Ba^{2+} = mol $BaCl_2$ = 0.0100 mol Ba^{2+}

mol Cl^- = 0.0100 mol $BaCl_2$ x $\frac{2\ \text{mol Cl}^-}{1\ \text{mol BaCl}_2}$ = 0.0200 mol Cl^-

mol $AgNO_3$ = (0.0500 L)(0.100 mol/L) = 0.00500 mol $AgNO_3$

mol Ag^+ = mol $AgNO_3$ = 0.00500 mol Ag^+

mol NO_3^- = mol $AgNO_3$ = 0.00500 mol NO_3^-

0.00500 mol Ag^+ requires only 0.00500 mol Cl^-, so Ag^+ is the limiting reactant and totally consumed.

mol Cl^- remaining after reaction = 0.0200 mol - 0.00500 mol = 0.0150 mol Cl^-

After step (3):

$Ba^{2+}(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2\ H^+(aq)$

mol H_2SO_4 = (0.0500 L)(0.100 mol/L) = 0.00500 mol H_2SO_4

mol SO_4^{2-} = mol H_2SO_4 = 0.00500 mol SO_4^{2-}

mol H^+ = 0.00500 mol H_2SO_4 x $\frac{2\ \text{mol H}^+}{1\ \text{mol H}_2\text{SO}_4}$ = 0.0100 mol H^+

0.0100 mol Ba^{2+} requires 0.0100 mol SO_4^{2-}, so SO_4^{2-} is the limiting reactant and is totally consumed.

mol Ba^{2+} remaining after reaction = 0.0100 mol - 0.00500 mol = 0.00500 mol Ba^{2+}

After step (4):

$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

mol NH_3 = (0.2500 L)(0.100 mol/L) = 0.0250 mol NH_3

0.0250 mol NH_3 requires 0.0250 mol H^+, so H^+ is the limiting reactant and is totally consumed.

mol NH_3 remaining after reaction = 0.0250 mol - 0.0100 mol = 0.0150 mol NH_3

mol NH_4^+ = mol H^+ before reaction = 0.0100 mol NH_4^+

total volume = 0.1000 L + 0.0500 L + 0.0500 L + 0.2500 L = 0.4500 L

$[Ba^{2+}] = \frac{0.00500\ mol}{0.4500\ L} = 0.0111\ M$

$[Cl^-] = \frac{0.0150\ mol}{0.4500\ L} = 0.0333\ M$

$[NO_3^-] = \frac{0.00500\ mol}{0.4500\ L} = 0.0111\ M$

$[NH_3] = \frac{0.0150\ mol}{0.4500\ L} = 0.0333\ M$

$[NH_4^+] = \frac{0.0100\ mol}{0.4500\ L} = 0.0222\ M$

4.110 (a) $Cr^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

$[Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^-] \times 6$ (oxidation half reaction)

$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq)$

$Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

$6\ e^- + 14\ H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.

$14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 6\ Cr^{2+}(aq) \rightarrow 8\ Cr^{3+}(aq) + 7\ H_2O(l)$

(b) total volume = 100.0 ml + 20.0 mL = 120.0 mL = 0.1200 L

Initial moles:

$0.120\ \frac{mol\ Cr(NO_3)_2}{1\ L} \times 0.1000\ L = 0.0120\ mol\ Cr(NO_3)_2$

$0.500\ \frac{mol\ HNO_3}{1\ L} \times 0.1000\ L = 0.0500\ mol\ HNO_3$

$0.250\ \frac{mol\ K_2Cr_2O_7}{1\ L} \times 0.0200\ L = 0.005\ 00\ mol\ K_2Cr_2O_7$

Check for the limiting reactant. 0.0120 mol of Cr^{2+} requires (0.0120)/6 = 0.00200 mol $Cr_2O_7^{2-}$ and (14/6)(0.0120) = 0.0280 mol H^+. Both are in excess of the required amounts, so Cr^{2+} is the limiting reactant.

	$14\ H^+(aq)$	$+\ Cr_2O_7^{2-}(aq)$	$+\ 6\ Cr^{2+}(aq)$	$\rightarrow\ 8\ Cr^{3+}(aq)$	$+\ 7\ H_2O(l)$
Initial moles	0.0500	0.00500	0.0120	0	
Change	-14x	-x	-6x	+8x	

Because Cr^{2+} is the limiting reactant, 6x = 0.0120 and x = 0.00200

Final moles	0.0220	0.00300	0	0.00160

mol K^+ = 0.00500 mol $K_2Cr_2O_7$ x $\frac{2 \text{ mol } K^+}{1 \text{ mol } K_2Cr_2O_7}$ = 0.0100 mol K^+

mol NO_3^- = 0.0120 mol $Cr(NO_3)_2$ x $\frac{2 \text{ mol } NO_3^-}{1 \text{ mol } Cr(NO_3)_2}$

+ 0.0500 mol HNO_3 x $\frac{1 \text{ mol } NO_3^-}{1 \text{ mol } HNO_3}$ = 0.0740 mol NO_3^-

mol H^+ = 0.0220 mol; mol $Cr_2O_7^{2-}$ = 0.00300 mol; mol Cr^{3+} = 0.01600 mol

Check for charge neutrality.
Total moles of +charge = 0.0100 + 0.0220 + 3 x (0.01600) = 0.0800 mol +charge
Total moles of -charge = 0.0740 + 2 x (0.00300) = 0.0800 mol -charge
The charges balance and there is electrical neutrality in the solution after the reaction.

K^+ molarity = $\frac{0.0100 \text{ mol } K^+}{0.1200 \text{ L}}$ = 0.0833 M

NO_3^- molarity = $\frac{0.0740 \text{ mol } NO_3^-}{0.1200 \text{ L}}$ = 0.617 M

H^+ molarity = $\frac{0.0220 \text{ mol } H^+}{0.1200 \text{ L}}$ = 0.183 M

$Cr_2O_7^{2-}$ molarity = $\frac{0.00300 \text{ mol } Cr_2O_7^{2-}}{0.1200 \text{ L}}$ = 0.0250 M

Cr^{3+} molarity = $\frac{0.0160 \text{ mol } Cr^{3+}}{0.1200 \text{ L}}$ = 0.133 M

4.111 (a) (1) $I^-(aq) \rightarrow I_3^-(aq)$
$3\ I^-(aq) \rightarrow I_3^-(aq)$
$3\ I^-(aq) \rightarrow I_3^-(aq) + 2\ e^-$ (oxidation half reaction)

$HNO_2(aq) \rightarrow NO(g)$
$HNO_2(aq) \rightarrow NO(g) + H_2O(l)$
$H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)$
$[e^- + H^+(aq) + HNO_2(aq) \rightarrow NO(g) + H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.
$3\ I^-(aq) + 2\ H^+(aq) + 2\ HNO_2(aq) \rightarrow I_3^-(aq) + 2\ NO(g) + 2\ H_2O(l)$

(2) $S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ e^-$ (oxidation half reaction)

$I_3^-(aq) \rightarrow I^-(aq)$

$I_3^-(aq) \rightarrow 3\ I^-(aq)$
$2\ e^- + I_3^-(aq) \rightarrow 3\ I^-(aq)$ (reduction half reaction)

Combine the two half reactions.
$2\ S_2O_3^{2-}(aq) + I_3^-(aq) \rightarrow S_4O_6^{2-}(aq) + 3\ I^-(aq)$

(b) 18.77 mL = 0.018 77 L; NO_2^-, 46.01 amu

$$0.1500\ \frac{\text{mol}\ S_2O_3^{2-}}{1\ \text{L}} \times 0.018\ 77\ \text{L} = 0.002\ 815\ 5\ \text{mol}\ S_2O_3^{2-}$$

$$\text{mass}\ NO_2^- = 0.002\ 815\ 5\ \text{mol}\ S_2O_3^{2-} \times \frac{1\ \text{mol}\ I_3^-}{2\ \text{mol}\ S_2O_3^{2-}} \times \frac{2\ \text{mol}\ NO_2^-}{1\ \text{mol}\ I_3^-} \times \frac{46.01\ \text{g}\ NO_2^-}{1\ \text{mol}\ NO_2^-} = 0.1295\ \text{g}\ NO_2^-$$

$$\text{mass \%}\ NO_2^- = \frac{0.1295\ \text{g}}{2.935\ \text{g}} \times 100\% = 4.412\%$$

4.112 (a) (1) $Cu(s) \rightarrow Cu^{2+}(aq)$
$[Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-] \times 3$ (oxidation half reaction)

$NO_3^-(aq) \rightarrow NO(g)$
$NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)$
$[3\ e^- + 4\ H^+(aq) + NO_3^-(aq) \rightarrow NO(g) + 2\ H_2O(l)] \times 2$
(reduction half reaction

Combine the two half reactions.
$3\ Cu(s) + 8\ H^+(aq) + 2\ NO_3^-(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l)$

(2) $Cu^{2+}(aq) + SCN^-(aq) \rightarrow CuSCN(s)$
$[e^- + Cu^{2+}(aq) + SCN^-(aq) \rightarrow CuSCN(s)] \times 2$ (reduction half reaction)

$HSO_3^-(aq) \rightarrow HSO_4^-(aq)$
$H_2O(l) + HSO_3^-(aq) \rightarrow HSO_4^-(aq)$
$H_2O(l) + HSO_3^-(aq) \rightarrow HSO_4^-(aq) + 2\ H^+(aq)$
$H_2O(l) + HSO_3^-(aq) \rightarrow HSO_4^-(aq) + 2\ H^+(aq) + 2\ e^-$
(oxidation half reaction)

Combine the two half reactions.
$2\ Cu^{2+}(aq) + 2\ SCN^-(aq) + H_2O(l) + HSO_3^-(aq) \rightarrow 2\ CuSCN(s) + HSO_4^-(aq) + 2\ H^+(aq)$

(3) $Cu^+(aq) \rightarrow Cu^{2+}(aq)$
$[Cu^+(aq) \rightarrow Cu^{2+}(aq) + e^-] \times 10$ (oxidation half reaction)

$IO_3^-(aq) \rightarrow I_2(aq)$
$2\ IO_3^-(aq) \rightarrow I_2(aq)$

$2\ IO_3^-(aq) \rightarrow I_2(aq) + 6\ H_2O(l)$
$12\ H^+(aq) + 2\ IO_3^-(aq) \rightarrow I_2(aq) + 6\ H_2O(l)$
$10\ e^- + 12\ H^+(aq) + 2\ IO_3^-(aq) \rightarrow I_2(aq) + 6\ H_2O(l)$ (reduction half reaction)

Combine the two half reactions.
$10\ Cu^+(aq) + 12\ H^+(aq) + 2\ IO_3^-(aq) \rightarrow 10\ Cu^{2+}(aq) + I_2(aq) + 6\ H_2O(l)$

(4) $I_2(aq) \rightarrow I^-(aq)$
$I_2(aq) \rightarrow 2\ I^-(aq)$
$2\ e^- + I_2(aq) \rightarrow 2\ I^-(aq)$ (reduction half reaction)

$S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq)$
$2\ S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ e^-$ (oxidation half reaction)

Combine the two half reactions.
$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq)$

(5) $2\ ZnNH_4PO_4 \rightarrow Zn_2P_2O_7 + H_2O + 2\ NH_3$

(b) 10.82 mL = 0.01082 L
mol $S_2O_3^{2-}$ = (0.1220 mol/L)(0.01082 L) = 0.00132 mol $S_2O_3^{2-}$

$$\text{mol } I_2 = 0.00132 \text{ mol } S_2O_3^{2-} \times \frac{1 \text{ mol } I_2}{2 \text{ mol } S_2O_3^{2-}} = 6.60 \times 10^{-4} \text{ mol } I_2$$

$$\text{mol } Cu^+ = 6.60 \times 10^{-4} \text{ mol } I_2 \times \frac{10 \text{ mol } Cu^+}{1 \text{ mol } I_2} = 6.60 \times 10^{-3} \text{ mol } Cu^+ \text{ (Cu)}$$

g Cu = $(6.60 \times 10^{-3}$ mol)(63.546 g/mol) = 0.419 g Cu

$$\text{mass \% Cu in brass} = \frac{0.419 \text{ g Cu}}{0.544 \text{ g brass}} \times 100\% = 77.1\% \text{ Cu}$$

(c) $Zn_2P_2O_7$, 304.72 amu

$$\text{mass \% Zn in } Zn_2P_2O_7 = \frac{2 \times 65.39 \text{ g}}{304.72 \text{ g}} \times 100\% = 42.92\%$$

mass of Zn in $Zn_2P_2O_7$ = (0.4292)(0.246 g) = 0.106 g Zn

$$\text{mass \% Zn in brass} = \frac{0.106 \text{ g Zn}}{0.544 \text{ g brass}} \times 100\% = 19.5\% \text{ Zn}$$

4.113 (a) $BaSO_4$, 233.38 amu

$$\text{mol S} = 7.19 \text{ g } BaSO_4 \times \frac{1 \text{ mol } BaSO_4}{233.38 \text{ g } BaSO_4} \times \frac{1 \text{ mol S}}{1 \text{ mol } BaSO_4} = 0.0308 \text{ mol S}$$

$$\text{theoretical mol S} = \frac{0.0308 \text{ mol S}}{0.913} = 0.0337 \text{ mol S}$$

(b) Assume n = 1:

mol Cl in MCl_5 = 0.0337 mol S x $\frac{5 \text{ mol Cl}}{1 \text{ mol S}}$ = 0.168 mol Cl

mass Cl = 0.168 mol Cl x $\frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}}$ = 5.97 g Cl

This is impossible because the initial mass of MCl_5 was only 4.61 g.

Assume n = 2:

mol Cl in MCl_5 = 0.0337 mol S x $\frac{5 \text{ mol Cl}}{2 \text{ mol S}}$ = 0.0842 mol Cl

mass Cl = 0.0842 mol Cl x $\frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}}$ = 2.99 g Cl

mass M = 4.61g - 2.99 g = 1.62 g M

mol M = 0.0337 mol S x $\frac{1 \text{ mol M}}{2 \text{ mol S}}$ = 0.0168 mol

M molar mass = $\frac{1.62 \text{ g}}{0.0168 \text{ mol}}$ = 96.4 g/mol; M atomic mass = 96.4 amu

96.4 is reasonable and suggests that M is Mo

Assume n = 3:

mol Cl in MCl_5 = 0.0337 mol S x $\frac{5 \text{ mol Cl}}{3 \text{ mol S}}$ = 0.0562 mol Cl

mass Cl = 0.0562 mol Cl x $\frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}}$ = 1.99 g Cl

mass M = 4.61g - 1.99 g = 2.62 g M

mol M = 0.0337 mol S x $\frac{1 \text{ mol M}}{3 \text{ mol S}}$ = 0.0112 mol

M molar mass = $\frac{2.62 \text{ g}}{0.0112 \text{ mol}}$ = 234 g/mol; M atomic mass = 234 amu

234 is between Pa and U, which is highly unlikely for a lubricant.

Assume n = 4:

mol Cl in MCl_5 = 0.0337 mol S x $\frac{5 \text{ mol Cl}}{4 \text{ mol S}}$ = 0.0421 mol Cl

mass Cl = 0.0421 mol Cl x $\frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}}$ = 1.49 g Cl

mass M = 4.61g - 1.49 g = 3.12 g M

mol M = 0.0337 mol S x $\frac{1 \text{ mol M}}{4 \text{ mol S}}$ = 0.00842 mol

M molar mass = $\frac{3.12 \text{ g}}{0.008\ 42 \text{ mol}}$ = 371 g/mol; M atomic mass = 371 amu

No known elements have a mass as great as 371 amu.

(c) M is most likely Mo and the metal sulfide is MoS_2.

(d) (1) $2\ MoCl_5(s) + 5\ Na_2S(s) \rightarrow 2\ MoS_2(s) + S(l) + 10\ NaCl(s)$

(2) $2\ MoS_2(s) + 7\ O_2(g) \rightarrow 2\ MoO_3(s) + 4\ SO_2(g)$
(3) $SO_2(g) + 2\ Fe^{3+}(aq) + 2\ H_2O(l) \rightarrow 2\ Fe^{2+}(aq) + SO_4^{2-}(aq) + 4\ H^+(aq)$
(4) $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Assignment 2. Questions from chapter 5 of McMurry and Fay
Question numbers are from the fourth edition.

Chapter 5. Periodicity and Atomic Structure

5.1 Gamma ray $\nu = \frac{c}{\lambda} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{3.56 \text{ x } 10^{-11} \text{ m}} = 8.43 \text{ x } 10^{18} \text{ s}^{-1} = 8.43 \text{ x } 10^{18} \text{ Hz}$

Radar wave $\nu = \frac{c}{\lambda} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{10.3 \text{ x } 10^{-2} \text{ m}} = 2.91 \text{ x } 10^{9} \text{ s}^{-1} = 2.91 \text{ x } 10^{9} \text{ Hz}$

5.2 $\nu = 102.5 \text{ MHz} = 102.5 \text{ x } 10^{6} \text{ Hz} = 102.5 \text{ x } 10^{6} \text{ s}^{-1}$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{102.5 \text{ x } 10^{6} \text{ s}^{-1}} = 2.93 \text{ m}$$

$\nu = 9.55 \text{ x } 10^{17} \text{ Hz} = 9.55 \text{ x } 10^{17} \text{ s}^{-1}$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{9.55 \text{ x } 10^{17} \text{ s}^{-1}} = 3.14 \text{ x } 10^{-10} \text{ m}$$

5.3 The wave with the shorter wavelength (b) has the higher frequency. The wave with the larger amplitude (b) represents the more intense beam of light. The wave with the shorter wavelength (b) represents blue light. The wave with the longer wavelength (a) represents red light.

5.4 Balmer series: m = 2; $R = 1.097 \text{ x } 10^{-2} \text{ nm}^{-1}$

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{7^2}\right]; \quad \frac{1}{\lambda} = 2.519 \text{ x } 10^{-3} \text{ nm}^{-1}; \quad \lambda = 397.0 \text{ nm}$$

5.5 Paschen series: m = 3; $R = 1.097 \text{ x } 10^{-2} \text{ nm}^{-1}$

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{4^2}\right]; \quad \frac{1}{\lambda} = 5.333 \text{ x } 10^{-4} \text{ nm}^{-1}; \quad \lambda = 1875 \text{ nm}$$

5.6 Paschen series: m = 3; $R = 1.097 \text{ x } 10^{-2} \text{ nm}^{-1}$

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{\infty^2}\right]; \quad \frac{1}{\lambda} = 1.219 \text{ x } 10^{-3} \text{ nm}^{-1}; \quad \lambda = 820.4 \text{ nm}$$

5.7 $\lambda = 91.2 \text{ nm} = 91.2 \text{ x } 10^{-9} \text{ m}$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{91.2 \text{ x } 10^{-9} \text{ m}} = 3.29 \text{ x } 10^{15} \text{ s}^{-1}$$

$E = h\nu = (6.626 \text{ x } 10^{-34} \text{ J} \equiv \text{s})(3.29 \text{ x } 10^{15} \text{ s}^{-1}) = 2.18 \text{ x } 10^{-18} \text{ J/photon}$

$E = (2.18 \text{ x } 10^{-18} \text{ J/photon})(6.022 \text{ x } 10^{23} \text{ photons/mol}) = 1.31 \text{ x } 10^{6} \text{ J/mol} = 1310 \text{ kJ/mol}$

5.8 IR, $\lambda = 1.55 \text{ x } 10^{-6} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{1.55 \text{ x } 10^{-6} \text{ m}}\right)(6.022 \text{ x } 10^{23} \text{ / mol})$$

E = 7.72 x 10^4 J/mol = 77.2 kJ/mol

UV, λ = 250 nm = 250 x 10^{s9} m

$$E = h\,\frac{c}{\lambda} = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})\left(\frac{3.00 \times 10^{8}\ \text{m/s}}{250 \times 10^{-9}\ \text{m}}\right)(6.022 \times 10^{23}\ /\ \text{mol})$$

E = 4.79 x 10^5 J/mol = 479 kJ/mol

X ray, λ = 5.49 nm = 5.49 x 10^{s9} m

$$E = h\,\frac{c}{\lambda} = (6.626 \times 10^{-34}\ \text{J}\bullet\text{s})\left(\frac{3.00 \times 10^{8}\ \text{m/s}}{5.49 \times 10^{-9}\ \text{m}}\right)(6.022 \times 10^{23}\ /\ \text{mol})$$

E = 2.18 x 10^7 J/mol = 2.18 x 10^4 kJ/mol

5.9 $$\lambda = \frac{h}{mv} = \frac{6.626\ \text{x}\ 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{(1150\ \text{kg})(24.6\ \text{m/s})} = 2.34 \times 10^{s38}\ \text{m}$$

5.10 $(\Delta x)(\Delta mv) \geq \frac{h}{4\pi}$; uncertainty in velocity = (45 m/s)(0.02) = 0.9 m/s

$$\Delta x \geq \frac{h}{4\pi(\Delta mv)} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4\pi(0.120\ \text{kg})(0.9\ \text{m/s})} = 5 \times 10^{-34}\ \text{m}$$

5.11

n	*l*	m_l	Orbital	No. of Orbitals
5	0	0	5s	1
	1	S1, 0, +1	5p	3
	2	S2, S1, 0, +1, +2	5d	5
	3	S3, S2, S1, 0, +1, +2, +3	5f	7
	4	S4, S3, S2, S1, 0, +1, +2, +3, +4	5g	9

There are 25 possible orbitals in the fifth shell.

5.12 (a) 2p (b) 4f (c) 3d

5.13 (a) 3s orbital: n = 3, *l* = 0, m_l = 0
(b) 2p orbital: n = 2, *l* = 1, m_l = S1, 0, +1
(c) 4d orbital: n = 4, *l* = 2, m_l = S2, S1, 0, +1, +2

5.14 The g orbitals have four nodal planes.

5.15 The figure represents a d orbital, n = 4 and *l* = 2.

5.16 m = 1, n = 4; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right];\quad \frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right];\quad \frac{1}{\lambda} = R\left[\frac{1}{1}\right] = 1.097 \times 10^{s2}\ \text{nm}^{s1};\ \lambda = 91.2\ \text{nm}$$

$$E = (6.626 \times 10^{-34}\ J\bullet s)\left(\frac{3.00 \times 10^{8}\ m/s}{91.2 \times 10^{-9}\ m}\right)(6.022 \times 10^{23}/\ mol)$$

$E = 1.31 \times 10^{6}$ J/mol = 1.31×10^{3} kJ/mol

5.17 (a) Ti, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^2$ or [Ar] $4s^2\,3d^2$

[Ar] ___ ___ ___ — — —
4s 3d

(b) Zn, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$ or [Ar] $4s^2\,3d^{10}$

[Ar] ___ ___ ___ ___ ___
4s 3d

(c) Sn, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^2$ or [Kr] $5s^2\,4d^{10}\,5p^2$

[Kr] ___ ___ ___ ___ ___ ___ — —
5s 4d 5p

(d) Pb,[Xe] $6s^2\,4f^{14}\,5d^{10}\,6p^2$

5.18 For Na^+, $1s^2\,2s^2\,2p^6$; for Cl^s, $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

5.19 The ground-state electron configuration contains 28 electrons. The atom is Ni.

5.20 Cr, Cu, Nb, Mo, Ru, Rh, Pd, Ag, La, Ce, Gd, Pt, Au, Ac, Th, Pa, U, Np, Cm

5.21 (a) Ba; atoms get larger as you go down a group.
(b) W; atoms get smaller as you go across a period.
(c) Sn; atoms get larger as you go down a group.
(d) Ce; atoms get smaller as you go across a period.

5.22 The aurora borealis begins on the surface of the sun with a massive solar flare. These flares eject a solar "gas" of energetic protons and electrons that reach earth after about 2 days and are then attracted toward the north and south magnetic poles. The energetic electrons are deflected by the earth's magnetic field into a series of sheetlike beams. The electrons then collide with O_2 and N_2 molecules in the upper atmosphere, exciting them, ionizing them, and breaking them apart into O and N atoms. The energetically excited atoms, ions, and molecules generated by collisions with electrons emit energy of characteristic wavelengths when they decay to their ground states. The O_2^+ ions emit a red light around 630 nm; N_2^+ ions emit violet and blue light at 391.4 nm and 470.0 nm; and O atoms emit a greenish-yellow light at 557.7 nm and a deep red light at 630.0 nm.

Understanding Key Concepts

5.23

5.24

5.25 The wave with the larger amplitude (a) has the greater intensity. The wave with the shorter wavelength (a) has the higher energy radiation. The wave with the shorter wavelength (a) represents yellow light. The wave with the longer wavelength (b) represents infrared radiation.

5.26 [Ar] $4s^2\ 3d^{10}\ 4p^1$ is Ga.

5.27 There are 34 total electrons in the atom, so there are also 34 protons in the nucleus. The atom is selenium (Se)

Se, [Ar] ___ ___ ___ ___ ___ ___ ___ ___ ___
4s 3d 4p

5.28 Ca and Br are in the same period, with Br to the far right of Ca. Ca is larger than Br. Sr is directly below Ca in the same group, and is larger than Ca. The result is
Sr (215 pm) > Ca (197 pm) > Br (114 pm)

5.29 (a) $3p_y$ n = 3, l = 1 (b) $4d_{z^2}$ n = 4, l = 2

Additional Problems
Electromagnetic Radiation

5.30 Violet has the higher frequency and energy. Red has the higher wavelength.

5.31 Ultraviolet light has the higher frequency and the higher energy. Infrared light has the higher wavelength.

5.32 $\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{5.5 \text{ x } 10^{15} \text{ s}^{-1}} = 5.5 \text{ x } 10^{s8} \text{ m}$

5.33 $\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{4.33 \text{ x } 10^{-3} \text{ m}} = 6.93 \text{ x } 10^{10} \text{ s}^{-1} = 6.93 \text{ x } 10^{10} \text{ Hz}$

5.34 (a) v = 99.5 MHz = 99.5 x 10^{6} s^{s1}
E = hv = (6.626 x 10^{s34} J≅s)(99.5 x 10^{6} s^{s1})(6.022 x 10^{23} /mol)
E = 3.97 H 10^{s2} J/mol = 3.97 H 10^{s5} kJ/mol
v = 1150 kHz = 1150 x 10^{3} s^{s1}
E = hv = (6.626 x 10^{s34} J≅s)(1150 x 10^{3} s^{s1})(6.022 x 10^{23} /mol)
E = 4.589 x 10^{s4} J/mol = 4.589 x 10^{s7} kJ/mol
The FM radio wave (99.5 MHz) has the higher energy.
(b) λ = 3.44 x 10^{s9} m

$$E = h\,\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ J•s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{3.44 \text{ x } 10^{-9} \text{ m}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

E = 3.48 x 10^{7} J/mol = 3.48 x 10^{4} kJ/mol
λ = 6.71 H 10^{s2} m

$$E = h\,\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ J•s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{6.71 \text{ x } 10^{-2} \text{ m}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

E = 1.78 J/mol = 1.78 x 10^{s3} kJ/mol
The X ray (λ = 3.44 x 10^{s9} m) has the higher energy.

5.35 v = 400 MHz = 400 x 10^{6} s^{s1}
E = (6.626 x 10^{s34} J≅s)(400 x 10^{6} s^{s1})(6.02 x 10^{23}/mol) = 0.160 J/mol = 1.60 x 10^{s4} kJ/mol

5.36 (a) $E = 90.5 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.02 \text{ x } 10^{23}} = 1.50 \text{ x } 10^{s19} \text{ J}$

$$\nu = \frac{E}{h} = \frac{1.50 \text{ x } 10^{-19} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J•s}} = 2.27 \text{ x } 10^{14} \text{ s}^{s1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{2.27 \text{ x } 10^{14} \text{ s}^{-1}} = 1.32 \text{ x } 10^{s6} \text{ m} = 1320 \text{ x } 10^{s9} \text{ m} = 1320 \text{ nm, near IR}$$

(b) $E = 8.05 \text{ x } 10^{s4} \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1 \text{ mol}}{6.02 \text{ x } 10^{23}} = 1.34 \text{ x } 10^{s24} \text{ J}$

$$\nu = \frac{E}{h} = \frac{1.34 \text{ x } 10^{-24} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s}} = 2.02 \text{ x } 10^{9} \text{ s}^{s1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{2.02 \text{ x } 10^{9} \text{ s}^{-1}} = 0.149 \text{ m, radio wave}$$

(c) $E = 1.83 \text{ x } 10^{3} \text{ kJ/mol x } \frac{1000 \text{ J}}{1 \text{ kJ}} \text{ x } \frac{1 \text{ mol}}{6.02 \text{ x } 10^{23}} = 3.04 \text{ x } 10^{s18} \text{ J}$

$$\nu = \frac{E}{h} = \frac{3.04 \text{ x } 10^{-18} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s}} = 4.59 \text{ x } 10^{15} \text{ s}^{s1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{4.59 \text{ x } 10^{15} \text{ s}^{-1}} = 6.54 \text{ x } 10^{s8} \text{ m} = 65.4 \text{ x } 10^{s9} \text{ m} = 65.4 \text{ nm, UV}$$

5.37 (a) $E = h\nu = (6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})(5.97 \text{ x } 10^{19} \text{ s}^{-1})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$

$E = 2.38 \text{ x } 10^{7} \text{ kJ/mol}$

(b) $E = h\nu = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})(1.26 \text{ x } 10^{6} \text{ s}^{-1})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$

$E = 5.03 \text{ x } 10^{s7} \text{ kJ/mol}$

(c) $E = h\nu = (6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{2.57 \text{ x } 10^{2} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$

$E = 4.66 \text{ x } 10^{s7} \text{ kJ/mol}$

5.38 $\lambda = \frac{h}{mv} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.11 \text{ x } 10^{-31} \text{ kg})(0.99 \text{ x } 3.00 \text{ x } 10^{8} \text{ m/s})} = 2.45 \text{ x } 10^{s12} \text{ m, } \gamma \text{ ray}$

5.39 $\lambda = \frac{h}{mv} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(1.673 \text{ x } 10^{-27} \text{ kg})(0.25 \text{ x } 3.00 \text{ x } 10^{8} \text{ m/s})} = 5.28 \text{ x } 10^{s15} \text{ m, } \gamma \text{ ray}$

5.40 156 km/h = 156 x 10^3 m/3600 s = 43.3 m/s; 145 g = 0.145 kg

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(0.145 \text{ kg})(43.3 \text{ m/s})} = 1.06 \text{ x } 10^{-34} \text{ m}$$

5.41 1.55 mg = 1.55 x 10^{s3} g = 1.55 x 10^{s6} kg

$$\lambda = \frac{h}{mv} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(1.55 \text{ x } 10^{-6} \text{ kg})(1.38 \text{ m/s})} = 3.10 \text{ x } 10^{s28} \text{ m}$$

5.42 145 g = 0.145 kg; 0.500 nm = 0.500 x 10^{s9} m

$$v = \frac{h}{m\lambda} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(0.145 \text{ kg})(0.500 \text{ x } 10^{-9} \text{ m})} = 9.14 \text{ x } 10^{-24} \text{ m/s}$$

5.43 750 nm = 750 x 10^{s9} m

$$v = \frac{h}{m\lambda} = \frac{6.626 \text{ x } 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.11 \text{ x } 10^{-31} \text{ kg})(750 \text{ x } 10^{-9} \text{ m})} = 970 \text{ m/s}$$

Atomic Spectra

5.44 For n = 3; λ = 656.3 nm = 656.3 x 10^{s9} m

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{656.3 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol})$$

$$E = 182.3 \text{ kJ/mol}$$

For n = 4; λ = 486.1 nm = 486.1 x 10^{s9} m

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{486.1 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol})$$

$$E = 246.1 \text{ kJ/mol}$$

For n = 5; λ = 434.0 nm = 434.0 x 10^{s9} m

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{434.0 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol})$$

$$E = 275.6 \text{ kJ/mol}$$

5.45 m = 2, n = 4; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{4}\right] = 2.74 \text{ x } 10^{s3} \text{ nm}^{s1}; \ \lambda = 364.6 \text{ nm}$$

5.46 From problem 5.45, for n = 4, λ = 364.6 nm = 364.6 x 10^{s9} m

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{364.6 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol})$$

$$E = 328.1 \text{ kJ/mol}$$

5.47 Brackett series: m = 4, n = 5; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{5^2}\right] = 2.468 \text{ x } 10^{s4} \text{ nm}^{s1}; \ \lambda = 4051 \text{ nm}$$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{4051 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol})$$

$$E = 29.55 \text{ kJ/mol, IR}$$

Brackett series: m = 4, n = 6; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{4^2} - \frac{1}{6^2}\right] = 3.809 \text{ x } 10^{s4} \text{ nm}^{s1}; \ \lambda = 2625 \text{ nm}$$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{2625 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 45.60 \text{ kJ / mol, IR}$$

5.48 $\lambda = 330 \text{ nm} = 330 \text{ x } 10^{s9} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{330 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 363 \text{ kJ / mol}$$

5.49 $795 \text{ nm} = 795 \text{ x } 10^{s9} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{3.00 \text{ x } 10^{8} \text{ m/s}}{795 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 151 \text{ kJ / mol}$$

Orbitals and Quantum Numbers

5.50 n is the principal quantum number. The size and energy level of an orbital depends on n. *l* is the angular-momentum quantum number. *l* defines the three-dimensional shape of an orbital.
m_l is the magnetic quantum number. m_l defines the spatial orientation of an orbital.
m_s is the spin quantum number. m_s indicates the spin of the electron and can have either of two values, +2 or S2.

5.51 The Heisenberg uncertainty principle states that one can never know both the position and the velocity of an electron beyond a certain level of precision. This means we cannot think of electrons circling the nucleus in specific orbital paths, but we can think of electrons as being found in certain three-dimensional regions of space around the nucleus, called orbitals.

5.52 The probability of finding the electron drops off rapidly as distance from the nucleus increases, although it never drops to zero, even at large distances. As a result, there is no definite boundary or size for an orbital. However, we usually imagine the boundary surface of an orbital enclosing the volume where an electron spends 95% of its time.

5.53 A 4s orbital has three nodal surfaces.

4s orbital

5.54 Part of the electron-nucleus attraction is canceled by the electron-electron repulsion, an effect we describe by saying that the electrons are shielded from the nucleus by the other electrons. The net nuclear charge actually felt by an electron is called the effective nuclear charge, Z_{eff}, and is often substantially lower than the actual nuclear charge, Z_{actual}.

$$Z_{eff} = Z_{actual} - \text{electron shielding}$$

5.55 Electron shielding gives rise to energy differences among 3s, 3p, and 3d orbitals in multielectron atoms because of the differences in orbital shape. For example, the 3s orbital is spherical and has a large probability density near the nucleus, while the 3p orbital is dumbbell shaped with a node at the nucleus. An electron in a 3s orbital can penetrate closer to the nucleus than an electron in a 3p orbital can and feels less of a shielding effect from other electrons. Generally, for any given value of the principal quantum number n, a lower value of l corresponds to a higher value of Z_{eff} and to a lower energy for the orbital.

5.56 (a) 4s n = 4; l = 0; m_l = 0; $m_s = \pm\frac{1}{2}$
(b) 3p n = 3; l = 1; m_l = −1, 0, +1; $m_s = \pm\frac{1}{2}$
(c) 5f n = 5; l = 3; m_l = −3, −2, −1, 0, +1, +2, +3; $m_s = \pm\frac{1}{2}$
(d) 5d n = 5; l = 2; m_l = −2, −1, 0, +1, +2; $m_s = \pm\frac{1}{2}$

5.57 (a) 3s (b) 2p (c) 4f (d) 4d

5.58 (a) is not allowed because for l = 0, m_l = 0 only.
(b) is allowed.
(c) is not allowed because for n = 4, l = 0, 1, 2, or 3 only.

5.59 Co $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
(a) is not allowed because for l = 0, m_l = 0 only.
(b) is not allowed because n = 4 and l = 2 is for a 4d orbital.
(c) is allowed because n = 3 and l = 1 is for a 3p orbital.

5.60 For n = 5, the maximum number of electrons will occur when the 5g orbital is filled:
[Rn] $7s^2\ 5f^{14}\ 6d^{10}\ 7p^6\ 8s^2\ 5g^{18}$ = 138 electrons

5.61 n = 4, l = 0 is a 4s orbital. The electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. The number of electrons is 20.

5.62 0.68 g = 0.68 x 10^{-3} kg

$$(\Delta x)(\Delta mv) \geq \frac{h}{4\pi}; \quad \Delta x \geq \frac{h}{4\pi(\Delta mv)} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4\pi\ (0.68 \times 10^{-3}\ \text{kg})(0.1\ \text{m/s})} = 8 \times 10^{-31}\ \text{m}$$

5.63 $4.0026 \text{ amu} \times \frac{1.660\ 540 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 6.6465 \times 10^{-27} \text{ kg}$; $(\Delta x)(\Delta mv) \geq \frac{h}{4\pi}$

$$\Delta x \geq \frac{h}{4\pi(\Delta mv)} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4\pi (6.6465 \times 10^{-27} \text{ kg})(0.01 \times 1.36 \times 10^{3} \text{ m/s})} = 5.833 \times 10^{-10} \text{ m}$$

Electron Configurations

5.64 The number of elements in successive periods of the periodic table increases by the progression 2, 8, 18, 32 because the principal quantum number n increases by 1 from one period to the next. As the principal quantum number increases, the number of orbitals in a shell increases. The progression of elements parallels the number of electrons in a particular shell.

5.65 The n and *l* quantum numbers determine the energy level of an orbital in a multielectron atom.

5.66 (a) 5d (b) 4s (c) 6s

5.67 (a) 2p < 3p < 5s < 4d (b) 2s < 4s < 3d < 4p (c) 3d < 4p < 5p < 6s

5.68 (a) 3d after 4s (b) 4p after 3d (c) 6d after 5f (d) 6s after 5p

5.69 (a) 3s before 3p (b) 3d before 4p (c) 6s before 4f (d) 4f before 5d

5.70 (a) Ti, Z = 22 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$
(b) Ru, Z = 44 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^6$
(c) Sn, Z = 50 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^2$
(d) Sr, Z = 38 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$
(e) Se, Z = 34 $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

5.71 (a) Z = 55, Cs [Kr] $5s^2\ 4d^{10}\ 5p^6\ 6s^1$ (b) Z = 40, Zr [Kr] $5s^2\ 4d^2$
(c) Z = 80, Hg [Xe] $6s^2\ 4f^{14}\ 5d^{10}$ (d) Z = 62, Sm [Xe] $6s^2\ 4f^6$

5.72 (a) Rb, Z = 37 [Kr] ⎯ (5s)
(b) W, Z = 74 [Xe] ⎯⎯ ⎯⎯⎯⎯⎯⎯⎯⎯⎯⎯⎯ ⎯⎯⎯⎯⎯ (6s, 4f, 5d)
(c) Ge, Z = 32 [Ar] ⎯⎯ ⎯⎯⎯⎯⎯ ⎯⎯⎯ (4s, 3d, 4p)
(d) Zr, Z = 40 [Kr] ⎯⎯ ⎯⎯ ⎯ (5s, 4d)

5.73 (a) Z = 25, Mn [Ar] ⎯⎯ ⎯⎯⎯⎯⎯ ⎯ (4s, 3d)
(b) Z = 56, Ba [Xe] ⎯⎯

6s

(c) Z = 28, Ni [Ar] ___ ___ ___ ___ ___ _
4s 3d

(d) Z = 47, Ag [Kr] ___ ___ ___ ___ ___ ___
5s 4d

5.74 4s > 4d > 4f

5.75 K < Ca < Se < Kr

5.76 Z = 116 [Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^4$

5.77 Z = 119 [Rn] $7s^2\,5f^{14}\,6d^{10}\,7p^6\,8s^1$

5.78 (a) O $1s^2\,2s^2\,2p^4$ ___ ___ ___ 2 unpaired e^s
2p

(b) Si $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$ ___ ___ _ 2 unpaired e^s
3p

(c) K [Ar] $4s^1$ 1 unpaired e^s

(d) As [Ar] $4s^2\,3d^{10}\,4p^3$ ___ ___ ___ 3 unpaired e^s
4p

5.79 (a) Z = 31, Ga (b) Z = 46, Pd

5.80 Order of orbital filling:
1s |2s |2p |3s |3p |4s |3d |4p |5s |4d |5p |6s |4f |5d |6p |7s |5f |6d |7p |8s |5g
Z = 121

5.81 A g orbital would begin filling at atomic number = 121 (see 5.80). There are nine g orbitals that can each hold two electrons. The first element to have a filled g orbital would be atomic number = 138.

Atomic Radii and Periodic Properties

5.82 Atomic radii increase down a group because the electron shells are farther away from the nucleus.

5.83 Across a period, the effective nuclear charge increases, causing a decrease in atomic radii.

5.84 F < O < S

5.85 (a) K, lower in group 1A (b) Ta, lower in group 5B
(c) V, farther to the left in same period

(d) Ba, four periods lower and only one group to the right

5.86 Mg has a higher ionization energy than Na because Mg has a higher Z_{eff} and a smaller size.

5.87 F has a higher electron affinity than C because of a higher effective nuclear charge and room in the valence shell for the additional electron. In addition, F^S achieves a noble gas electron configuration.

General Problems

5.88 Balmer series: m = 2; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]; \quad \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{6^2}\right] = 2.438 \text{ x } 10^{s3} \text{ nm}^{s1}$$

$\lambda = 410.2 \text{ nm} = 410.2 \text{ x } 10^{s9} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{410.2 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 291.6 \text{ kJ / mol}$$

5.89 Pfund series: m = 5; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]$$

n = 6, $\frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{6^2}\right] = 1.341 \text{ x } 10^{s4} \text{ nm}^{s1}$; $\lambda = 7458 \text{ nm} = 7458 \text{ x } 10^{s9} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{7458 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 16.04 \text{ kJ / mol}$$

n = 7, $\frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{7^2}\right] = 2.149 \text{ x } 10^{s4} \text{ nm}^{s1}$; $\lambda = 4653 \text{ nm} = 4653 \text{ x } 10^{s9} \text{ m}$

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ Jcdot s})\left(\frac{2.998 \text{ x } 10^{8} \text{ m/s}}{4653 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23} / \text{mol})$$

$$E = 25.71 \text{ kJ / mol}$$

These lines in the Pfund series are in the infrared region of the electromagnetic spectrum.

5.90 Pfund series: m = 5, n = 4; R = 1.097 x 10^{s2} nm^{s1}

$$\frac{1}{\lambda} = R\left[\frac{1}{5^2} - \frac{1}{\infty^2}\right] = R\left[\frac{1}{25}\right] = 4.388 \text{ x } 10^{s4} \text{ nm}^{s1}; \ \lambda = 2279 \text{ nm}$$

5.91 (a) $E = \left(142 \frac{\text{kJ}}{\text{mol}}\right)\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right)\left(\frac{1 \text{ mol}}{6.02 \text{ x } 10^{23}}\right) = 2.36 \text{ x } 10^{\bullet 19} \text{ J}$

$E = h\frac{c}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J \bullet s)(3.00 \times 10^{8}\ m/s)}{2.36 \times 10^{-19}\ J}$

$\lambda = 8.42 \times 10^{-7}$ m (infrared)

(b) $E = \left(4.55 \times 10^{-2}\ \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1\ mol}{6.02 \times 10^{23}}\right) = 7.56 \times 10^{-23}\ J$

$E = h\frac{c}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J \bullet s)(3.00 \times 10^{8}\ m/s)}{7.56 \times 10^{-23}\ J}$

$\lambda = 2.63 \times 10^{-3}$ m (microwave)

(c) $E = \left(4.81 \times 10^{4}\ \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1\ mol}{6.02 \times 10^{23}}\right) = 7.99 \times 10^{-17}\ J$

$E = h\frac{c}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J \bullet s)(3.00 \times 10^{8}\ m/s)}{7.99 \times 10^{-17}\ J}$

$\lambda = 2.49 \times 10^{-9}$ m (X ray)

5.92 (a) $E = h\nu = (6.626 \times 10^{-34}\ J \cong s)(3.79 \times 10^{11}\ s^{-1})\left(\frac{1\ kJ}{1000\ J}\right)(6.022 \times 10^{23}/mol) = 0.151$ kJ/mol

(b) $E = h\nu = (6.626 \times 10^{-34}\ J \cong s)(5.45 \times 10^{4}\ s^{-1})\left(\frac{1\ kJ}{1000\ J}\right)(6.022 \times 10^{23}/mol) = 2.17 \times 10^{-8}$ kJ/mol

(c) $E = h\nu = (6.626 \times 10^{-34}\ J \cong s)\left(\frac{3.00 \times 10^{8}\ m/s}{4.11 \times 10^{-5}\ m}\right)\left(\frac{1\ kJ}{1000\ J}\right)(6.022 \times 10^{23}/mol) = 2.91$ kJ/mol

5.93 $\nu = 9{,}192{,}631{,}770\ s^{-1} = 9.19263 \times 10^{9}\ s^{-1}$

$E = h\nu = (6.626 \times 10^{-34}\ J \cong s)(9.19263 \times 10^{9}\ s^{-1})\left(\frac{1\ kJ}{1000\ J}\right)(6.022 \times 10^{23}/mol) = 3.668 \times 10^{-3}$ kJ/mol

5.94 (a) Ra [Rn] $7s^2$ [Rn] ___ (7s)

(b) Sc [Ar] $4s^2\ 3d^1$ [Ar] ___ _ (4s, 3d)

(c) Lr [Rn] $7s^2\ 5f^{14}\ 6d^1$ [Rn] ___ ___ ___ ___ ___ ___ ___ ___ _ (7s, 5f, 6d)

(d) B [He] $2s^2\ 2p^1$ [He] ___ _ (2s, 2p)

(e) Te [Kr] $5s^2\ 4d^{10}\ 5p^4$ [Kr] ___ ___ ___ ___ ___ ___ ___ ___ _ (5s, 4d, 5p)

5.95 (a) row 1 n = 1, $l = 0$ 1s 2 elements
$l = 1$ 1p 6 elements
$l = 2$ 1d 10 elements

row 2 n = 2, $l = 0$ 2s 2 elements
$l = 1$ 2p 6 elements
$l = 2$ 2d 10 elements
$l = 3$ 2f 14 elements

There would be 50 elements in the first two rows.

(b) There would be 18 elements in the first row [see (a) above]. The fifth element in the second row would have atomic number = 23.

(c) Z = 12 ___ ___ ___ ___ ___ ___ ___ _
1s 1p 1d

5.96 206.5 kJ = 206.5 x 10^3 J; $E = \frac{206.5 \text{ x } 10^3 \text{ J}}{1 \text{ mol}} \text{ x } \frac{1 \text{ mol}}{6.022 \text{ x } 10^{23}} = 3.429 \text{ x } 10^{s19} \text{ J}$

$E = h\frac{c}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{(6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})(3.00 \text{ x } 10^8 \text{ m/s})}{3.429 \text{ x } 10^{-19} \text{ J}} = 5.797 \text{ x } 10^{s7} \text{ m} = 580. \text{ nm}$

5.97 780 nm is at the red end of the visible region of the electromagnetic spectrum.
780 nm = 780 x 10^{s9} m

$$E = h\frac{c}{\lambda} = (6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})\left(\frac{3.00 \text{ x } 10^8 \text{ m/s}}{780 \text{ x } 10^{-9} \text{ m}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)(6.022 \text{ x } 10^{23}/\text{mol}) = 153 \text{ kJ/mol}$$

5.98 (a) Sr, Z = 38 [Kr] ___
5s

(b) Cd, Z = 48 [Kr] ___ ___ ___ ___ ___ ___
5s 4d

(c) Z = 22, Ti [Ar] ___ ___ _
4s 3d

(d) Z = 34, Se [Ar] ___ ___ ___ ___ ___ ___ ___ ___ _
4s 3d 4p

5.99 La ([Xe] $6s^2\ 5d^1$) is directly below Y ([Kr] $5s^2\ 4d^1$) in the periodic table. Both have similar valence electron configurations, but for La the valence electrons are one shell farther out leading to its larger radius.
Although Hf ([Xe] $6s^2\ 4f^{14}\ 5d^2$) is directly below Zr ([Kr] $5s^2\ 4d^2$) in the periodic table, Zr and Hf have almost identical atomic radii because the 4f electrons in Hf are not effective in shielding the valence electrons. The valence electrons in Hf are drawn in closer to the nucleus by the higher Z_{eff}.

5.100 For K, $Z_{eff} = \sqrt{\frac{(418.8 \text{ kJ/mol})(4^2)}{1312 \text{ kJ/mol}}} = 2.26$; For Kr, $Z_{eff} = \sqrt{\frac{(1350.7 \text{ kJ/mol})(4^2)}{1312 \text{ kJ/mol}}} = 4.06$

5.101 75 W = 75 J/s; 550 nm = 550 x 10^{s9} m; (0.05)(75 J/s) = 3.75 J/s

$$E = h\frac{c}{\lambda} = (6.626 \times 10^{-34}\ J\bullet s)\left(\frac{3.00 \times 10^{8}\ m/s}{550 \times 10^{-9}\ m}\right) = 3.61 \times 10^{\bullet 19}\ J/photon$$

$$\text{number of photons} = \frac{3.75\ J/s}{3.61 \times 10^{\bullet 19}\ J/photon} = 1.0 \times 10^{19}\ photons/s$$

5.102 q = (350 g)(4.184 J/g≅°C)(95°C S 20°C) = 109,830 J

λ = 15.0 cm = 15.0 x 10^{s2} m

$$E = (6.626 \times 10^{s34}\ J\cong s)\left(\frac{3.00 \times 10^{8}\ m/s}{15.0 \times 10^{-2}\ m}\right) = 1.33 \times 10^{s24}\ J/photon$$

$$\text{number of photons} = \frac{109{,}830\ J}{1.33 \times 10^{-24}\ J/photon} = 8.3 \times 10^{28}\ photons$$

5.103 $$E = \left(310\ \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1\ mol}{6.022 \times 10^{23}}\right) = 5.15 \times 10^{\bullet 19}\ J$$

$$E = h\frac{c}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ J\bullet s)(3.00 \times 10^{8}\ m/s)}{5.15 \times 10^{-19}\ J} = 3.86 \times 10^{s7}\ m = 386\ nm$$

5.104 48.2 nm = 48.2 x 10^{s9} m

$$E(photon) = 6.626 \times 10^{-34}\ J\bullet s \times \frac{3.00 \times 10^{8}\ m/s}{48.2 \times 10^{-9}\ m} \times \frac{1\ kJ}{1000\ J} \times \frac{6.022 \times 10^{23}}{mol} = 2.48 \times 10^{3}\ kJ/mol$$

$$E_K = E(electron) = \text{‰}\,(9.109 \times 10^{-31}\ kg)\,(2.371 \times 10^{6}\ m/s)^2\left(\frac{1\ kJ}{1000\ J}\right)\left(\frac{6.022 \times 10^{23}}{mol}\right)$$

$$E_K = 1.54 \times 10^{3}\ kJ/mol$$

$E(photon) = E_i + E_K$; $E_i = E(photon)$ B $E_K = (2.48 \times 10^3)$ S (1.54×10^3) = 940 kJ/mol

5.105 Charge on electron = 1.602 x 10^{s19} C; 1 V ≅C = 1 J = 1 kg m^2/s^2

(a) E_K = (30,000 V)(1.602 x 10^{s19} C) = 4.806 x 10^{s15} J

$$E_K = 2mv^2; \quad v = \sqrt{\frac{2\ E_K}{m}} = \sqrt{\frac{2 \times 4.806 \times 10^{-15}\ kg\ m^2/s^2}{9.109 \times 10^{-31}\ kg}} = 1.03 \times 10^{8}\ m/s$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ kg\ m^2/s}{(9.109 \times 10^{-31}\ kg)(1.03 \times 10^{8}\ m/s)} = 7.06 \times 10^{s12}\ m$$

(b) $$E = h\frac{c}{\lambda} = (6.626 \times 10^{-34}\ J\bullet s)\left(\frac{3.00 \times 10^{8}\ m/s}{1.54 \times 10^{-10}\ m}\right) = 1.29 \times 10^{\bullet 15}\ J/photon$$

5.106 Substitute the equation for the orbit radius, r, into the equation for the energy level, E, to get $E = \dfrac{-Ze^2}{2\left(\dfrac{n^2 a_o}{Z}\right)} = \dfrac{-Z^2e^2}{2a_o n^2}$

Let E_1 be the energy of an electron in a lower orbit and E_2 the energy of an electron in a higher orbit. The difference between the two energy levels is

$$\Delta E = E_2 - E_1 = \frac{-Z^2e^2}{2a_o n_2^2} - \frac{-Z^2e^2}{2a_o n_1^2} = \frac{-Z^2e^2}{2a_o n_2^2} + \frac{Z^2e^2}{2a_o n_1^2} = \frac{Z^2e^2}{2a_o n_1^2} - \frac{Z^2e^2}{2a_o n_2^2}$$

$$\Delta E = \frac{Z^2e^2}{2a_o}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Because Z, e, and a_o are constants, this equation shows that ΔE is proportional to $\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$ where n_1 and n_2 are integers with $n_2 > n_1$. This is similar to the Balmer-Rydberg equation where $1/\lambda$ or ν for the emission spectra of atoms is proportional to $\left[\dfrac{1}{m^2} - \dfrac{1}{n^2}\right]$ where m and n are integers with $n > m$.

5.107 (a) 1s 2s 2p 3s 3p 4s

Two partially filled orbitals.

(b) The element in the 3rd column and 4th row under these new rules would have an atomic number of 30 and be in the s-block.

5.108 (a) 3d, n = 3, l = 2

(b) 2p, n = 2, l = 1, m_l = −1, 0, +1
3p, n = 3, l = 1, m_l = −1, 0, +1
3d, n = 3, l = 2, m_l = −2, −1, 0, +1, +2

(c) N, $1s^2\,2s^2\,2p^3$ so the 3s, 3p, and 3d orbitals are empty.

(d) C, $1s^2\,2s^2\,2p^2$ so the 1s and 2s orbitals are filled.

(e) Be, $1s^2\,2s^2$ so the 2s orbital contains the outermost electrons.

(f) 2p and 3p (___ ___ ___) and 3d (___ ___ ___ ___ ___).

5.109 $\lambda = 1.03 \times 10^{-7}\ m = 103 \times 10^{-9}\ m = 103\ nm$

$\dfrac{1}{\lambda} = R\left[\dfrac{1}{m^2} - \dfrac{1}{n^2}\right]$, $R = 1.097 \times 10^{-2}\ nm^{-1}$

$\dfrac{1}{103\ nm} = (1.097 \times 10^{-2}\ nm^{-1})\left[\dfrac{1}{1^2} - \dfrac{1}{n^2}\right]$, solve for n.

$\dfrac{(1/103\ nm)}{(1.097 \times 10^{-2}\ nm^{-1})} - 1 = -\dfrac{1}{n^2}$

$\frac{1}{n^2} = 0.115$; $n^2 = \frac{1}{0.115}$; $n = \sqrt{\frac{1}{0.115}} = 2.95$

The electron jumps to the third shell.

5.110 (a) $E = h\nu$; $\nu = \frac{E}{h} = \frac{7.21 \times 10^{-19}\ J}{6.626 \times 10^{-34}\ J \bullet s} = 1.09 \times 10^{15}\ s^{-1}$

(b) $E(photon) = E_i + E_K$; from (a), $E_i = 7.21 \times 10^{-19}$ J

$E(photon) = h\frac{c}{\lambda} = (6.626 \times 10^{-34}\ J \bullet s)\left(\frac{3.00 \times 10^{8}\ m/s}{2.50 \times 10^{-7}\ m}\right) = 7.95 \times 10^{-19}$ J

$E_K = E(photon) - E_i = (7.95 \times 10^{-19}\ J) - (7.21 \times 10^{-19}\ J) = 7.4 \times 10^{-20}$ J

Calculate the electron velocity from the kinetic energy, E_K.

$E_K = 7.4 \times 10^{-20}\ J = 7.4 \times 10^{-20}\ kgAm^2/s^2 = 2mv^2 = 2(9.109 \times 10^{-31}\ kg)v^2$

$v = \sqrt{\frac{2 \times (7.4 \times 10^{-20}\ kg \bullet m^2/s^2)}{9.109 \times 10^{-31}\ kg}} = 4.0 \times 10^{5}$ m/s

deBroglie wavelength $= \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ kg \bullet m^2/s}{(9.109 \times 10^{-31}\ kg)(4.0 \times 10^{5}\ m/s)} = 1.8 \times 10^{-9}$ m = 1.8 nm

Multi-Concept Problem

5.111 (a) $E = h\nu$; $\nu = \frac{E}{h} = \frac{4.70 \times 10^{-16}\ J}{6.626 \times 10^{-34}\ J \bullet s} = 7.09 \times 10^{17}\ s^{-1}$

(b) $\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\ m/s}{7.09 \times 10^{17}\ s^{-1}} = 4.23 \times 10^{-10}$ m $= 0.423 \times 10^{-9}$ m $= 0.423$ nm

(c) $\lambda = \frac{h}{mv}$; $\nu = \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34}\ kg \bullet m^2/s}{(9.11 \times 10^{-31}\ kg)(4.23 \times 10^{-10}\ m)} = 1.72 \times 10^{6}$ m/s

(d) $KE = \frac{mv^2}{2} = \frac{(9.11 \times 10^{-31}\ kg)(1.72 \times 10^{6}\ m/s)^2}{2} = 1.35 \times 10^{-18}$ kg A $m^2/s^2 = 1.35 \times 10^{-18}$ J

5.112 (a) 5f subshell: n = 5, l = 3, m_l = −3, −2, −1, 0, +1, +2, +3

3d subshell: n = 3, l = 2, m_l = −2, −1, 0, +1, +2

(b) In the H atom the subshells in a particular energy level are all degenerate, i.e., all have the same energy. Therefore, you only need to consider the principal quantum number, n, to calculate the wavelength emitted for an electron that drops from the 5f to the 3d subshell.

m = 3, n = 5; $R = 1.097 \times 10^{-2}\ nm^{-1}$

$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]$; $\frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{5^2}\right]$; $\frac{1}{\lambda} = 7.801 \times 10^{-4}\ nm^{-1}$; $\lambda = 1282$ nm

(c) m = 3, n = 4; $R = 1.097 \times 10^{-2}\ nm^{-1}$

$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right]$; $\frac{1}{\lambda} = R\left[\frac{1}{3^2} - \frac{1}{\infty^2}\right]$; $\frac{1}{\lambda} = R\left[\frac{1}{3^2}\right] = 1.219 \times 10^{s3}\ nm^{s1}$; $\lambda = 820.3$ nm

$E = (6.626 \times 10^{-34}\ J \bullet s)\left(\frac{3.00 \times 10^{8}\ m/s}{820.3 \times 10^{-9}\ m}\right)(6.022 \times 10^{23}/\ mol) = 1.46 \times 10^{5}$ J/mol = 146 kJ/mol

5.113 (a) [Kr] $5s^2\ 4d^{10}\ 5p^6$ (b) [Kr] $5s^2\ 4d^{10}\ 5p^5\ 6s^1$

(c) Both Xe^* and Cs have a single electron in the 6s orbital with similar effective nuclear charges. Therefore the 6s electrons in both cases are held with similar strengths and require almost the same energy to remove.

5.114 (a) Cl_2, 70.91 amu

$M + Cl_2 \mid MCl_2$

mol Cl_2 = 0.8092 g $Cl_2 \times \frac{1\ mol\ Cl_2}{70.91\ g\ Cl_2}$ = 0.01141 mol Cl_2

mol M = 0.01141 mol $Cl_2 \times \frac{1\ mol\ M}{1\ mol\ Cl_2}$ = 0.01141 mol M

molar mass of M = $\frac{1.000\ g}{0.01141\ mol}$ = 87.64 g/mol

atomic mass of M = 87.64 amu; M = Sr

(b) q = $\frac{9.46\ kJ}{0.01141\ mol}$ = 829 kJ/mol

5.115 (a) $H_3MO_3(aq) \mid H_3MO_4(aq)$

$H_3MO_3(aq) + H_2O(l) \mid H_3MO_4(aq)$

$H_3MO_3(aq) + H_2O(l) \mid H_3MO_4(aq) + 2\ H^+(aq)$

$[H_3MO_3(aq) + H_2O(l) \mid H_3MO_4(aq) + 2\ H^+(aq) + 2\ e^s] \times 5$ (oxidation half reaction)

$MnO_4^s(aq) \mid Mn^{2+}(aq)$

$MnO_4^s(aq) \mid Mn^{2+}(aq) + 4\ H_2O(l)$

$MnO_4^s(aq) + 8\ H^+(aq) \mid Mn^{2+}(aq) + 4\ H_2O(l)$

$[MnO_4^s(aq) + 8\ H^+(aq) + 5\ e^s \mid Mn^{2+}(aq) + 4\ H_2O(l)] \times 2$ (reduction half reaction)

Combine the two half reactions.

$5\ H_3MO_3(aq) + 5\ H_2O(l) + 2\ MnO_4^s(aq) + 16\ H^+(aq) \mid 5\ H_3MO_4(aq) + 10\ H^+(aq) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$

$5\ H_3MO_3(aq) + 2\ MnO_4^s(aq) + 6\ H^+(aq) \mid 5\ H_3MO_4(aq) + 2\ Mn^{2+}(aq) + 3\ H_2O(l)$

(b) 10.7 mL = 0.0107 L

mol MnO_4^s = (0.0107 L)(0.100 mol/L) = 1.07×10^{s3} mol MnO_4^s

mol H_3MO_3 = 1.07 x 10^{s3} mol MnO_4^{s} x $\frac{5 \text{ mol } H_3MO_3}{2 \text{ mol } MnO_4^-}$ = 2.67 x 10^{s3} mol H_3MO_3

mol M_2O_3 = 2.67 x 10^{s3} mol H_3MO_3 x $\frac{1 \text{ mol } M_2O_3}{2 \text{ mol } H_3MO_3}$ = 1.34 x 10^{s3} mol M_2O_3

(c) mol M in M_2O_3 = 1.34 x 10^{s3} mol M_2O_3 x $\frac{2 \text{ mol M}}{1 \text{ mol } M_2O_3}$ = 2.68 x 10^{s3} mol M

M molar mass = $\frac{0.200 \text{ g}}{2.68 \text{ x } 10^{-3} \text{ mol}}$ = 74.6 g/mol; M atomic mass = 74.6 amu

M is As.

(d) E = hv = (6.626 x 10^{s34} JAs)(9.07 x 10^{14} s^{s1}) = 6.01 x 10^{s19} J/photon
E = (6.01 x 10^{s19} J/photon)(6.022 x 10^{23} photons/mol)(1 kJ/1000 J) = 362 kJ/mol

6 Ionic Bonds and Some Main-Group Chemistry

6.1 (a) Ra^{2+} [Rn] (b) La^{3+} [Xe] (c) Ti^{4+} [Ar] (d) N^{3-} [Ne]
Each ion has the ground-state electron configuration of the noble gas closest to it in the periodic table.

6.2 The neutral atom contains 30 e^- and is Zn. The ion is Zn^{2+}.

6.3 (a) O^{2-}; decrease in effective nuclear charge and an increase in electron-electron repulsions lead to the larger anion.
(b) S; atoms get larger as you go down a group.
(c) Fe; in Fe^{3+} electrons are removed from a larger valence shell and there is an increase in effective nuclear charge leading to the smaller cation.
(d) H^-; decrease in effective nuclear charge and an increase in electron-electron repulsions lead to the larger anion.

6.4 K^+ is smaller than neutral K because the ion has one less electron. K^+ and Cl^- are isoelectronic, but K^+ is smaller than Cl^- because of its higher effective nuclear charge. K is larger than Cl^- because K has one additional electron and that electron begins the next shell (period). K^+, r = 133 pm; Cl^-, r = 184 pm; K, r = 227 pm

6.5 (a) Br (b) S (c) Se (d) Ne

6.6 (a) Be $1s^2\,2s^2$ N $1s^2\,2s^2\,2p^3$
Be would have the larger third ionization energy because this electron would come from the 1s orbital.
(b) Ga [Ar] $4s^2\,3d^{10}\,4p^1$ Ge [Ar] $4s^2\,3d^{10}\,4p^2$
Ga would have the larger fourth ionization energy because this electron would come from the 3d orbitals.

6.7 (b) Cl has the highest E_{i1} and smallest E_{i4}.

6.8 Ca (red) would have the largest third ionization energy of the three because the electron being removed is from a filled valence shell. For Al (green) and Kr (blue), the electron being removed is from a partially filled valence shell. The third ionization energy for Kr would be larger than that for Al because the electron being removed from Kr is coming out of a set of filled 4p orbitals while the electron being removed from Al is coming out of a half-filled 3s orbital. In addition, Z_{eff} is larger for Kr than for Al. The ease of losing its third electron is Al < Kr < Ca.

6.9 Cr [Ar] $4s^1\ 3d^5$ Mn [Ar] $4s^2\ 3d^5$ Fe [Ar] $4s^2\ 3d^6$
Cr can accept an electron into a 4s orbital. The 4s orbital is lower in energy than a 3d orbital. Both Mn and Fe accept the added electron into a 3d orbital that contains an electron, but Mn has a lower value of Z_{eff}. Therefore, Mn has a less negative E_{ea} than either Cr or Fe.

6.10 The least favorable E_{ea} is for Kr (red) because it is a noble gas with filled set of 4p orbitals. The most favorable E_{ea} is for Ge (blue) because the 4p orbitals would become half filled. In addition, Z_{eff} is larger for Ge than it is for K (green).

6.11 (a) KCl has the higher lattice energy because of the smaller K^+.
(b) CaF_2 has the higher lattice energy because of the smaller Ca^{2+}.
(c) CaO has the higher lattice energy because of the higher charge on both the cation and anion.

6.12

$K(s) \rightarrow K(g)$	+89.2 kJ/mol
$K(g) \rightarrow K^+(g) + e^-$	+418.8 kJ/mol
$\frac{1}{2}[F_2(g) \rightarrow 2\ F(g)]$	+79 kJ/mol
$F(g) + e^- \rightarrow F^-(g)$	-328 kJ/mol
$K^+(g) + F^-(g) \rightarrow KF(s)$	-821 kJ/mol
Sum =	-562 kJ/mol for $K(s) + \frac{1}{2} F_2(g) \rightarrow KF(s)$

6.13 The anions are larger than the cations. Cl^- is larger than O^{2-} because it is below it in the periodic table. Therefore, (a) is NaCl and (b) is MgO. Because of the higher ion charge and shorter cation – anion distance, MgO has the larger lattice energy.

6.14 (a) Li_2O, O -2 (b) K_2O_2, O -1 (c) CsO_2, O -½

6.15 (a) $2\ Cs(s) + 2\ H_2O(l) \rightarrow 2\ Cs^+(aq) + 2\ OH^-(aq) + H_2(g)$
(b) $Na(s) + N_2(g) \rightarrow$ N. R.
(c) $Rb(s) + O_2(g) \rightarrow RbO_2(s)$
(d) $2\ K(s) + 2\ NH_3(g) \rightarrow 2\ KNH_2(s) + H_2(g)$
(e) $2\ Rb(s) + H_2(g) \rightarrow 2\ RbH(s)$

6.16 (a) $Be(s) + Br_2(l) \rightarrow BeBr_2(s)$
(b) $Sr(s) + 2\ H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$
(c) $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$

6.17 $BeCl_2(s) + 2\ K(s) \rightarrow Be(s) + 2\ KCl(s)$

6.18 $Mg(s) + S(s) \rightarrow MgS(s)$; In MgS, the oxidation number of S is -2.

6.19 $2\ Al(s) + 6\ H^+(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ H_2(g)$
H^+ gains electrons and is the oxidizing agent. Al loses electrons and is the reducing agent.

6.20 $2\ Al(s) + 3\ S(s) \rightarrow Al_2S_3(s)$

6.21 (a) $Br_2(l) + Cl_2(g) \rightarrow 2\ BrCl(g)$
(b) $2\ Al(s) + 3\ F_2(g) \rightarrow 2\ AlF_3(s)$
(c) $H_2(g) + I_2(s) \rightarrow 2\ HI(g)$

6.22 $Br_2(l) + 2\ NaI(s) \rightarrow 2\ NaBr(s) + I_2(s)$
Br_2 gains electrons and is the oxidizing agent. I^- (from NaI) loses electrons and is the reducing agent.

6.23 (a) XeF_2 F -1, Xe +2 (b) XeF_4 F -1, Xe +4
(c) $XeOF_4$ F -1, O -2, Xe +6

6.24 (a) Rb would lose one electron and adopt the Kr noble-gas configuration.
(b) Ba would lose two electrons and adopt the Xe noble-gas configuration.
(c) Ga would lose three electrons and adopt an Ar-like noble-gas configuration (note that Ga^{3+} has ten 3d electrons in addition to the two 3s and six 3p electrons).
(d) F would gain one electron and adopt the Ne noble-gas configuration.

6.25 Group 6A elements will gain 2 electrons.

6.26 Only about 10% of current world salt production comes from evaporation of seawater. Most salt is obtained by mining the vast deposits of halite, or rock salt, formed by evaporation of ancient inland seas. These salt beds can be up to hundreds of meters thick and may occur anywhere from a few meters to thousands of meters below the earth's surface.

Understanding Key Concepts

6.27

6.28 (a) shows an extended array, which represents an ionic compound.
(b) shows discrete units, which represent a covalent compound.

6.29

6.30

(a) Al^{3+} (b) Cr^{3+} (c) Sn^{2+} (d) Ag^{+}

6.31 The first sphere gets larger on going from reactant to product. This is consistent with it being a nonmetal gaining an electron and becoming an anion. The second sphere gets smaller on going from reactant to product. This is consistent with it being a metal losing an electron and becoming a cation.

6.32 (a) I_2 (b) Na (c) NaCl (d) Cl_2

6.33 (c) has the largest lattice energy because the charges are closest together.
(a) has the smallest lattice energy because the charges are farthest apart.

6.34 Green CBr_4: C, +4; Br, -1
Blue SrF_2: Sr, +2; F, -1
Red PbS: Pb, +2; S, -2 or PbS_2: Pb, +4; S, -2

6.35

Additional Problems
Ionization Energy and Electron Affinity

6.36 (a) La^{3+}, [Xe] (b) Ag^{+}, [Kr] $4d^{10}$ (c) Sn^{2+}, [Kr] $5s^2\,4d^{10}$

6.37 (a) Se^{2-}, [Kr] (b) N^{3-}, [Ne]

6.38 Cr^{2+} [Ar] $3d^4$ ↑ ↑ ↑ ↑ (3d)

Fe^{2+} [Ar] $3d^6$ ↑↓ ↑ ↑ ↑ ↑ (3d)

6.39 Z = 30, Zn

6.40 Ionization energies have a positive sign because energy is required to remove an electron from an atom of any element.

6.41 Electron affinities have a negative sign because energy is released when an electron is added.

6.42 The largest E_{i1} are found in Group 8A because of the largest values of Z_{eff}.
The smallest E_{i1} are found in Group 1A because of the smallest values of Z_{eff}.

6.43 Fr would have the smallest ionization energy, and He would have the largest.

6.44 (a) K [Ar] $4s^1$ Ca [Ar] $4s^2$
Ca has the smaller second ionization energy because it is easier to remove the second 4s valence electron in Ca than it is to remove the second electron in K from the filled 3p orbitals.
(b) Ca [Ar] $4s^2$ Ga [Ar] $4s^2\,3d^{10}\,4p^1$
Ca has the larger third ionization energy because it is more difficult to remove the third electron in Ca from the filled 3p orbitals than it is to remove the third electron (second 4s valence electron) from Ga.

6.45 Sn has a smaller fourth ionization energy than Sb because of a smaller Z_{eff}.
Br has a larger sixth ionization energy than Se because of a larger Z_{eff}.

6.46 (a) $1s^2\,2s^2\,2p^6\,3s^2\,3p^3$ is P (b) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6$ is Ar (c) $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$ is Ca

Ar has the highest E_{i2}. Ar has a higher Z_{eff} than P. The 4s electrons in Ca are easier to remove than any 3p electrons.
Ar has the lowest E_{i7}. It is difficult to remove 3p electrons from Ca, and it is difficult to remove 2p electrons from P.

6.47 The atom in the third row with the lowest E_{i4} is the 4A element, Si. $1s^2\,2s^2\,2p^6\,3s^2\,3p^2$

6.48 Using Figure 6.3 as a reference:

	Lowest E_{i1}	Highest E_{i1}
(a)	K	Li
(b)	B	Cl
(c)	Ca	Cl

6.49 (a) Group 2A (b) Group 6A

6.50 The relationship between the electron affinity of a univalent cation and the ionization energy of the neutral atom is that they have the same magnitude but opposite sign.

6.51 The relationship between the ionization energy of a univalent anion and the electron affinity of the neutral atom is that they have the same magnitude but opposite sign.

6.52 Na^+ has a more negative electron affinity than either Na or Cl because of its positive charge.

6.53 Br would have a more negative electron affinity than Br^- because Br^- has no room in its valence shell for an additional electron.

6.54 Energy is usually released when an electron is added to a neutral atom but absorbed when an electron is removed from a neutral atom because of the positive Z_{eff}.

6.55 E_{i1} increases steadily across the periodic table from Group 1A to Group 8A because electrons are being removed from the same shell and Z_{eff} is increasing. The electron affinity increases irregularly from 1A to 7A and then falls dramatically for Group 8A because the additional electron goes into the next higher shell.

6.56 (a) F; nonmetals have more negative electron affinities than metals.
(b) Na; Ne (noble gas) has a positive electron affinity.
(c) Br; nonmetals have more negative electron affinities than metals.

6.57 Zn, Cd, and Hg all have filled s and d subshells. An additional electron would have to go into the higher energy p subshell. This is unfavorable and results in near-zero electron affinities.

Lattice Energy and Ionic Bonds

6.58 $MgCl_2$ > LiCl > KCl > KBr

6.59 $AlBr_3$ > CaO > $MgBr_2$ > LiBr

6.60

$Li \rightarrow Li^+ + e^-$	+520 kJ/mol
$Br + e^- \rightarrow Br^-$	-325 kJ/mol
	+195 kJ/mol

6.61 The total energy = (376 kJ/mol) + (-349 kJ/mol) = +27 kJ/mol, which is unfavorable because it is positive.

6.62

$Li(s) \rightarrow Li(g)$	+159.4 kJ/mol
$Li(s) \rightarrow Li(g) + e^-$	+520 kJ/mol
$\frac{1}{2}[Br_2(l) \rightarrow Br_2(g)]$	+15.4 kJ/mol
$\frac{1}{2}[Br_2(g) \rightarrow 2\ Br(g)]$	+112 kJ/mol
$Br(g) + e^- \rightarrow Br^-(g)$	-325 kJ/mol
$Li^+(g) + Br^-(g) \rightarrow LiBr(s)$	-807 kJ/mol
	Sum = -325 kJ/mol for $Li(s) + \frac{1}{2}\ Br_2(l) \rightarrow LiBr(s)$

6.63 (a)

$Li(s) \rightarrow Li(g)$	+159.4 kJ/mol
$Li(g) \rightarrow Li^+(g) + e^-$	+520 kJ/mol
$\frac{1}{2}[F_2(g) \rightarrow 2\ F(g)]$	+79 kJ/mol
$F(g) + e^- \rightarrow F^-(g)$	-328 kJ/mol
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	-1036 kJ/mol
	Sum = -606 kJ/mol for $Li(s) + \frac{1}{2}\ F_2(g) \rightarrow LiF(s)$

(b)

$Ca(s) \rightarrow Ca(g)$	+178.2 kJ/mol
$Ca(g) \rightarrow Ca^+(g) + e^-$	+589.8 kJ/mol
$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$	+1145 kJ/mol
$F_2(g) \rightarrow 2\ F(g)$	+158 kJ/mol
$2[F(g) + e^- \rightarrow F^-(g)]$	2(-328) kJ/mol
$Ca^{2+}(g) + 2\ F^- \rightarrow CaF_2(s)$	-2630 kJ/mol
	Sum = -1215 kJ/mol for $Ca(s) + F_2(g) \rightarrow CaF_2(s)$

6.64

$Na(s) \rightarrow Na(g)$	+107.3 kJ/mol
$Na(g) \rightarrow Na^+(g) + e^-$	+495.8 kJ/mol
$\frac{1}{2}[H_2(g) \rightarrow 2\ H(g)]$	½(+435.9) kJ/mol
$H(g) + e^- \rightarrow H^-(g)$	-72.8 kJ/mol
$Na^+(g) + H^-(g) \rightarrow NaH(s)$	-U

Sum = -60 kJ/mol for $Na(s) + \frac{1}{2} H_2(g) \rightarrow NaH(s)$

$-U = -60 - 107.3 - 495.8 - 435.9/2 + 72.8 = -808$ kJ/mol; $U = 808$ kJ/mol

6.65

$Ca(s) \rightarrow Ca(g)$	+178.2 kJ/mol
$Ca(g) \rightarrow Ca^+(g) + e^-$	+589.8 kJ/mol
$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$	+1145 kJ/mol
$H_2(g) \rightarrow 2\ H(g)$	+435.9 kJ/mol
$2[H(g) + e^- \rightarrow H^-(g)]$	2(-72.8) kJ/mol
$Ca^{2+}(g) + 2\ H^-(g) \rightarrow CaH_2(s)$	-U

Sum = -186.2 kJ/mol for $Ca(s) + H_2(g) \rightarrow CaH_2(s)$

$-U = -186.2 - 178.2 - 589.8 - 1145 - 435.9 + 2(72.8) = -2390$ kJ/mol; $U = 2390$ kJ/mol

6.66

$Cs(s) \rightarrow Cs(g)$	+76.1 kJ/mol
$Cs(g) \rightarrow Cs^+(g) + e^-$	+375.7 kJ/mol
$\frac{1}{2}[F_2(g) \rightarrow 2\ F(g)]$	+79 kJ/mol
$F(g) + e^- \rightarrow F^-(g)$	-328 kJ/mol
$Cs^+(g) + F^-(g) \rightarrow CsF(s)$	-740 kJ/mol

Sum = -537 kJ/mol for $Cs(s) + \frac{1}{2} F_2(g) \rightarrow CsF(s)$

6.67

$Cs(s) \rightarrow Cs(g)$	+76.1 kJ/mol
$Cs(g) \rightarrow Cs^+(g) + e^-$	+375.7 kJ/mol
$Cs^+(g) \rightarrow Cs^{2+}(g) + e^-$	+2422 kJ/mol
$F_2(g) \rightarrow 2\ F(g)$	+158 kJ/mol
$2[F(g) + e^- \rightarrow F^-(g)]$	2(-328) kJ/mol
$Cs^{2+}(g) + 2\ F^-(g) \rightarrow CsF_2(s)$	-2347 kJ/mol

Sum = +29 kJ/mol for $Cs(s) + F_2(g) \rightarrow CsF_2(s)$

The overall reaction absorbs 29 kJ/mol.
In the reaction of cesium with fluorine, CsF will form because the overall energy for the formation of CsF is negative, whereas it is positive for CsF_2.

6.68

$Ca(s) \rightarrow Ca(g)$	+178.2 kJ/mol
$Ca(g) \rightarrow Ca^+(g) + e^-$	+589.8 kJ/mol
$\frac{1}{2}[Cl_2(g) \rightarrow 2\ Cl(g)]$	+121.5 kJ/mol
$Cl(g) + e^- \rightarrow Cl^-(g)$	-348.6 kJ/mol
$Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$	-717 kJ/mol

Sum = -176 kJ/mol for $Ca(s) + \frac{1}{2} Cl_2(g) \rightarrow CaCl(s)$

6.69 $Ca(s) \rightarrow Ca(g) + e^-$ +178.2 kJ/mol

$Ca(g) \rightarrow Ca^{+}(g) + e^{-}$	+589.8	kJ/mol
$Ca^{+}(g) \rightarrow Ca^{2+}(g)$	+1145	kJ/mol
$Cl_2(g) \rightarrow 2\ Cl(g)$	+243	kJ/mol
$2[Cl(g) + e^{-} \rightarrow Cl^{-}(g)]$	2(-348.6)	kJ/mol
$Ca^{2+}(g) + 2\ Cl^{-}(g) \rightarrow CaCl_2(s)$	-2258	kJ/mol
	Sum = -799	kJ/mol for $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$

In the reaction of calcium with chlorine, $CaCl_2$ will form because the overall energy for the formation of $CaCl_2$ is much more negative than for the formation of CaCl.

6.70

6.71

Main-Group Chemistry

6.72 Solids: I_2; Liquids: Br_2; Gases: F_2, Cl_2, He, Ne, Ar, Kr, Xe

6.73 (a) Li is used in automotive grease. Li_2CO_3 is a manic depressive drug.

(b) K salts are used in plant fertilizers.
(c) $SrCO_3$ is used in color TV picture tubes. Sr salts are used for red fireworks.
(d) Liquid He (bp = 4.2 K) is used for low temperature studies and for cooling superconducting magnets.

6.74 (a) At is in Group 7A. The trend going down the group is gas → liquid → solid. At, being at the bottom of the group, should be a solid.
(b) At would likely be dark, like I_2, maybe with a metallic sheen.
(c) At is likely to react with Na just like the other halogens, yielding NaAt.

6.75 Predicted for Fr: melting point ≈ 23 °C; boiling point ≈ 650 °C; density ≈ 2 g/cm^3; atomic radius ≈ 275 pm

6.76 (a) $2\ NaCl \xrightarrow[580°C]{\text{electrolysis in } CaCl_2} 2\ Na(l) + Cl_2(g)$

(b) $2\ Al_2O_3 \xrightarrow[980°C]{\text{electrolysis in } Na_3AlF_6} 4\ Al(l) + 3\ O_2(g)$

(c) Ar is obtained from the distillation of liquid air.
(d) $2\ Br^-(aq) + Cl_2(g) \rightarrow Br_2(l) + 2\ Cl^-(aq)$

6.77 Group 1A metals react by losing an electron. Down Group 1A, the valence electron is more easily removed. This trend parallels chemical reactivity.
Group 7A nonmetals react by gaining an electron. The electron affinity generally increases up the group. This trend parallels chemical reactivity.

6.78 Main-group elements tend to undergo reactions that leave them with eight valence electrons. That is, main-group elements react so that they attain a noble gas electron configuration with filled s and p sublevels in their valence electron shell.
The octet rule works for valence shell electrons because taking electrons away from a filled octet is difficult because they are tightly held by a high Z_{eff}; adding more electrons to a filled octet is difficult because, with s and p sublevels full, there is no low-energy orbital available.

6.79 Main-group nonmetals in the third period and below occasionally break the octet rule.

6.80 (a) $2\ K(s) + H_2(g) \rightarrow 2\ KH(s)$
(b) $2\ K(s) + 2\ H_2O(l) \rightarrow 2\ K^+(aq) + 2\ OH^-(aq) + H_2(g)$
(c) $2\ K(s) + 2\ NH_3(g) \rightarrow 2\ KNH_2(s) + H_2(g)$
(d) $2\ K(s) + Br_2(l) \rightarrow 2\ KBr(s)$

(e) $K(s) + N_2(g) \rightarrow$ N. R.
(f) $K(s) + O_2(g) \rightarrow KO_2(s)$

6.81 (a) $Ca(s) + H_2(g) \rightarrow CaH_2(s)$
(b) $Ca(s) + 2\ H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq) + H_2(g)$
(c) $Ca(s) + He(g) \rightarrow$ N. R.
(d) $Ca(s) + Br_2(l) \rightarrow CaBr_2(s)$
(e) $2\ Ca(s) + O_2(g) \rightarrow 2\ CaO(s)$

6.82 (a) $Cl_2(g) + H_2(g) \rightarrow 2\ HCl(g)$
(b) $Cl_2(g) + Ar(g) \rightarrow$ N. R.
(c) $Cl_2(g) + Br_2(l) \rightarrow 2\ BrCl(g)$
(d) $Cl_2(g) + N_2(g) \rightarrow$ N. R.

6.83 (a) $2\ Cl^-(aq) + F_2(g) \rightarrow 2\ F^-(aq) + Cl_2(g)$
F_2 gains electrons and is the oxidizing agent. Cl^- loses electrons and is the reducing agent.
(b) $2\ Br^-(aq) + I_2(s) \rightarrow$ N. R.
(c) $2\ I^-(aq) + Br_2(aq) \rightarrow 2\ Br^-(aq) + I_2(aq)$
Br_2 gains electrons and is the oxidizing agent. I^- loses electrons and is the reducing agent.

6.84 $AlCl_3 + 3\ Na \rightarrow Al + 3\ NaCl$
Al^{3+} (from $AlCl_3$) gains electrons and is reduced. Na loses electrons and is oxidized.

6.85 $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$
$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$

6.86 $CaIO_3$, 215.0 amu; 1.00 kg = 1000 g

$$\% \text{ I} = \frac{126.9\ \text{g}}{215.0\ \text{g}} \times 100\% = 59.02\%;\ (0.5902)(1000\ \text{g}) = 590\ \text{g I}_2$$

6.87 $2\ Li(s) + 2\ H_2O(l) \rightarrow 2\ LiOH(aq) + H_2(g)$; 455 mL = 0.455 L
mass of $H_2 = (0.0893\ \text{g/L})(0.455\ \text{L}) = 0.0406\ \text{g}\ H_2$

$$0.0406\ \text{g}\ H_2 \times \frac{1\ \text{mol}\ H_2}{2.016\ \text{g}\ H_2} \times \frac{2\ \text{mol Li}}{1\ \text{mol}\ H_2} \times \frac{6.94\ \text{g Li}}{1\ \text{mol Li}} = 0.280\ \text{g Li}$$

6.88 $Ca(s) + H_2(g) \rightarrow CaH_2(s)$; H_2, 2.016 amu; CaH_2, 42.09 amu

$$5.65\ \text{g Ca} \times \frac{1\ \text{mol Ca}}{40.08\ \text{g Ca}} = 0.141\ \text{mol Ca}$$

$$3.15\ \text{L}\ H_2 \times 0.0893\ \frac{\text{g}\ H_2}{1\ \text{L}} \times \frac{1\ \text{mol}\ H_2}{2.016\ \text{g}\ H_2} = 0.140\ \text{mol}\ H_2$$

Because the reaction stoichiometry between Ca and H_2 is one to one, H_2 is the limiting reactant.

$$0.140 \text{ mol } H_2 \times \frac{1 \text{ mol } CaH_2}{1 \text{ mol } H_2} \times \frac{42.09 \text{ g } CaH_2}{1 \text{ mol } CaH_2} \times 0.943 = 5.56 \text{ g } CaH_2$$

6.89 $6\ Li(s) + N_2(g) \rightarrow 2\ Li_3N(s)$; N_2, 28.01 amu; Li_3N, 34.83 amu

$$2.87 \text{ g Li} \times \frac{1 \text{ mol Li}}{6.941 \text{ g Li}} \times \frac{1 \text{ mol } N_2}{6 \text{ mol Li}} \times \frac{28.01 \text{ g } N_2}{1 \text{ mol } N_2} \times \frac{1 \text{ L}}{1.25 \text{ g } N_2} = 1.54 \text{ L } N_2$$

6.90 (a) $Mg(s) + 2\ H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
H^+ gains electrons and is the oxidizing agent. Mg loses electrons and is the reducing agent.
(b) $Kr(g) + F_2(g) \rightarrow KrF_2(s)$
F_2 gains electrons and is the oxidizing agent. Kr loses electrons and is the reducing agent.
(c) $I_2(s) + 3\ Cl_2(g) \rightarrow 2\ ICl_3(l)$
Cl_2 gains electrons and is the oxidizing agent. I_2 loses electrons and is the reducing agent.

6.91 (a) $2\ XeF_2(s) + 2\ H_2O(l) \rightarrow 2\ Xe(g) + 4\ HF(aq) + O_2(g)$
Xe in XeF_2 gains electrons and is the oxidizing agent. O in H_2O loses electrons and is the reducing agent.
(b) $NaH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2(g)$
H in H_2O gains electrons and is the oxidizing agent. H in NaH loses electrons and is the reducing agent.
(c) $2\ TiCl_4(l) + H_2(g) \rightarrow 2\ TiCl_3(s) + 2\ HCl(g)$
Ti in $TiCl_4$ gains electrons and is the oxidizing agent. H_2 loses electrons and is the reducing agent.

General Problems

6.92 Cu^{2+} has fewer electrons and a larger effective nuclear charge; therefore it has the smaller ionic radius.

6.93 $S^{2-} > Ca^{2+} > Sc^{3+} > Ti^{4+}$, Z_{eff} increases on going from S^{2-} to Ti^{4+}.

6.94

$Mg(s) \rightarrow Mg(g)$	+147.7 kJ/mol
$Mg(g) \rightarrow Mg^+(g) + e^-$	+737.7 kJ/mol
$\frac{1}{2}[F_2(g) \rightarrow 2\ F(g)]$	+79 kJ/mol
$F(g) + e^- \rightarrow F^-(g)$	-328 kJ/mol
$Mg^+(g) + F^-(g) \rightarrow MgF(s)$	-930 kJ/mol
Sum =	-294 kJ/mol for $Mg(s) + \frac{1}{2}\ F_2(g) \rightarrow MgF(s)$

$Mg(s) \rightarrow Mg(g)$	+147.7 kJ/mol
$Mg(g) \rightarrow Mg^+(g) + e^-$	+737.7 kJ/mol

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ +1450.7 kJ/mol
$F_2(g) \rightarrow 2\ F(g)$ +158 kJ/mol
$2[F(g) + e^- \rightarrow F^-(g)]$ 2(-328) kJ/mol
$Mg^{2+}(g) + 2\ F^-(g) \rightarrow MgF_2(s)$ -2952 kJ/mol
Sum = -1114 kJ/mol for $Mg(s) + F_2(g) \rightarrow MgF_2(s)$

6.95 In the reaction of magnesium with fluorine, MgF_2 will form because the overall energy for the formation of MgF_2 is much more negative than for the formation of MgF.

6.96 (a) Na is used in table salt (NaCl), glass, rubber, and pharmaceutical agents.
(b) Mg is used as a structural material when alloyed with Al.
(c) F_2 is used in the manufacture of Teflon, $(C_2F_4)_n$, and in toothpaste as SnF_2.

6.97 (a) $2\ HF(l) \xrightarrow[100°C]{\text{electrolysis}} H_2(g) + F_2(g)$

(b) $3\ CaO(l) + 2\ Al(l) \xrightarrow{\text{high temperature}} 3\ Ca(l) + Al_2O_3(s)$

(c) $2\ NaCl(l) \xrightarrow[580°C]{\text{electrolysis in } CaCl_2} 2\ Na(l) + Cl_2(g)$

6.98 (a) $2\ Li(s) + H_2(g) \rightarrow 2\ LiH(s)$
(b) $2\ Li(s) + 2\ H_2O(l) \rightarrow 2\ Li^+(aq) + 2\ OH^-(aq) + H_2(g)$
(c) $2\ Li(s) + 2\ NH_3(g) \rightarrow 2\ LiNH_2(s) + H_2(g)$
(d) $2\ Li(s) + Br_2(l) \rightarrow 2\ LiBr(s)$
(e) $6\ Li(s) + N_2(g) \rightarrow 2\ Li_3N(s)$
(f) $4\ Li(s) + O_2(g) \rightarrow 2\ Li_2O(s)$

6.99 (a) $F_2(g) + H_2(g) \rightarrow 2\ HF(g)$ (b) $F_2(g) + 2\ Na(s) \rightarrow 2\ NaF(s)$
(c) $F_2(g) + Br_2(l) \rightarrow 2\ BrF(g)$ (d) $F_2(g) + 2\ NaBr(s) \rightarrow 2\ NaF(g) + Br_2(l)$

6.100 When moving diagonally down and right on the periodic table, the increase in atomic radius caused by going to a larger shell is offset by a decrease caused by a higher Z_{eff}. Thus, there is little net change.

6.101 $Na(s) \rightarrow Na(g)$ +107.3 kJ/mol
$Na(g) + e^- \rightarrow Na^-(g)$ -52.9 kJ/mol
$\frac{1}{2}[Cl_2(g) \rightarrow 2\ Cl(g)]$ +122 kJ/mol
$Cl(g) \rightarrow Cl^+(g) + e^-$ +1251 kJ/mol
$Na^-(g) + Cl^+(g) \rightarrow ClNa(s)$ -787 kJ/mol
Sum = +640 kJ/mol for $Na(s) + \frac{1}{2}\ Cl_2(g) \rightarrow Cl^+Na^-(s)$
The formation of Cl^+Na^- from its elements is not favored because the net energy change is

positive whereas for the formation of Na^+Cl^- it is negative.

6.102

6.103 94.2 mL = 0.0942 L

$$0.0942\ \text{L}\ Cl_2 \times \frac{1\ \text{mol}\ Cl_2}{22.4\ \text{L}} \times \frac{2\ \text{mol}\ Cl^-}{1\ \text{mol}\ Cl_2} = 8.41 \times 10^{-3}\ \text{mol}\ Cl^-$$

Possible formulas for the metal halide are MCl, MCl_2, MCl_3, etc.

For MCl, mol M = mol Cl^- = 8.41×10^{-3} mol M

$$\text{molar mass of M} = \frac{0.719\ \text{g}}{8.41 \times 10^{-3}\ \text{mol}} = 85.5\ \text{g/mol}$$

For MCl_2, mol M = 8.41×10^{-3} mol Cl^- $\times \frac{1\ \text{mol M}}{2\ \text{mol}\ Cl^-}$ 1111 = 4.20×10^{-3} mol M

$$\text{molar mass of M} = \frac{0.719\ \text{g}}{4.20 \times 10^{-3}\ \text{mol}} = 171\ \text{g/mol}$$

For MCl_3, mol M = 8.41×10^{-3} mol Cl^- $\times \frac{1\ \text{mol M}}{3\ \text{mol}\ Cl^-}$ = 2.80×10^{-3} mol M

$$\text{molar mass of M} = \frac{0.719\ \text{g}}{2.80 \times 10^{-3}\ \text{mol}} = 257\ \text{g/mol}$$

The best match for a metal is with 85.5 g/mol, which is Rb.

6.104

$Mg(s) \rightarrow Mg(g)$	+147.7 kJ/mol
$Mg(g) \rightarrow Mg^+(g) + e^-$	+738 kJ/mol
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	+1451 kJ/mol
$\frac{1}{2}[O_2(g) \rightarrow 2\ O(g)]$	+249.2 kJ/mol
$O(g) + e^- \rightarrow O^-(g)$	-141.0 kJ/mol
$O^-(g) + e^- \rightarrow O^{2-}(g)$	E_{ea2}
$Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$	-3791 kJ/mol
$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	-601.7 kJ/mol

147.7 + 738 + 1451 + 249.2 - 141.0 + E_{ea2} - 3791 = -601.7

E_{ea2} = -147.7 - 738 - 1451 - 249.2 + 141.0 + 3791 - 601.7 = +744 kJ/mol

Because E_{ea2} is positive, O^{2-} is not stable in the gas phase. It is stable in MgO because of the large lattice energy that results from the +2 and -2 charge of the ions and their small size.

6.105 (a) (i) Ra because it is farthest down (7th period) in the periodic table.
(ii) In because it is farthest down (5th period) in the periodic table.
(b) (i) Tl and Po are farthest down (6th period) but Tl is larger because it is to the left of Po and thus has the smaller ionization energy.
(ii) Cs and Bi are farthest down (6th period) but Cs is larger because it is to the left of Bi and thus has the smaller ionization energy.

6.106 (a) The more negative the E_{ea}, the greater the tendency of the atom to accept an electron, and the more stable the anion that results. Be, N, O, and F are all second row elements. F has the most negative E_{ea} of the group because the anion that forms, F^-, has a complete octet of electrons and its nucleus has the highest effective nuclear charge.
(b) Se^{2-} and Rb^+ are below O^{2-} and F^- in the periodic table and are the larger of the four. Se^{2-} and Rb^+ are isoelectronic, but Rb^+ has the higher effective nuclear charge so it is smaller. Therefore Se^{2-} is the largest of the four ions.

6.107

$Ca(s) \rightarrow Ca(g)$	+178 kJ/mol
$Ca(g) \rightarrow Ca^+(g)$	+590 kJ/mol
$Ca^+(g) \rightarrow Ca^{2+}(g)$	+1145 kJ/mol
$2\ C(s) \rightarrow 2\ C(g)$	2(+717 kJ/mol)
$2\ C(g) \rightarrow C_2(g)$	-614 kJ/mol
$C_2(g) \rightarrow C_2^-(g)$	-315 kJ/mol
$C_2^-(g) \rightarrow C_2^{2-}(g)$	+410 kJ/mol
$Ca^{2+}(g) + C_2^{2-}(g) \rightarrow CaC_2(s)$	-U
$Ca(s) + 2\ C(s) \rightarrow CaC_2(s)$	-60 kJ/mol

$-U = -60 - 178 - 590 - 1145 - 2(717) + 614 + 315 - 410 = -2888$ kJ/mol
$U = 2888$ kJ/mol

6.108

$Cr(s) \rightarrow Cr(g)$	+397 kJ/mol
$Cr(g) \rightarrow Cr^+(g)$	+652 kJ/mol
$Cr^+(g) \rightarrow Cr^{2+}(g)$	+1588 kJ/mol
$Cr^{2+}(g) \rightarrow Cr^{3+}(g)$	+2882 kJ/mol
$\frac{1}{2}(I_2(s) \rightarrow I_2(g))$	+62/2 kJ/mol
$\frac{1}{2}\ (I_2(g) \rightarrow 2\ I(g))$	+151/2 kJ/mol
$I(g) + e^- \rightarrow I^-(g)$	-295 kJ/mol
$Cl_2(g) \rightarrow 2\ Cl(g)$	+243 kJ/mol
$2(Cl(g) + e^- \rightarrow Cl^-(g))$	2(-349) kJ/mol
$Cr^{3+}(g) + 2\ Cl^-(g) + I^-(g) \rightarrow CrCl_2I(s)$	-U
$Cr(s) + Cl_2(g) + \frac{1}{2}\ I_2(g) \rightarrow CrCl_2I(s)$	- 420 kJ/mol

$-U = -420 - 397 - 652 - 1588 - 2882 - 62/2 - 151/2 + 295 - 243 + 2(349) = -5295.5$ kJ/mol
$U = 5295$ kJ/mol

Multi-Concept Problems

6.109 (a) $E = (703\ kJ/mol)(1000\ J/1\ kJ)/(6.022 \times 10^{23}\ photons/mol) = 1.17 \times 10^{-18}$ J/photon

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})(3.00 \text{ x } 10^{8} \text{ m/s})}{1.17 \text{ x } 10^{-18} \text{ J}} = 1.70 \text{ x } 10^{-7} \text{ m} = 170 \text{ x } 10^{-9} \text{ m} = 170 \text{ nm}$$

(b) Bi [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^3$
Bi^+ [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$

(c) n = 6, l = 1

(d) Element 115 would be directly below Bi in the periodic table. The valence electron is farther from the nucleus and less strongly held than in Bi. The ionization energy for element 115 would be less than that for Bi.

6.110 (a) Fe [Ar] $4s^2\ 3d^6$
Fe^{2+} [Ar] $3d^6$
Fe^{3+} [Ar] $3d^5$

(b) A 3d electron is removed on going from Fe^{2+} to Fe^{3+}. For the 3d electron, n = 3 and l = 2.

(c) $E(\text{J/photon}) = 2952 \text{ kJ/mol} \text{ x } \frac{1 \text{ mol photons}}{6.022 \text{ x } 10^{23} \text{ photons}} \text{ x } \frac{1000 \text{ J}}{1 \text{ kJ}} = 4.90 \text{ x } 10^{-18} \text{ J/photon}$

$$E = \frac{h\,c}{\lambda}$$

$$\lambda = \frac{h\,c}{E} = \frac{(6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s})(3.00 \text{ x } 10^{8} \text{ m/s})}{4.90 \text{ x } 10^{-18} \text{ J}} = 4.06 \text{ x } 10^{-8} \text{ m} = 40.6 \text{ x } 10^{-9} \text{ m} = 40.6 \text{ nm}$$

(d) Ru is directly below Fe in the periodic table and the two metals have similar electron configurations. The electron removed from Ru to go from Ru^{2+} to Ru^{3+} is a 4d electron. The electron with the higher principal quantum number, n = 4, is farther from the nucleus, less tightly held, and requires less energy to remove.

6.111 (a) 58.4 nm = 58.4 x 10^{-9} m

$$E(\text{photon}) = 6.626 \text{ x } 10^{-34} \text{ J·s x } \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{58.4 \text{ x } 10^{-9} \text{ m}} \text{ x } \frac{1 \text{ kJ}}{1000 \text{ J}} \text{ x } \frac{6.022 \text{ x } 10^{23}}{\text{mol}} = 2049 \text{ kJ/mol}$$

$$E_K = E(\text{electron}) = \tfrac{1}{2}(9.109 \text{ x } 10^{-31} \text{ kg})(2.450 \text{ x } 10^{6} \text{ m/s})^2 \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)\left(\frac{6.022 \text{ x } 10^{23}}{\text{mol}}\right)$$

E_K = 1646 kJ/mol

$E(\text{photon}) = E_i + E_K$; $E_i = E(\text{photon}) - E_K = 2049 - 1646 = 403$ kJ/mol

(b) 142 nm = 142 x 10^{-9} m

$$E(\text{photon}) = 6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{s} \text{ x } \frac{3.00 \text{ x } 10^{8} \text{ m/s}}{142 \text{ x } 10^{-9} \text{ m}} \text{ x } \frac{1 \text{ kJ}}{1000 \text{ J}} \text{ x } \frac{6.022 \text{ x } 10^{23}}{\text{mol}} = 843 \text{ kJ/mol}$$

$$E_K = E(\text{electron}) = \tfrac{1}{2}(9.109 \times 10^{-31}\ \text{kg})(1.240 \times 10^{6}\ \text{m/s})^2\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)\left(\frac{6.022 \times 10^{23}}{\text{mol}}\right)$$

$$E_K = 422\ \text{kJ/mol}$$

$E(\text{photon}) = E_i + E_K$; $\quad E_i = E(\text{photon}) - E_K = 843 - 422 = 421\ \text{kJ/mol}$

6.112 AgCl, 143.32 amu

(a) mass Cl in AgCl = 1.126 g AgCl x $\dfrac{35.453\,\text{g Cl}}{143.32\,\text{g AgCl}}$ = 0.279 g Cl

%Cl in alkaline earth chloride = $\dfrac{0.279\,\text{g Cl}}{0.436\,\text{g}}$ x 100% = 64.0% Cl

(b) Because M is an alkaline earth metal, M is a 2+ cation.
For MCl_2, mass of M = 0.436 g - 0.279 g = 0.157 g M

mol M = 0.279 g Cl x $\dfrac{1\,\text{mol Cl}}{35.453\,\text{g Cl}}$ x $\dfrac{1\,\text{mol M}}{2\,\text{mol Cl}}$ = 0.003 93 mol M

molar mass for M = $\dfrac{0.157\,\text{g}}{0.003\ 93\,\text{mol}}$ = 39.9 g/mol; M = Ca

(c) $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$
$CaCl_2(aq) + 2\ AgNO_3(aq) \rightarrow 2\ AgCl(s) + Ca(NO_3)_2(aq)$

(d) 1.005 g Ca x $\dfrac{1\,\text{mol Ca}}{40.078\,\text{g Ca}}$ = 0.0251 mol Ca

1.91×10^{22} Cl_2 molecules x $\dfrac{1\,\text{mol Cl}_2}{6.022 \times 10^{23}\,\text{Cl}_2\,\text{molecules}}$ = 0.0317 mol Cl_2

Because the stoichiometry between Ca and Cl_2 is one to one, the Cl_2 is in excess.

Mass Cl_2 unreacted = (0.0317 - 0.0251) mol Cl_2 x $\dfrac{70.91\,\text{g Cl}_2}{1\,\text{mol Cl}_2}$ = 0.47 g Cl_2 unreacted

6.113 (a) (i) $M_2O_3(s) + 3\ C(s) + 3\ Cl_2(g) \rightarrow 2\ MCl_3(l) + 3\ CO(g)$
(ii) $2\ MCl_3(l) + 3\ H_2(g) \rightarrow 2\ M(s) + 6\ HCl(g)$
(b) $HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl(aq)$
144.2 mL = 0.1442 L
mol NaOH = (0.511 mol/L)(0.1442 L) = 0.07369 mol NaOH

mol HCl = 0.07369 mol NaOH x $\dfrac{1\ \text{mol HCl}}{1\ \text{mol NaOH}}$ = 0.07369 mol HCl

mol M = 0.07369 mol HCl x $\dfrac{2\ \text{mol M}}{6\ \text{mol HCl}}$ = 0.02456 mol M

mol M_2O_3 = 0.02456 mol M x $\dfrac{2\ \text{mol MCl}_3}{2\ \text{mol M}}$ x $\dfrac{1\ \text{mol M}_2\text{O}_3}{2\ \text{mol MCl}_3}$ = 0.01228 mol M_2O_3

molar mass $M_2O_3 = \frac{0.855\ g}{0.01228\ mol} = 69.6$ g/mol; molecular mass $M_2O_3 = 69.6$ amu

atomic mass of M = $\frac{69.6\ amu\ -\ (3\ x\ 16.0\ amu)}{2} = 10.8$ amu; M = B

(c) mass of M = 0.02456 mol M x $\frac{10.81\ g\ M}{1\ mol\ M} = 0.265$ g M

6.114 (a)

$Sr(s) \rightarrow Sr(g)$	+164.44	kJ/mol
$Sr(g) \rightarrow Sr^+(g) + e^-$	+549.5	kJ/mol
$Sr^+(g) \rightarrow Sr^{2+}(g) + e^-$	+1064.2	kJ/mol
$Cl_2(g) \rightarrow 2\ Cl(g)$	+243	kJ/mol
$2[Cl(g) + e^- \rightarrow Cl^-(g)]$	2(-348.6)	kJ/mol
$Sr^{2+}(g) + 2\ Cl^-(g) \rightarrow SrCl_2(s)$	-2156	kJ/mol
	Sum = -832	kJ/mol for $Sr(s) + Cl_2(g) \rightarrow SrCl_2(s)$

(b) Sr, 87.62 amu; Cl_2, 70.91 amu; $SrCl_2$, 158.53 amu

20.0 g Sr x $\frac{1\ mol\ Sr}{87.62\ g\ Sr} = 0.228$ mol Sr and 25.0 g Cl_2 x $\frac{1\ mol\ Cl_2}{70.91\ g\ Cl_2} = 0.353$ mol Cl_2

Because there is a 1:1 stoichiometry between the reactants, the one with the smaller mole amount is the limiting reactant. Sr is the limiting reactant.

0.228 mol Sr x $\frac{1\ mol\ SrCl_2}{1\ mol\ Sr}$ x $\frac{158.53\ g\ SrCl_2}{1\ mol\ SrCl_2} = 36.1$ g $SrCl_2$

(c) 0.228 mol $SrCl_2$ x $\frac{-832\ kJ}{1\ mol\ SrCl_2} = -190$ kJ

190 kJ is released during the reaction of 20.0 g of Sr with 25.0 g Cl_2.

6.115 (a) The alkali metal is Li because it is the only alkali metal to form the nitride, M_3N.

(b) $4\ Li(s) + O_2(g) \rightarrow 2\ Li_2O(s)$

$6\ Li(s) + N_2(g) \rightarrow 2\ Li_3N(s)$

$Li_2O(s) + H_2O(l) \rightarrow 2\ LiOH(aq)$

$Li_3N(s) + 3\ H_2O(l) \rightarrow NH_3(aq) + 3\ LiOH(aq)$

(c) 96.8 mL = 0.0968 L

mol HCl = (0.0968 L)(0.100 mol/L) = 0.009 68 mol HCl

Note, that the HCl neutralized only 20% (0.20) of the total sample.

Let Y = mol Li_2O and let Z = mol Li_3N

mol HCl = 2Y + 4Z = 0.009 68 mol

mol Li = 2Y + 3Z = (0.20)(0.265 g Li) x $\frac{1\ mol\ Li}{6.941\ g\ Li} = 0.007\ 64$ mol Li

2Y + 4Z = 0.009 68

2Y + 3Z = 0.007 64

2Y = 0.007 64 - 3Z (substitute 2Y into the first equation and solve for Z)

0.007 64 - 3Z + 4Z = 0.009 68

Z = 0.009 68 - 0.007 64 = 0.002 04 mol Li_3N

$$Y = (0.007\ 64 - 3Z)/2 = [0.007\ 64 - 3(0.002\ 04)]/2 = 0.000\ 76 \text{ mol } Li_2O$$

$$X_{Li_2O} = \frac{\text{mol } Li_2O}{\text{mol } Li_2O + \text{mol } Li_3N} = \frac{0.000\ 76 \text{ mol}}{0.000\ 76 \text{ mol} + 0.002\ 04 \text{ mol}} = 0.271$$

$$X_{Li_3N} = 1.000 - 0.271 = 0.729$$

7 Covalent Bonds and Molecular Structure

7.1 (a) $SiCl_4$

chlorine	EN = 3.0	
silicon	EN = 1.8	
	ΔEN = 1.2	The Si–Cl bond is polar covalent.

(b) CsBr

bromine	EN = 2.8	
cesium	EN = 0.7	
	ΔEN = 2.1	The Cs^+Br^- bond is ionic.

(c) $FeBr_3$

bromine	EN = 2.8	
iron	EN = 1.8	
	ΔEN = 1.0	The Fe–Br bond is polar covalent.

(d) CH_4

carbon	EN = 2.5	
hydrogen	EN = 2.1	
	ΔEN = 0.4	The C–H bond is polar covalent.

7.2 (a) CCl_4

chlorine	EN = 3.0
carbon	EN = 2.5
	ΔEN = 0.5

(b) $BaCl_2$

chlorine	EN = 3.0
barium	EN = 0.9
	ΔEN = 2.1

(c) $TiCl_3$

chlorine	EN = 3.0
titanium	EN = 1.5
	ΔEN = 1.5

(d) Cl_2O

oxygen	EN = 3.5
chlorine	EN = 3.0
	ΔEN = 0.5

Increasing ionic character: $CCl_4 \sim ClO_2 < TiCl_3 < BaCl_2$

7.3 H is positively polarized (blue). O is negatively polarized (red). This is consistent with the electronegativity values for O (3.5) and H (2.1). The more negatively polarized atom should be the one with the larger electronegativity.

7.4 (a) (b)

7.5

7.6 (a) (b) (c)

(d) (e) (f)

7.7

7.8 Molecular formula: $C_4H_5N_3O$;

7.9

7.10 (a) (b)

(c) (d)

7.11 (a) (b) (c)

(d)

7.12

7.13 (a)

(b)

(c)

(d)

7.14

7.15	For nitrogen:	Isolated nitrogen valence electrons	5
		Bound nitrogen bonding electrons	8
		Bound nitrogen nonbonding electrons	0
		Formal charge = 5 - ½(8) - 0 = +1	
	For singly bound oxygen:	Isolated oxygen valence electrons	6
		Bound oxygen bonding electrons	2
		Bound oxygen nonbonding electrons	6
		Formal charge = 6 - ½(2) - 6 = -1	
	For doubly bound oxygen:	Isolated oxygen valence electrons	6
		Bound oxygen bonding electrons	4
		Bound oxygen nonbonding electrons	4
		Formal charge = 6 - ½(4) - 4 = 0	

7.16	(a)		
	For nitrogen:	Isolated nitrogen valence electrons	5
		Bound nitrogen bonding electrons	4
		Bound nitrogen nonbonding electrons	4
		Formal charge = 5 - ½(4) - 4 = -1	
	For carbon:	Isolated carbon valence electrons	4
		Bound carbon bonding electrons	8
		Bound carbon nonbonding electrons	0
		Formal charge = 4 - ½ (8) - 0 = 0	
	For oxygen:	Isolated oxygen valence electrons	6
		Bound oxygen bonding electrons	4
		Bound oxygen nonbonding electrons	4
		Formal charge = 6 - ½(4) - 4 = 0	
	(b)		
	For left oxygen:	Isolated oxygen valence electrons	6
		Bound oxygen bonding electrons	2
		Bound oxygen nonbonding electrons	6
		Formal charge = 6 - ½(2) - 6 = -1	
	For central oxygen:	Isolated oxygen valence electrons	6
		Bound oxygen bonding electrons	6
		Bound oxygen nonbonding electrons	2
		Formal charge = 6 - ½(6) - 2 = +1	

For right oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4

Formal charge = 6 - ½(4) - 4 = 0

7.17

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) O_3	2	1	bent
(b) H_3O^+	3	1	trigonal pyramidal
(c) XeF_2	2	3	linear
(d) PF_6^-	6	0	octahedral
(e) $XeOF_4$	5	1	square pyramidal
(f) AlH_4^-	4	0	tetrahedral
(g) BF_4^-	4	0	tetrahedral
(h) $SiCl_4$	4	0	tetrahedral
(i) ICl_4^-	4	2	square planar
(j) $AlCl_3$	3	0	trigonal planar

7.18

7.19 (a) tetrahedral (b) seesaw

7.20 Each C is sp^3 hybridized. The C–C bond is formed by the overlap of one singly occupied sp^3 hybrid orbital from each C. The C–H bonds are formed by the overlap of one singly occupied sp^3 orbital on C with a singly occupied H 1s orbital.

7.21

The carbon in formaldehyde is sp^2 hybridized.

7.22

In HCN the carbon is sp hybridized.

7.23 The central I in I_3^- has two single bonds and three lone pairs of electrons. The hybridization of the central I is sp^3d. A sketch of the ion showing the orbitals involved in bonding is shown below.

7.24

	Single Bonds	Lone Pairs	Hybridization of S
SF_2	2	2	sp^3
SF_4	4	1	sp^3d
SF_6	6	0	sp^3d^2

7.25 (a) sp (b) sp^3d

7.26 For He_2^+ σ^*_{1s} ↑
σ_{1s} ↑↓

He_2^+ Bond order = $\frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right)-\left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2} = \frac{2-1}{2} = 1/2$

He_2^+ should be stable with a bond order of 1/2.

7.27 For B_2

σ^*_{2p} —
π^*_{2p} — —
σ_{2p} —
π_{2p} ↑ ↑
σ^*_{2s} ↑↓
σ_{2s} ↑↓

B_2 Bond order = $\frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right)-\left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2} = \frac{4-2}{2} = 1$

B_2 is paramagnetic because it has two unpaired electrons in the π_{2p} molecular orbitals.

For C_2

σ^*_{2p} —
π^*_{2p} — —
σ_{2p} —
π_{2p} ↑↓ ↑↓
σ^*_{2s} ↑↓
σ_{2s} ↑↓

C_2 Bond order = $\frac{6-2}{2} = 2$; C_2 is diamagnetic because all electrons are paired.

7.28

7.29 Handed biomolecules have specific shapes that only match complementary-shaped receptor sites in living systems. The mirror-image forms of the molecules can't fit into the receptor sites and thus don't elicit the same biological response.

7.30 The mirror image of molecule (a) has the same shape as (a) and is identical to it in all respects so there is no handedness associated with it. The mirror image of molecule (b) is different than (b) so there is a handedness to this molecule.

Understanding Key Concepts

7.31 As the electrostatic potential maps are drawn, the Li and Cl are at the tops of each map. The red area is for a negatively polarized region (associated with Cl). The blue area is for a positively polarized region (associated with Li). Map (a) is for CH_3Cl and Map (b) is for CH_3Li.

7.32 (a) square pyramidal (b) trigonal pyramidal
(c) square planar (d) trigonal planar

7.33 (a) trigonal bipyramidal (b) tetrahedral
(c) square pyramidal (4 ligands in the horizontal plane, including one hidden)

7.34 Molecular model (c) does not have a tetrahedral central atom. It is square planar.

7.35 (a) sp^2 (b) sp^3d^2 (c) sp^3

7.36 (a) $C_8H_9NO_2$

(b) & (c)

7.37 (a) $C_{13}H_{10}N_2O_4$
(b) and (c)

All carbons that have only single bonds are sp^3 hybridized and have a tetrahedral geometry. All carbons that have double bonds are sp^2 hybridized and have a trigonal planar geometry. The two nitrogens are sp^2 hybridized and have a trigonal planar geometry.

Additional Problems
Electronegativity and Polar Covalent Bonds

7.38 Electronegativity increases from left to right across a period and decreases down a group.

7.39 Z = 119 would be below francium and have a very low electronegativity.

7.40 K < Li < Mg < Pb < C < Br

7.41 Cl > C > Cu > Ca > Cs

7.42 (a) HF fluorine EN = 4.0
hydrogen EN = 2.1
ΔEN = 1.9 HF is polar covalent.

(b) HI iodine EN = 2.5
hydrogen EN = 2.1
ΔEN = 0.4 HI is polar covalent.

(c) $PdCl_2$ chlorine EN = 3.0
palladium EN = 2.2
ΔEN = 0.8 $PdCl_2$ is polar covalent.

(d) BBr_3 bromine EN = 2.8
boron EN = 2.0
ΔEN = 0.8 BBr_3 is polar covalent.

(e) NaOH $Na^+ – OH^-$ is ionic
OH^- oxygen EN = 3.5
hydrogen EN = 2.1
ΔEN = 1.4 OH^- is polar covalent.

(f) CH_3Li lithium EN = 1.0
carbon EN = 2.5
ΔEN = 1.5 CH_3Li is polar covalent.

7.43 The electronegativity for each element is shown in parentheses.
(a) C (2.5), H (2.1), Cl (3.0): The C–Cl bond is more polar than the C–H bond because of the larger electronegativity difference between the bonded atoms.
(b) Si (1.8), Li (1.0), Cl (3.0): The Si–Cl bond is more polar than the Si–Li bond because of the larger electronegativity difference between the bonded atoms.
(c) N (3.0), Cl (3.0), Mg (1.2): The N–Mg bond is more polar than the N–Cl bond because of the larger electronegativity difference between the bonded atoms.

7.44 (a) $\overset{\delta-}{C}-\overset{\delta+}{H}$ $\overset{\delta+}{C}-\overset{\delta-}{Cl}$ (b) $\overset{\delta-}{Si}-\overset{\delta+}{Li}$ $\overset{\delta+}{Si}-\overset{\delta-}{Cl}$

(c) N – Cl $\overset{\delta-}{N}-\overset{\delta+}{Mg}$

7.45 (a) $\overset{\delta-}{F}-\overset{\delta+}{H}$ (b) $\overset{\delta-}{I}-\overset{\delta+}{H}$ (c) $\overset{\delta-}{Cl}-\overset{\delta+}{Pd}$

(d) $\overset{\delta-}{Br}-\overset{\delta+}{B}$ (e) $\overset{\delta-}{O}-\overset{\delta+}{H}$

Electron-Dot Structures and Resonance

7.46 The octet rule states that main-group elements tend to react so that they attain a noble gas electron configuration with filled s and p sublevels (8 electrons) in their valence electron shells. The transition metals are characterized by partially filled d orbitals that can be used to expand their valence shell beyond the normal octet of electrons.

7.47 (a) $AlCl_3$ Al has only 6 electrons around it. (b) PCl_5 P has 10 electrons around it.

7.48 (a) (b) (c)

(d) (e) (f)

7.49 (a) (b) (c)

(d) (e)

(f)

7.50 (a)

(b)

(c)

7.51 (a)

(b)

(c)

(d)

7.52

7.53 ; CS_2 has two double bonds.

7.54 (a) yes (b) yes (c) yes (d) yes

7.55 (a) yes (b) no (c) yes

7.56 (a) The anion has 32 valence electrons. Each Cl has seven valence electrons (28 total). The minus one charge on the anion accounts for one valence electron. This leaves three valence electrons for X. X is Al.
(b) The cation has eight valence electrons. Each H has one valence electron (4 total).

X is left with four valence electrons. Since this is a cation, one valence electron was removed from X. X has five valence electrons. X is P.

7.57 (a) This fourth-row element has six valence electrons. It is Se.
(b) This fourth-row element has eight valence electrons. It is Kr.

7.58 (a) (b)

7.59 (a) (b)

Formal Charges

7.60

For carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	6
	Bound carbon nonbonding electrons	2
	Formal charge = 4 - ½(6) - 2 = -1	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	6
	Bound oxygen nonbonding electrons	2
	Formal charge = 6 - ½(6) - 2 = +1	

7.61 (a)

For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For nitrogen:	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	6
	Bound nitrogen nonbonding electrons	2
	Formal charge = 5 - ½(6) - 2 = 0	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4

	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	

(b)

For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For nitrogen:	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	4
	Bound nitrogen nonbonding electrons	4
	Formal charge = 5 - ½(4) - 4 = -1	
For carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	

(c)

For chlorine:	Isolated chlorine valence electrons	7
	Bound chlorine bonding electrons	2
	Bound chlorine nonbonding electrons	6
	Formal charge = 7 - ½(2) - 6 = 0	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For phosphorus:	Isolated phosphorus valence electrons	5
	Bound phosphorus bonding electrons	8
	Bound phosphorus nonbonding electrons	0
	Formal charge = 5 - ½(8) - 0 = +1	

7.62

For both oxygens:	Isolated oxygen valence electrons	6

	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For chlorine:	Isolated chlorine valence electrons	7
	Bound chlorine bonding electrons	4
	Bound chlorine nonbonding electrons	4
	Formal charge = 7 - ½(4) - 4 = +1	
For left oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For right oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For chlorine:	Isolated chlorine valence electrons	7
	Bound chlorine bonding electrons	6
	Bound chlorine nonbonding electrons	4
	Formal charge = 7 - ½(6) - 4 = 0	

7.63

For sulfur:	Isolated sulfur valence electrons	6
	Bound sulfur bonding electrons	8
	Bound sulfur nonbonding electrons	2
	Formal charge = 6 - ½(8) - 2 = 0	
For doubly bound oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For oxygen bound to hydrogen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	

For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For sulfur:	Isolated sulfur valence electrons	6
	Bound sulfur bonding electrons	6
	Bound sulfur nonbonding electrons	2
	Formal charge = 6 - ½(6) - 2 = +1	
For oxygen not bound to hydrogen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = - 1	
For oxygen bound to hydrogen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	

7.64 (a)

For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For nitrogen: (central)	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	8
	Bound nitrogen nonbonding electrons	0
	Formal charge = 5 - ½(8) - 0 = +1	
For nitrogen: (terminal)	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	4
	Bound nitrogen nonbonding electrons	4
	Formal charge = 5 - ½(4) - 4 = -1	

For carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	

(b)

For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For nitrogen: (central)	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	6
	Bound nitrogen nonbonding electrons	2
	Formal charge = 5 - ½(6) - 2 = 0	
For nitrogen: (terminal)	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	4
	Bound nitrogen nonbonding electrons	4
	Formal charge = 5 - ½(4) - 4 = -1	
For carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	6
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(6) - 0 = +1	

Structure (a) is more important because of the octet of electrons around carbon.

7.65

For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For left carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	

For right carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	6
	Bound carbon nonbonding electrons	2
	Formal charge = 4 - ½(6) - 2 = -1	

For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For left carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	
For right carbon:	Isolated carbon valence electrons	4
	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	

The second structure is more important because of the -1 formal charge on the more electronegative oxygen.

The VSEPR Model

7.66 From data in Table 7.4:
(a) trigonal planar (b) trigonal bipyramidal (c) linear (d) octahedral

7.67 From data in Table 7.4:
(a) T shaped (b) bent (c) square planar

7.68 From data in Table 7.4:

(a) tetrahedral, 4	(b) octahedral, 6	(c) bent, 3 or 4
(d) linear, 2 or 5	(e) square pyramidal, 6	(f) trigonal pyramidal, 4

7.69 From data in Table 7.4:

(a) seesaw, 5	(b) square planar, 6	(c) trigonal bipyramidal, 5
(d) T shaped, 5	(e) trigonal planar, 3	(f) linear, 2 or 5

7.70

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) H_2Se	2	2	bent
(b) $TiCl_4$	4	0	tetrahedral
(c) O_3	2	1	bent
(d) GaH_3	3	0	trigonal planar

7.71

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) XeO_4	4	0	tetrahedral
(b) SO_2Cl_2	4	0	tetrahedral
(c) OsO_4	4	0	tetrahedral
(d) SeO_2	2	1	bent

7.72

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) SbF_5	5	0	trigonal bipyramidal
(b) IF_4^+	4	1	see saw
(c) SeO_3^{2-}	3	1	trigonal pyramidal
(d) CrO_4^{2-}	4	0	tetrahedral

7.73

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) NO_3^-	3	0	trigonal planar
(b) NO_2^+	2	0	linear
(c) NO_2^-	2	1	bent

7.74

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) PO_4^{3-}	4	0	tetrahedral
(b) MnO_4^-	4	0	tetrahedral
(c) SO_4^{2-}	4	0	tetrahedral
(d) SO_3^{2-}	3	1	trigonal pyramidal
(e) ClO_4^-	4	0	tetrahedral
(f) SCN^- (C is the central atom)	2	0	linear

7.75

	Number of Bonded Atoms	Number of Lone Pairs	Shape
(a) XeF_3^+	3	2	T shaped
(b) SF_3^+	3	1	trigonal pyramidal
(c) ClF_2^+	2	2	bent

(d) CH_3^+	3	0	trigonal planar

7.76 (a) In SF_2 the sulfur is bound to two fluorines and contains two lone pairs of electrons. SF_2 is bent and the F–S–F bond angle is approximately 109°.
(b) In N_2H_2 each nitrogen is bound to the other nitrogen and one hydrogen. Each nitrogen has one lone pair of electrons. The H–N–N bond angle is approximately 120°.
(c) In KrF_4 the krypton is bound to four fluorines and contains two lone pairs of electrons. KrF_4 is square planar, and the F–Kr–F bond angle is 90°.
(d) In NOCl the nitrogen is bound to one oxygen and one chlorine and contains one lone pair of electrons. NOCl is bent, and the Cl–N–O bond angle is approximately 120°.

7.77 (a) In PCl_6^- the phosphorus is bound to six chlorines. There are no lone pairs of electrons on the phosphorus. PCl_6^- is octahedral, and the Cl–P–Cl bond angle is 90°.
(b) In ICl_2^- the iodine is bound to two chlorines and contains three lone pairs of electrons. ICl_2^- is linear, and the Cl–I–Cl bond angle is 180°.
(c) In SO_4^{2-} the sulfur is bound to four oxygens. There are no lone pairs of electrons on the sulfur. SO_4^{2-} is tetrahedral, and the O–S–O bond angle is 109.5^o.
(d) In BO_3^{3-} the boron is bound to three oxygens. There are no lone pairs of electrons on the boron. BO_3^{3-} is trigonal planar, and the O–B–O bond angle is 120°.

7.78

$H - C_a - H$	$\sim 120^o$	$C_b - C_c - N$	180°
$H - C_a - C_b$	$\sim 120^o$	$C_a - C_b - H$	$\sim 120^o$
$C_a - C_b - C_c$	$\sim 120^o$	$H - C_b - C_c$	$\sim 120^o$

7.79

7.80 All six carbons in cyclohexane are bonded to two other carbons and two hydrogens (i.e. four charge clouds). The geometry about each carbon is tetrahedral with a C–C–C bond angle of approximately 109°. Because the geometry about each carbon is tetrahedral, the cyclohexane ring cannot be flat.

7.81 All six carbon atoms are sp^2 hybridized and the bond angles are ~120°. The geometry about each carbon is trigonal planar.

Hybrid Orbitals and Molecular Orbital Theory

7.82 In a π bond, the shared electrons occupy a region above and below a line connecting the two nuclei. A σ bond has its shared electrons located along the axis between the two

nuclei.

7.83 Electrons in a bonding molecular orbital spend most of their time in the region between the two nuclei, helping to bond the atoms together. Electrons in an antibonding molecular orbital cannot occupy the central region between the nuclei and cannot contribute to bonding.

7.84 See Table 7.5.
(a) sp (b) sp^3d (c) sp^3d^2 (d) sp^3

7.85 See Table 7.5.
(a) tetrahedral (b) octahedral (c) linear

7.86 See Table 7.5.
(a) sp^3 (b) sp^3d^2 (c) sp^2 or sp^3 (d) sp or sp^3d (e) sp^3d^2

7.87 See Tables 7.4 and 7.5.
(a) seesaw, 5 charge clouds, sp^3d
(b) square planar, 6 charge clouds, sp^3d^2
(c) trigonal bipyramidal, 5 charge clouds, sp^3d
(d) T shaped, 5 charge clouds, sp^3d
(e) trigonal planar, 3 charge clouds, sp^2

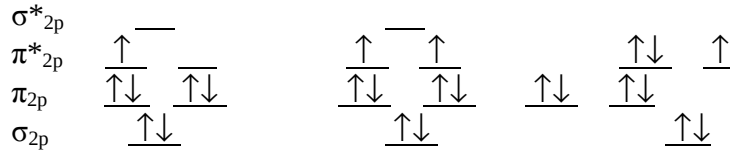
7.88 (a) sp^2 (b) sp^3 (c) sp^3d^2 (d) sp^2

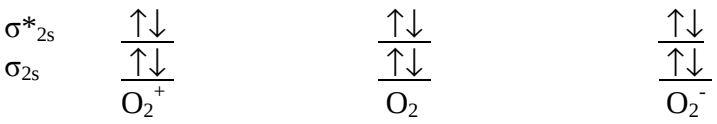
7.89 (a) sp^3 (b) sp^2 (c) sp^2 (d) sp^3

7.90 The C is sp^2 hybridized and the N atoms are sp^3 hybridized.

7.91 (a)
(b) H–C–H, ~109°; O–C–O, ~120°; H–N–H, ~107°
(c) N, sp^3; left C, sp^3; right C, sp^2

7.92





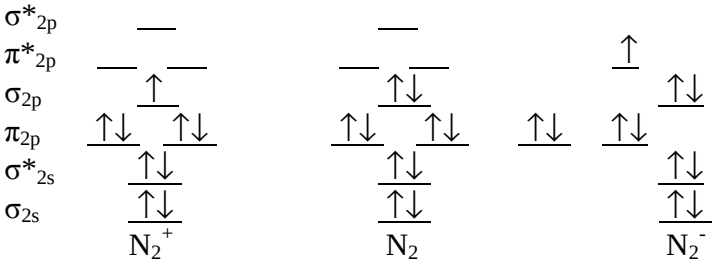
$$\text{Bond order} = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2}$$

O_2^+ bond order $= \frac{8-3}{2} = 2.5$; O_2 bond order $= \frac{8-4}{2} = 2$

O_2^- bond order $= \frac{8-5}{2} = 1.5$

All are stable with bond orders between 1.5 and 2.5. All have unpaired electrons.

7.93



$$\text{Bond order} = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2}$$

N_2^+ bond order $= \frac{7-2}{2} = 2.5$; N_2 bond order $= \frac{8-2}{2} = 3$

N_2^- bond order $= \frac{8-3}{2} = 2.5$

All are stable with bond orders of either 3 or 2.5. N_2^+ and N_2^- contain unpaired electrons.

7.94 p orbitals in allyl cation

allyl cation showing only the σ bonds (each C is sp^2 hybridized)

delocalized MO model for π bonding in the allyl cation

7.95 p orbitals in NO_2^-

NO_2^- showing only the σ bonds (N is sp^2 hybridized)

delocalized MO model for π bonding in NO_2^-

General Problems

7.96

7.97 In ascorbic acid (Problem 7.96) all carbons that have only single bonds are sp^3 hybridized. The three carbons that have double bonds are sp^2 hybridized.

7.98 Every carbon is sp^2 hybridized. There are 18 σ bonds and 5 π bonds.

7.99

For

For oxygen: (top)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For oxygen: (middle)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For oxygen: (left)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For oxygen: (right)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For sulfur:	Isolated sulfur valence electrons	6
	Bound sulfur bonding electrons	8
	Bound sulfur nonbonding electrons	0
	Formal charge = 6 - ½(8) - 0 = +2	

For

For oxygen: (top)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For oxygen: (middle)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For oxygen: (left)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6

Formal charge = 6 - ½(2) - 6 = -1

For oxygen: (right)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	
For sulfur:	Isolated sulfur valence electrons	6
	Bound sulfur bonding electrons	8
	Bound sulfur nonbonding electrons	0
	Formal charge = 6 - ½(8) - 0 = +2	

For

For oxygen: (top)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For oxygen: (middle)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	6
	Bound oxygen nonbonding electrons	2
	Formal charge = 6 - ½(6) - 2 = +1	
For oxygen: (left)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For oxygen: (right)	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	
For sulfur:	Isolated sulfur valence electrons	6
	Bound sulfur bonding electrons	8
	Bound sulfur nonbonding electrons	0
	Formal charge = 6 - ½(8) - 0 = +2	

7.100

For		
For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For carbon:	Isolated carbon valence electrons	4
(left)	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	
For nitrogen:	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	6
	Bound nitrogen nonbonding electrons	2
	Formal charge = 5 - ½(6) - 2 = 0	
For carbon:	Isolated carbon valence electrons	4
(right)	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	4
	Bound oxygen nonbonding electrons	4
	Formal charge = 6 - ½(4) - 4 = 0	

For		
For hydrogen:	Isolated hydrogen valence electrons	1
	Bound hydrogen bonding electrons	2
	Bound hydrogen nonbonding electrons	0
	Formal charge = 1 - ½(2) - 0 = 0	
For carbon:	Isolated carbon valence electrons	4
(left)	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	

For nitrogen:	Isolated nitrogen valence electrons	5
	Bound nitrogen bonding electrons	8
	Bound nitrogen nonbonding electrons	0
	Formal charge = 5 - ½(8) - 0 = +1	
For carbon:	Isolated carbon valence electrons	4
(right)	Bound carbon bonding electrons	8
	Bound carbon nonbonding electrons	0
	Formal charge = 4 - ½(8) - 0 = 0	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	2
	Bound oxygen nonbonding electrons	6
	Formal charge = 6 - ½(2) - 6 = -1	

7.101 They are geometric isomers not resonance forms. In resonance forms the atoms have the same geometrical arrangement.

7.102 (a)

For boron:	Isolated boron valence electrons	3
	Bound boron bonding electrons	8
	Bound boron nonbonding electrons	0
	Formal charge = 3 – ½(8) – 0 = -1	
For oxygen:	Isolated oxygen valence electrons	6
	Bound oxygen bonding electrons	6
	Bound oxygen nonbonding electrons	2
	Formal charge = 6 – ½ (6) – 2 = +1	

(b) In BF_3 the B has three bonding pairs of electrons and no lone pairs. The B is sp^2 hybridized and BF_3 is trigonal planar.

is bent about the oxygen because of two bonding pairs and two lone pairs of electrons. The O is sp^3 hybridized.
In the product, B is sp^3 hybridized (with four bonding pairs of electrons), and the geometry about it is tetrahedral. The O is also sp^3 hybridized (with three bonding pairs and one lone pair of electrons), and the geometry about it is trigonal pyramidal.

7.103 Both the B and N are sp^2 hybridized. All bond angles are ~120°. The overall geometry of

the molecule is planar.

7.104 The triply bonded carbon atoms are sp hybridized. The theoretical bond angle for C–C≡C is 180°. Benzyne is so reactive because the C–C≡C bond angle is closer to 120° and is very strained.

7.105 (a) (b) (c)

7.106

7.107 Li_2

σ^*_{2s} ___
σ_{2s} ↑↓
σ^*_{1s} ↑↓
σ_{1s} ↑↓

$$Li_2 \text{ Bond order } = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2} = \frac{4 - 2}{2} = 1$$

The bond order for Li_2 is 1, and the molecule is likely to be stable.

7.108 C_2^{2-}

σ^*_{2p} ___
π^*_{2p} ___ ___
σ_{2p} ↑↓
π_{2p} ↑↓ ↑↓
σ^*_{2s} ↑↓
σ_{2s} ↑↓

$$\text{Bond order } = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2}$$

C_2^{2-} bond order $= \frac{8 - 2}{2} = 3$; there is a triple bond between the two carbons.

7.109 (a) (b) (c)

Structure (a) is different from structures (b) and (c) because both chlorines are on the same carbon. Structures (b) and (c) are different because in (b) both chlorines are on the same side of the molecule ("cis") and in (c) they are on opposite sides of the molecule

("trans"). There is no rotation around the carbon-carbon double bond.

7.110 $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

Energy change = *D* (Reactant bonds) - *D* (Product bonds)

Energy change = $[4\ D_{C\text{-}H} + D_{Cl\text{-}Cl}] - [3\ D_{C\text{-}H} + D_{C\text{-}Cl} + D_{H\text{-}Cl}]$

Energy change = [(4 mol)(410 kJ/mol) + (1 mol)(243 kJ/mol]

- [(3 mol)(410 kJ/mol) + (1 mol)(330 kJ/mol) + (1 mol)(432 kJ/mol)] = -109 kJ

7.111

7.112 (a) (b) (c)

(d) (e) (f)

(g) (h)

Structures (a) – (d) make more important contributions to the resonance hybrid because of only -1 and 0 formal charges on the oxygens.

7.113 (a) (1) (2) (3)

(b) Structure (1) makes the greatest contribution to the resonance hybrid because of the -1 formal charge on the oxygen. Structure (3) makes the least contribution to the resonance hybrid because of the +1 formal charge on the oxygen.

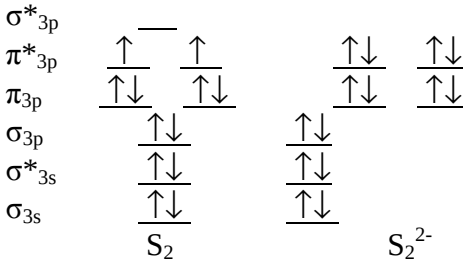
(c) and (d) OCN^- is linear because the C has 2 charge clouds. It is sp hybridized in all three resonance structures. It forms two π bonds.

7.114

21 σ bonds
5 π bonds
Each C with a double bond is sp^2 hybridized.
The $–CH_3$ carbon is sp^3 hybridized.

7.115

7.116 (a)



(b) S_2 would be paramagnetic with two unpaired electrons in the π^*_{3p} MOs.

(c) $$\text{Bond order} = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2}$$

$$S_2 \text{ bond order} = \frac{8 - 4}{2} = 2$$

(d) $$S_2^{2-} \text{ bond order} = \frac{8 - 6}{2} = 1$$

The two added electrons go into the antibonding π^*_{3p} MOs, the bond order drops from 2 to 1, and the bond length in S_2^{2-} should be longer than the bond length in S_2.

7.117 (a) CO

σ^*_{2p} ___

π^*_{2p} ___ ___

σ_{2p} ↑↓

π_{2p} ↑↓ ↑↓

σ^*_{2s} ↑↓

σ_{2s} ↑↓

(b) All electrons are paired, CO is diamagnetic.

(c)

$$\text{Bond order} = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{2}$$

$$\text{CO bond order} = \frac{8 - 2}{2} = 3$$

The bond order here matches that predicted by the electron-dot structure ( ).

(d)

7.118 (a)

The left S has 5 electron clouds (4 bonding, 1 lone pair). The S is sp^3d hybridized and the geometry about this S is seesaw. The right S has 4 electron clouds (2 bonding, 2 lone pairs). The S is sp^3 hybridized and the geometry about this S is bent.

(b)

The left C has 4 electron clouds (4 bonding, 0 lone pairs). This C is sp^3 hybridized and its geometry is tetrahedral. The right C has 3 electron clouds (3 bonding, 0 lone pairs). This C is sp^2 hybridized and its geometry is trigonal planar. The central two C's have 2 electron clouds (2 bonding, 0 lone pairs). These C's are sp hybridized and the geometry about both is linear.

7.119

Multi-Concept Problems

7.120 (a)

(b) The oxygen in OH has a half-filled 2p orbital that can accept the additional electron. For a 2p orbital, n = 2 and l = 1.

(c) The electron affinity for OH is slightly more negative than for an O atom because when OH gains an additional electron, it achieves an octet configuration.

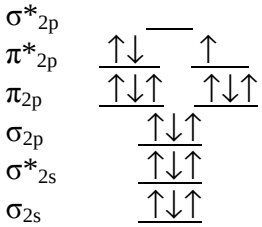
7.121 (a) (4 orbitals)(3 electrons) = 12 outer-shell electrons

(b) 3 electrons

(c) $1s^3\ 2s^3\ 2p^6$;

(d)

(e)



$$\text{Bond order} = \frac{\left(\begin{array}{c}\text{number of}\\ \text{bonding electrons}\end{array}\right) - \left(\begin{array}{c}\text{number of}\\ \text{antibonding electrons}\end{array}\right)}{3}$$

$$X_2 \text{ bond order} = \frac{12 - 6}{3} = 2$$

7.122 (a)

(b) Each Cr atom has 6 pairs of electrons around it. The likely geometry about each Cr atom is tetrahedral because each Cr has 4 charge clouds.

7.123 (a) $XOCl_2 + 2\,H_2O \rightarrow 2\,HCl + H_2XO_3$

(b) 96.1 mL = 0.0961 L

mol NaOH = (0.1225 mol/L)(0.0961 L) = 0.01177 mol NaOH

$$\text{mol } H^+ = 0.01177 \text{ mol NaOH} \times \frac{1 \text{ mol } H^+}{1 \text{ mol NaOH}} = 0.01177 \text{ mol } H^+$$

Of the total H^+ concentration, half comes from HCl and half comes from H_2XO_3.

$$\text{mol } H_2XO_3 = \frac{0.01177 \text{ mol } H^+}{2} \times \frac{1 \text{ mol } H_2XO_3}{2 \text{ mol } H^+} = 2.943 \times 10^{-3} \text{ mol } H_2XO_3$$

$$\text{mol } XOCl_2 = 2.943 \times 10^{-3} \text{ mol } H_2XO_3 \times \frac{1 \text{ mol } XOCl_2}{1 \text{ mol } H_2XO_3} = 2.943 \times 10^{-3} \text{ mol } XOCl_2$$

$$\text{molar mass } XOCl_2 = \frac{0.350 \text{ g } XOCl_2}{2.943 \times 10^{-3} \text{ mol } XOCl_2} = 118.9 \text{ g/mol}$$

molecular mass of $XOCl_2$ = 118.9 amu

atomic mass of X = 118.9 amu - 16.0 amu - 2(35.45 amu) = 32.0 amu: X = S

(c)

(d) trigonal pyramidal

7.124 (a)

(b) All three molecules are planar. The first two structures are polar because they both have an unsymmetrical distribution of atoms about the center of the molecule (the middle of the double bond), and bond polarities do not cancel. Structure 3 is nonpolar because the H's and Cl's, respectively, are symmetrically distributed about the center of the molecule, both being opposite each other. In this arrangement, bond polarities cancel.

(c) 200 nm = 200×10^{-9} m

$$E = \frac{h\,c}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \bullet \text{s})(3.00 \times 10^{8} \text{ m/s})}{200 \times 10^{-9} \text{ m}} (6.022 \times 10^{23} \text{ / mol})$$

E = 5.99×10^5 J/mol = 599 kJ/mol

(d)
The π bond must be broken before rotation can occur.

8 Thermochemistry: Chemical Energy

8.1 Convert lb to kg. $2300\ \text{lb} \times \frac{453.59\ \text{g}}{1\ \text{lb}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 1043\ \text{kg}$

Convert mi/h to m/s. $55\ \frac{\text{mi}}{\text{h}} \times \frac{1\ \text{km}}{0.62137\ \text{mi}} \times \frac{1000\ \text{m}}{1\text{km}} \times \frac{1\ \text{h}}{3600\ \text{s}} = 24.6\ \text{m/s}$

$1\ \text{kg}\cdot\text{m}^2/\text{s}^2 = 1\ \text{J}$; $E = \frac{1}{2}mv^2 = \frac{1}{2}(1043\ \text{kg})(24.6\ \text{m/s})^2 = 3.2 \times 10^5\ \text{J}$

$E = 3.2 \times 10^5\ \text{J} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 3.2 \times 10^2\ \text{kJ}$

8.2 (a) and (b) are state functions; (c) is not.

8.3 $\Delta V = (4.3\ \text{L} - 8.6\ \text{L}) = -4.3\ \text{L}$

$w = -P\Delta V = -(44\ \text{atm})(-4.3\ \text{L}) = +189.2\ \text{L}\cdot\text{atm}$

$w = (189.2\ \text{L}\cdot\text{atm})\left(101\ \frac{\text{J}}{\text{L}\bullet\text{atm}}\right) = +1.9 \times 10^4\ \text{J}$

The positive sign for the work indicates that the surroundings does work on the system. Energy flows into the system.

8.4 $w = -P\Delta V = -(2.5\ \text{atm})(3\ \text{L} - 2\ \text{L}) = -2.5\ \text{L}\cdot\text{atm}$

$w = (-2.5\ \text{L}\cdot\text{atm})\left(101\ \frac{\text{J}}{\text{L}\bullet\text{atm}}\right) = -252.5\ \text{J} = -250\ \text{J} = -0.25\ \text{kJ}$

The negative sign indicates that the expanding system loses work energy and does work on the surroundings.

8.5 (a) $w = -P\Delta V$ is positive and $P\Delta V$ is negative for this reaction because the system volume is decreased at constant pressure.

(b) $P\Delta V$ is small compared to ΔE.

$\Delta H = \Delta E + P\Delta V$; ΔH is negative. Its value is slightly more negative than ΔE.

8.6 $\Delta H^o = -484\ \frac{\text{kJ}}{2\ \text{mol}\ H_2}$

$P\Delta V = (1.00\ \text{atm})(-5.6\ \text{L}) = -5.6\ \text{L}\cdot\text{atm}$

$P\Delta V = (-5.6\ \text{L}\cdot\text{atm})\left(101\ \frac{\text{J}}{\text{L}\bullet\text{atm}}\right) = -565.6\ \text{J} = -570\ \text{J} = -0.57\ \text{kJ}$

$w = -P\Delta V = 570\ \text{J} = 0.57\ \text{kJ}$

$\Delta H = \frac{-121\ \text{kJ}}{0.50\ \text{mol}\ H_2}$

$\Delta E = \Delta H - P\Delta V = -121\ \text{kJ} - (-0.57\ \text{kJ}) = -120.43\ \text{kJ} = -120\ \text{kJ}$

8.7 $\Delta V = 448\ \text{L}$ and assume $P = 1.00\ \text{atm}$

$w = -P\Delta V = -(1.00\ atm)(448\ L) = -448\ L \cdot atm$

$w = -(448\ L \cdot atm)(101\ \frac{J}{L \bullet atm}) = -4.52 \times 10^4\ J$

$w = -4.52 \times 10^4\ J \times \frac{1\ kJ}{1000\ J} = -45.2\ kJ$

8.8 (a) C_3H_8, 44.10 amu; $\Delta H^o = -2219\ kJ/mol\ C_3H_8$

$15.5\ g \times \frac{1\ mol\ C_3H_8}{44.10\ g\ C_3H_8} \times \frac{-2219\ kJ}{1\ mol\ C_3H_8} = -780.\ kJ$

780. kJ of heat is evolved.

(b) $Ba(OH)_2 \cdot 8\ H_2O$, 315.5 amu; $\Delta H^o = +80.3\ kJ/mol\ Ba(OH)_2 \cdot 8\ H_2O$

$4.88\ g \times \frac{1\ mol\ Ba(OH)_2 \bullet 8\ H_2O}{315.5\ g\ Ba(OH)_2 \bullet 8\ H_2O} \times \frac{80.3\ kJ}{1\ mol\ Ba(OH)_2 \bullet 8\ H_2O} = +1.24\ kJ$

1.24 kJ of heat is absorbed.

8.9 CH_3NO_2, 61.04 amu

$q = 100.0\ g\ CH_3NO_2 \times \frac{1\ mol\ CH_3NO_2}{61.04\ g\ CH_3NO_2} \times \frac{2441.6\ kJ}{4\ mol\ CH_3NO_2} = 1.000 \times 10^3\ kJ$

8.10 $q = (\text{specific heat}) \times m \times \Delta T = (4.18\ \frac{J}{g \bullet {}^oC})(350\ g)(3^oC - 25^oC) = -3.2 \times 10^4\ J$

$q = -3.2 \times 10^4\ J \times \frac{1\ kJ}{1000\ J} = -32\ kJ$

8.11 $q = (\text{specific heat}) \times m \times \Delta T$; $\text{specific heat} = \frac{q}{m \times \Delta T} = \frac{96\ J}{(75\ g)(10\ {}^oC)} = 0.13\ J/(g \cdot {}^oC)$

8.12 25.0 mL = 0.0250 L and 50.0 mL = 0.0500 L

mol H_2SO_4 = (1.00 mol/L)(0.0250 L) = 0.0250 mol H_2SO_4

mol NaOH = (1.00 mol/L)(0.0500 L) = 0.0500 mol NaOH

NaOH and H_2SO_4 are present in a 2:1 mol ratio. This matches the stoichiometric ratio in the balanced equation.

$q = (\text{specific heat}) \times m \times \Delta T$

m = (25.0 mL + 50.0 mL)(1.00 g/mL) = 75.0 g

$q = (4.18\ \frac{J}{g \bullet {}^oC})(75.0\ g)(33.9\ {}^oC - 25.0\ {}^oC) = 2790\ J$

$\text{mol } H_2SO_4 = 0.0250\ L \times 1.00\ \frac{mol}{L}\ H_2SO_4 = 0.0250\ mol\ H_2SO_4$

$\text{Heat evolved per mole of } H_2SO_4 = \frac{2.79 \times 10^3\ J}{0.0250\ mol\ H_2SO_4} = 1.1 \times 10^5\ J / mol\ H_2SO_4$

Because the reaction evolves heat, the sign for ΔH is negative.

$$\Delta H = -1.1 \times 10^5 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -1.1 \times 10^2 \text{ kJ}$$

8.13

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ $\quad \Delta H^o_1 = -98.3$ kJ

$\underline{CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl(g)}$ $\quad \Delta H^o_2 = -104$ kJ

Sum $CH_4(g) + 2\,Cl_2(g) \rightarrow CH_2Cl_2(g) + 2\,HCl(g)$

$\Delta H^o = \Delta H^o_1 + \Delta H^o_2 = -202$ kJ

8.14 (a) $A + 2\,B \rightarrow D$; $\Delta H^o = -100$ kJ + (-50 kJ) = -150 kJ

(b) The red arrow corresponds to step 1: $A + B \rightarrow C$

The green arrow corresponds to step 2: $C + B \rightarrow D$

The blue arrow corresponds to the overall reaction.

(c) The top energy level represents A + 2 B.

The middle energy level represents C + B.

The bottom energy level represents D.

8.15

8.16 $4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$

$\Delta H^o_{rxn} = [4\,\Delta H^o_f(NO) + 6\,\Delta H^o_f(H_2O)] - [4\,\Delta H^o_f(NH_3)]$

$\Delta H^o_{rxn} = [(4 \text{ mol})(90.2 \text{ kJ/mol}) + (6 \text{ mol})(-241.8 \text{ kJ/mol})] - [(4 \text{ mol})(-46.1 \text{ kJ/mol})]$

$\Delta H^o_{rxn} = -905.6$ kJ

8.17 $6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$

$\Delta H^o_{rxn} = \Delta H^o_f(C_6H_{12}O_6) - [6\,\Delta H^o_f(CO_2) + 6\,\Delta H^o_f(H_2O(l))]$

$\Delta H^o_{rxn} = [(1 \text{ mol})(-1260 \text{ kJ/mol})] - [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-285.8 \text{ kJ/mol})]$

$\Delta H^o_{rxn} = +2815.8 \text{ kJ} = +2816 \text{ kJ}$

8.18 $H_2C{=}CH_2(g) + H_2O(g) \rightarrow C_2H_5OH(g)$

$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)

$\Delta H^o_{rxn} = (D_{C=C} + 4\,D_{C-H} + 2\,D_{O-H}) - (D_{C-C} + D_{C-O} + 5\,D_{C-H} + D_{O-H})$

$\Delta H^o_{rxn} = [(1 \text{ mol})(611 \text{ kJ/mol}) + (4 \text{ mol})(410 \text{ kJ/mol}) + (2 \text{ mol})(460 \text{ kJ/mol})]$

$- [(1 \text{ mol})(350 \text{ kJ/mol}) + (1 \text{ mol})(350 \text{ kJ/mol}) + (5 \text{ mol})(410 \text{ kJ/mol}) + (1 \text{ mol})(460 \text{ kJ/mol})]$

$\Delta H^o_{rxn} = -39$ kJ

8.19 $2\,NH_3(g) + Cl_2(g) \rightarrow N_2H_4(g) + 2\,HCl(g)$

$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)

$\Delta H^o_{rxn} = (6\,D_{N-H} + D_{Cl-Cl}) - (D_{N-N} + 4\,D_{N-H} + 2\,D_{H-Cl})$

$\Delta H^o_{rxn} = [(6 \text{ mol})(390 \text{ kJ/mol}) + (1 \text{ mol})(243 \text{ kJ/mol})]$

- [(1 mol)(240 kJ/mol) + (4 mol)(390 kJ/mol) + (2 mol)(432 kJ/mol)] = -81 kJ

8.20 $C_4H_{10}(l) + \frac{13}{2} O_2(g) \rightarrow 4 CO_2(g) + 5 H_2O(g)$

$\Delta H^o_{rxn} = [4 \Delta H^o_f (CO_2) + 5 \Delta H^o_f (H_2O)] - \Delta H^o_f (C_4H_{10})$

$\Delta H^o_{rxn} = [(4 \text{ mol})(-393.5 \text{ kJ/mol}) + (5 \text{ mol})(-241.8 \text{ kJ/mol})] - [(1 \text{ mol})(-147.5 \text{ kJ/mol})]$

$\Delta H^o_{rxn} = -2635.5 \text{ kJ}$

$\Delta H^o_C = -2635.5 \text{ kJ/mol}$

C_4H_{10}, 58.12 amu; $\Delta H^o_C = \left(-2635.5 \frac{\text{kJ}}{\text{mol}} \right)\left(\frac{1 \text{ mol}}{58.12 \text{ g}} \right) = -45.35 \text{ kJ/g}$

$\Delta H^o_C = \left(-45.35 \frac{\text{kJ}}{\text{g}} \right)\left(0.579 \frac{\text{g}}{\text{mL}} \right) = -26.3 \text{ kJ/mL}$

8.21 ΔS^o is negative because the reaction decreases the number of moles of gaseous molecules.

8.22 The reaction proceeds from a solid and a gas (reactants) to all gas (product). This is more disordered and ΔS^o is positive.

8.23 (a) Because ΔG^o is negative, the reaction is spontaneous.
(b) Because ΔG^o is positive, the reaction is nonspontaneous.

8.24 $\Delta G^o = \Delta H^o - T\Delta S^o = (-92.2 \text{ kJ}) - (298 \text{ K})(-0.199 \text{ kJ/K}) = -32.9 \text{ kJ}$

Because ΔG^o is negative, the reaction is spontaneous.

Set $\Delta G^o = 0$ and solve for T.

$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$

$T = \frac{\Delta H^o}{\Delta S^o} = \frac{-92.2 \text{ kJ}}{-0.199 \text{ kJ/K}} = 463 \text{ K} = 190^oC$

8.25 (a) $2 A_2 + B_2 \rightarrow 2 A_2B$
(b) Because the reaction is exothermic, ΔH is negative. There are more reactant molecules than product molecules. The randomness of the system decreases on going from reactant to product, therefore ΔS is negative.
(c) Because $\Delta G = \Delta H - T\Delta S$, a reaction with both ΔH and ΔS negative is favored at low temperatures where the negative ΔH term is larger than the positive - $T\Delta S$, and ΔG is negative.

Understanding Key Concepts

8.26. (a) $w = -P\Delta V$, $\Delta V > 0$; therefore $w < 0$ and the system is doing work on the surroundings.
(b) Since the temperature has increased there has been an enthalpy change. The system evolved heat, the reaction is exothermic, and $\Delta H < 0$.

8.27

8.28

8.29

8.30 $\Delta H = \Delta E + P\Delta V$

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

$$\Delta V = \frac{\Delta H - \Delta E}{P} = \frac{[-35.0\ kJ - (-34.8\ kJ)]}{1\,atm} \times \frac{1\,L \bullet atm}{101 \times 10^{-3}\ kJ} = -2\ L$$

$\Delta V = -2\ L = V_{final} - V_{initial} = V_{final} - 5\ L$; $V_{final} = -2\ L - (-5\ L) = 3\ L$

The volume decreases from 5 L to 3 L.

8.31 $\Delta H^o = +55$ kJ

ΔS^o is positive because the chemical system becomes more disordered in going from

reactant to products.
$\Delta G^o = \Delta H^o - T\Delta S^o$; For the reaction to be spontaneous, ΔG^o must be negative. Because ΔH^o and ΔS^o are both positive, the reaction is spontaneous at some higher temperatures but nonspontaneous at some lower temperatures.

8.32 The change is the spontaneous conversion of a liquid to a gas. ΔG is negative because the change is spontaneous. The conversion of a liquid to a gas is endothermic, therefore ΔH is positive. ΔS is positive because the gas is more disordered than the liquid.

8.33 (a) $2\ A_3 \rightarrow 3\ A_2$
(b) Because the reaction is spontaneous, ΔG is negative. ΔS is positive because the number of molecules increases in going from reactant to products. ΔH could be either positive or negative and the reaction would still be spontaneous. ΔH is probably positive because there is more bond breaking than bond making

Additional Problems
Heat, Work, and Energy

8.34 Heat is the energy transferred from one object to another as the result of a temperature difference between them. Temperature is a measure of the kinetic energy of molecular motion.
Energy is the capacity to do work or supply heat. Work is defined as the distance moved times the force that opposes the motion (w = d x F).
Kinetic energy is the energy of motion. Potential energy is stored energy.

8.35 Internal energy is the sum of kinetic and potential energies for each particle in the system.

8.36 Car: $E_K = \frac{1}{2}(1400\ \text{kg})\left(\frac{115\ \text{x}\ 10^3\ \text{m}}{3600\ \text{s}}\right)^2 = 7.1 \times 10^5\ \text{J}$

Truck: $E_K = \frac{1}{2}(12{,}000\ \text{kg})\left(\frac{38\ \text{x}\ 10^3\ \text{m}}{3600\ \text{s}}\right)^2 = 6.7 \times 10^5\ \text{J}$

The car has more kinetic energy.

8.37 Heat = q = 7.1×10^5 J (from Problem 8.34)
q = (specific heat) x m x ΔT

$$m = \frac{q}{(\text{specific heat}) \times \Delta T} = \frac{7.1 \times 10^5\ \text{J}}{\left(4.18\ \frac{\text{J}}{\text{g} \bullet\ ^\circ\text{C}}\right)(50\ ^\circ\text{C} - 20\ ^\circ\text{C})} = 5.7 \times 10^3\ \text{g of water}$$

8.38 $w = -P\Delta V = -(3.6\ \text{atm})(3.4\ \text{L} - 3.2\ \text{L}) = -0.72\ \text{L} \cdot \text{atm}$

$$w = (-0.72\ L \cdot atm)\left(\frac{101\ J}{1\ L \bullet atm}\right) = -72.7\ J = -70\ J;$$ The energy change is negative.

8.39 $V_{initial}$ = 50.0 mL + 50 mL = 100.0 mL = 0.1000 L
V_{final} = 50.0 mL = 0.0500 L
$\Delta V = V_{final} - V_{initial}$ = (0.0500 L - 0.1000 L) = -0.0500 L
$w = -P\Delta V$ = -(1.5 atm)(-0.0500 L) = +0.075 L· atm

$$w = (+0.075\ L \cdot atm)\left(101\ \frac{J}{1\ L \bullet atm}\right) = +7.6\ J$$

The positive sign for the work indicates that the surroundings does work on the system. Energy flows into the system.

Energy and Enthalpy

8.40 $\Delta E = q_v$ is the heat change associated with a reaction at constant volume. Since $\Delta V = 0$, no PV work is done.
$\Delta H = q_p$ is the heat change associated with a reaction at constant pressure. Since $\Delta V \neq 0$, PV work can also be done.

8.41 ΔH is negative for an exothermic reaction. ΔH is positive for an endothermic reaction.

8.42 $\Delta H = \Delta E + P\Delta V$; ΔH and ΔE are nearly equal when there are no gases involved in a chemical reaction, or, if gases are involved, $\Delta V = 0$ (that is, there are the same number of reactant and product gas molecules).

8.43 Heat is lost on going from $H_2O(g) \rightarrow H_2O(l) \rightarrow H_2O(s)$.
$H_2O(g)$ has the highest enthalpy content. $H_2O(s)$ has the lowest enthalpy content.

8.44 $P\Delta V$ = -7.6 J (from Problem 8.39)
$\Delta H = \Delta E + P\Delta V$
$\Delta E = \Delta H - P\Delta V$ = -0.31 kJ - (- 7.6 x 10^{-3} kJ) = -0.30 kJ

8.45 ΔH = -244 kJ and $w = -P\Delta V$ = 35 kJ; therefore $P\Delta V$ = -35 kJ
$\Delta E = \Delta H - P\Delta V$ = -244 kJ - (-35 kJ) = -209 kJ
For the system: ΔH = -244 kJ and ΔE = -209 kJ
ΔH and ΔE for the surroundings are just the opposite of what they are for the system.
For the surroundings: ΔH = 244 kJ and ΔE = 209 kJ

8.46 ΔH = -1255.5 kJ/mol C_2H_2; C_2H_2, 26.04 amu
$w = -P\Delta V$ = -(1.00 atm)(-2.80 L) = 2.80 L· atm

$$w = (2.80\ L \cdot atm)\left(\frac{101\ J}{1\ L \bullet atm}\right) = 283\ J = 0.283\ kJ$$

$$6.50\ g \times \frac{1\ mol\ C_2H_2}{26.04\ g\ C_2H_2} = 0.250\ mol\ C_2H_2$$

q = (-1255.5 kJ/mol)(0.250 mol) = -314 kJ
$\Delta E = \Delta H - P\Delta V$ = -314 kJ - (-0.283 kJ) = -314 kJ

8.47 C_2H_4, 28.05 amu; HCl, 36.46 amu

$w = -P\Delta V = -(1.00 \text{ atm})(-71.5 \text{ L}) = 71.5 \text{ L} \cdot \text{atm}$

$$w = (71.5 \text{ L} \cdot \text{atm})\left(\frac{101 \text{ J}}{1 \text{ L} \bullet \text{atm}}\right) = 7222 \text{ J} = 7.22 \text{ kJ}$$

$$89.5 \text{ g } C_2H_4 \times \frac{1 \text{ mol } C_2H_4}{28.05 \text{ g } C_2H_4} = 3.19 \text{ mol } C_2H_4$$

$$125 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 3.43 \text{ mol HCl}$$

Because the reaction stoichiometry between C_2H_4 and HCl is one to one, C_2H_4 is the limiting reactant.

ΔH^o = -72.3 kJ/mol C_2H_4

q = (-72.3 kJ/mol)(3.19 mol) = -231 kJ

$\Delta E = \Delta H - P\Delta V$ = -231 kJ - (-7.22 kJ) = -224 kJ

8.48 $C_4H_{10}O$, 74.12 amu; mass of $C_4H_{10}O$ = (0.7138 g/mL)(100 mL) = 71.38 g

$$\text{mol } C_4H_{10}O = 71.38 \text{ g} \times \frac{1 \text{ mol}}{74.12 \text{ g}} = 0.9626 \text{ mol}$$

$q = n \times \Delta H_{vap}$ = 0.9626 mol x 26.5 kJ/mol = 25.5 kJ

8.49 Assume 100 mL of H_2O = 100 g; H_2O, 18.02 amu

$$100 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{40.7 \text{ kJ}}{1 \text{ mol } H_2O} = 226 \text{ kJ}$$

The heat to vaporize 100 mL of H_2O is much greater than that to vaporize 100 mL of diethyl ether.

8.50 Al, 26.98 amu

$$\text{mol Al} = 5.00 \text{ g} \times \frac{1 \text{ mol}}{26.98 \text{ g}} = 0.1853 \text{ mol}$$

$$q = n \times \Delta H^o = 0.1853 \text{ mol Al} \times \frac{-1408.4 \text{ kJ}}{2 \text{ mol Al}} = -131 \text{ kJ}$$; 131 kJ is released.

8.51 Na, 22.99 amu; ΔH^o = -368.4 kJ/2 mol Na = -184.2 kJ/mol Na

$$1.00 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{-184.2 \text{ kJ}}{1 \text{ mol Na}} = -8.01 \text{ kJ}$$

8.01 kJ of heat is evolved. The reaction is exothermic.

8.52 Fe_2O_3, 159.7 amu

$$\text{mol } Fe_2O_3 = 2.50 \text{ g} \times \frac{1 \text{ mol}}{159.7 \text{ g}} = 0.015\,65 \text{ mol}$$

$q = n \times \Delta H^o = 0.015\ 65\ \text{mol } Fe_2O_3 \times \frac{-24.8\ \text{kJ}}{1\ \text{mol } Fe_2O_3} = -0.388\ \text{kJ}$; 0.388 kJ is evolved.

Because ΔH is negative, the reaction is exothermic.

8.53 CaO, 56.08 amu

$\text{mol CaO} = 233.0\ \text{g} \times \frac{1\ \text{mol}}{56.08\ \text{g}} = 4.155\ \text{mol}$

$q = n \times \Delta H^o = 4.155\ \text{mol CaO} \times \frac{464.8\ \text{kJ}}{1\ \text{mol CaO}} = 1931\ \text{kJ}$; 1931 kJ is absorbed.

Because ΔH is positive, the reaction is endothermic.

Calorimetry and Heat Capacity

8.54 Heat capacity is the amount of heat required to raise the temperature of a substance a given amount. Specific heat is the amount of heat necessary to raise the temperature of exactly 1 g of a substance by exactly 1°C.

8.55 A measurement carried out in a bomb calorimeter is done at constant volume and therefore ΔE is obtained.

8.56 Na, 22.99 amu

$\text{specific heat} = 28.2\ \frac{\text{J}}{\text{mol} \bullet\ ^\circ\text{C}} \times \frac{1\ \text{mol}}{22.99\ \text{g}} = 1.23\ \text{J/(g} \bullet\ ^\circ\text{C)}$

8.57 $q = (\text{specific heat}) \times m \times \Delta T$

$\text{specific heat} = \frac{q}{m \times \Delta T} = \frac{89.7\ \text{J}}{(33.0\ \text{g})(5.20\ ^\circ\text{C})} = 0.523\ \text{J/(g} \cdot\ ^\circ\text{C)}$

$C_m = [0.523\ \text{J/(g} \cdot\ ^\circ\text{C)}](47.88\ \text{g/mol}) = 25.0\ \text{J/(mol} \cdot\ ^\circ\text{C)}$

8.58 Mass of solution = 50.0 g + 1.045 g = 51.0 g

$q = (\text{specific heat}) \times m \times \Delta T$

$q = \left(4.18\ \frac{\text{J}}{\text{g} \bullet\ ^\circ\text{C}}\right)(51.0\ \text{g})(32.3\ ^\circ\text{C} - 25.0\ ^\circ\text{C}) = 1.56 \times 10^3\ \text{J} = 1.56\ \text{kJ}$

CaO, 56.08 amu; $\text{mol CaO} = 1.045\ \text{g} \times \frac{1\ \text{mol}}{56.08\ \text{g}} = 0.018\,63\ \text{mol}$

$\text{Heat evolved per mole of CaO} = \frac{1.56\ \text{kJ}}{0.018\,63\ \text{mol}} = 83.7\ \text{kJ / mol CaO}$

Because the reaction evolves heat, the sign for ΔH is negative. $\Delta H = -83.7\ \text{kJ}$

8.59 C_6H_6, 78.11 amu; $2\ C_6H_6(l) + 15\ O_2(g) \rightarrow 12\ CO_2(g) + 6\ H_2O(g)$

$\Delta E = q_V = \_ q_{H_2O} = -\left(4.18 \frac{J}{g \bullet {}^oC}\right)(250.0\ g)(7.48^oC) = -7817\ J = -7.82\ kJ$

$0.187\ g\ C_6H_6 \times \frac{1\ mol\ C_6H_6}{78.11\ g\ C_6H_6} = 0.002\ 39\ mol\ C_6H_6$

ΔE(per mole) = (-7.82 kJ)/(0.002 39 mol) = -3.27×10^3 kJ/mol

ΔE (per gram C_6H_6) = (-3.27×10^3 kJ/mol)/(78.11 g/mol) = - 41.9 kJ/g

8.60 NaOH, 40.00 amu; HCl, 36.46 amu

$8.00\ g\ NaOH \times \frac{1\ mol\ NaOH}{40.00\ g\ NaOH} = 0.200\ mol\ NaOH$

$8.00\ g\ HCl \times \frac{1\ mol\ HCl}{36.46\ g\ HCl} = 0.219\ mol\ HCl$

Because the reaction stoichiometry between NaOH and HCl is one to one, the NaOH is the limiting reactant.

$q_P = -q_{soln} = -(\text{specific heat}) \times m \times \Delta T = -\left(4.18 \frac{J}{g \bullet {}^oC}\right)(316\ g)(33.5^oC \_ 25.0^oC) = -11.2\ kJ$

$\Delta H = q_p/n = (-11.2\ kJ)/(0.200\ mol) = -56\ kJ/mol$

When 10.00 g of HCl in 248.0 g of water is added the same temperature increase is observed because the mass of NaOH is the same and it is still the limiting reactant. The mass of the solution is also the same.

8.61 NH_4NO_3, 80.04 amu; assume 125 mL = 125 g H_2O

$50.0\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.04\ g\ NH_4NO_3} = 0.625\ mol\ NH_4NO_3$

$q_p = \Delta H \times n = (+25.7\ kJ/mol)(0.625\ mol) = 16.1\ kJ = 16{,}100\ J$

$q_{soln} = -q_p = -16{,}100\ J$

$q_{soln} = (\text{specific heat}) \times m \times \Delta T$

$\Delta T = \frac{q_{soln}}{(\text{specific heat}) \times m} = \frac{\_16{,}100\ J}{\left(4.18 \frac{J}{g \bullet {}^oC}\right)(50\ g + 125\ g)} = -22.0^oC$

$\Delta T = -22.0^oC = T_{final} - T_{initial} = T_{final} - 25.0^oC$

$T_{final} = -22.0^oC + 25.0^oC = 3.0^oC$

Hess's Law and Heats of Formation

8.62 The standard state of an element is its most stable form at 1 atm and the specified temperature, usually 25°C.

8.63 A compound's standard heat of formation is the amount of heat associated with the formation of 1 mole of a compound from its elements (in their standard states).

8.64 Hess's Law – the overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.

Hess's Law works because of the law of conservation of energy.

8.65 Elements always have $\Delta H^o_f = 0$ because the standard state of elements is the reference point from which all enthalpy changes are measured.

8.66

	$S(s) + O_2(g) \rightarrow SO_2(g)$	$\Delta H^o_1 = -296.8$ kJ
	$SO_2 + \frac{1}{2} O_2(g) \rightarrow SO_3(g)$	$\Delta H^o_2 = -98.9$ kJ
Sum	$S(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$	$\Delta H^o_3 = \Delta H^o_1 + \Delta H^o_2$

$\Delta H^o_f = \Delta H^o_3 = -296.8$ kJ + (-98.9 kJ) = -395.7 kJ/mol

8.67 $\Delta H^o_{rxn} = [12\ \Delta H^o_f(CO_2) + 6\ \Delta H^o_f(H_2O)] - [2\ \Delta H^o_f(C_6H_6)]$

-6534 kJ = [(12 mol)(-393.5 kJ/mol) + (6 mol)(-285.8 kJ/mol)] - [(2 mol)($\Delta H^o_f(C_6H_6)$)]

Solve for $\Delta H^o_f(C_6H_6)$.

-6534 kJ = -6436.8 kJ - [(2 mol)($\Delta H^o_f(C_6H_6)$)]

97.2 kJ = (2 mol)($\Delta H^o_f(C_6H_6)$)

$\Delta H^o_f(C_6H_6) = +48.6$ kJ/mol

8.68

	$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$	$\Delta H^o_1 = -227.8$ kJ
	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	$\Delta H^o_2 = \Delta H^o_f = -285.8$ kJ
	$S(s) + 3/2\ O_2(g) \rightarrow SO_3(g)$	$\Delta H^o_3 = \Delta H^o_f = -395.7$
Sum	$S(s) + H_2(g) + 2\ O_2(g) \rightarrow H_2SO_4(aq)$	$\Delta H^o_f\ (H_2SO_4) = ?$

$\Delta H^o_f\ (H_2SO_4) = \Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 = -909.3$ kJ

8.69 $\Delta H^o_{rxn} = [\Delta H^o_f(CH_3CO_2H) + \Delta H^o_f(H_2O)] - \Delta H^o_f(CH_3CH_2OH)$

$\Delta H^o_{rxn} = [(1\text{ mol})(-484.5\text{ kJ/mol}) + (1\text{mol})(-285.8\text{ kJ/mol})] - [(1\text{ mol})(-277.7\text{ kJ/mol})]$

$\Delta H^o_{rxn} = -492.6$ kJ

8.70 $C_8H_8(l) + 10\ O_2(g) \rightarrow 8\ CO_2(g) + 4\ H_2O(l)$

$\Delta H^o_{rxn} = \Delta H^o_c = -4395.2$ kJ

$\Delta H^o_{rxn} = [8\ \Delta H^o_f(CO_2) + 4\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_8H_8)$

-4395.2 kJ = [(8 mol)(-393.5 kJ/mol) + (4 mol)(-285.8 kJ/mol)]- [(1 mol)($\Delta H^o_f(C_8H_8)$)]

Solve for $\Delta H^o_f(C_8H_8)$

-4395.2 kJ = -4291.2 kJ - (1 mol)($\Delta H^o_f(C_8H_8)$)

-104.0 kJ = -(1 mol)($\Delta H^o_f(C_8H_8)$)

$$\Delta H^o_f(C_8H_8) = \frac{-104.0\text{ kJ}}{1\text{ mol}} = +104.0\text{ kJ/mol}$$

8.71 $C_5H_{12}O(l) + 15/2\ O_2(g) \rightarrow 5\ CO_2(g) + 6\ H_2O(l)$

$\Delta H^o_{rxn} = [5\ \Delta H^o_f(CO_2) + 6\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_5H_{12}O)$

$\Delta H^o_{rxn} = [(5\text{ mol})(-393.5\text{ kJ/mol}) + (6\text{ mol})(-285.8\text{ kJ/mol})] - [(1\text{ mol})(-313.6\text{ kJ/mol})]$

$\Delta H^o_{rxn} = -3369$ kJ

8.72 $\Delta H^o_{rxn} = \Delta H^o_f(\text{MTBE}) - [\Delta H^o_f(\text{2-Methylpropene}) + \Delta H^o_f(CH_3OH)]$

-57.8 kJ = -313.6 kJ - [(1 mol)(ΔH^o_f(2-Methylpropene)) + (-238.7 kJ)]

Solve for ΔH^o_f(2-Methylpropene).
-17.1 kJ = (1 mol)(ΔH^o_f(2-Methylpropene))
ΔH^o_f(2-Methylpropene) = -17.1 kJ/mol

8.73 $C_{51}H_{88}O_6(l) + 70\ O_2(g) \rightarrow 51\ CO_2(g) + 44\ H_2O(l)$
$\Delta H^o_{rxn} = [51\ \Delta H^o_f(CO_2) + 44\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_{51}H_{88}O_6)$
$\Delta H^o_{rxn} = [(51\ mol)(-393.5\ kJ/mol) + (44\ mol)(-285.8\ kJ/mol)] - [(1\ mol)(-1310\ kJ/mol)]$
$\Delta H^o_{rxn} = -3.133 \times 10^4$ kJ/mol $C_{51}H_{88}O_6$
$C_{51}H_{88}O_6$, 797.25 amu

$$q = -3.133 \times 10^4 \frac{kJ}{mol} \times \frac{1\ mol}{797.25\ g} \times 0.94 \frac{g}{mL} = \_37\ kJ / mL\ ;\ 37\ kJ\ released\ per\ mL$$

Bond Dissociation Energies

8.74 $H_2C{=}CH_2(g) + H_2(g) \rightarrow CH_3CH_3(g)$
$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)
$\Delta H^o_{rxn} = (D_{C=C} + 4\ D_{C-H} + D_{H-H}) - (6\ D_{C-H} + D_{C-C})$
$\Delta H^o_{rxn} = [(1\ mol)(611\ kJ/mol) + (4\ mol)(410\ kJ/mol) + (1\ mol)(436\ kJ/mol)]$
$- [(6\ mol)(410\ kJ/mol) + (1\ mol)(350\ kJ/mol)] = -123\ kJ$

8.75 $CH_3CH{=}CH_2 + H_2O \rightarrow CH_3CH(OH)CH_3$
$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)
$\Delta H^o_{rxn} = (D_{C=C} + D_{C-C} + 6\ D_{C-H} + 2\ D_{O-H}) - (2\ D_{C-C} + 7\ D_{C-H} + D_{C-O} + D_{O-H})$
$\Delta H^o_{rxn} = [(1\ mol)(611\ kJ/mol) + (1\ mol)(350\ kJ/mol) + (6\ mol)(410\ kJ/mol)$
$+ (2\ mol)(460\ kJ/mol)] - [(2\ mol)(350\ kJ/mol) + (7\ mol)(410\ kJ/mol)$
$+ (1\ mol)(350\ kJ/mol) + (1\ mol)(460\ kJ/mol)] = -39\ kJ$

8.76 $C_4H_{10} + 13/2\ O_2 \rightarrow 4\ CO_2 + 5\ H_2O$
$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)
$\Delta H^o_{rxn} = (3\ D_{C-C} + 10\ D_{C-H} + 13/2\ D_{O=O}) - (8\ D_{C=O} + 10\ D_{O-H})$
$\Delta H^o_{rxn} = [(3\ mol)(350\ kJ/mol) + (10\ mol)(410\ kJ/mol) + (13/2\ mol)(498\ kJ/mol)]$
$- [(8\ mol)(804\ kJ/mol) + (10\ mol)(460\ kJ/mol)] = -2645\ kJ$

8.77 $CH_3CO_2H + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + H_2O$
$\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)
$\Delta H^o_{rxn} = (D_{C=O} + 2\ D_{C-O} + 8\ D_{C-H} + 2\ D_{O-H}) - (D_{C=O} + 2\ D_{C-O} + 8\ D_{C-H} + 2\ D_{O-H}) = 0\ kJ$

Free Energy and Entropy

8.78 Entropy is a measure of molecular disorder.

8.79 $\Delta G = \Delta H - T\Delta S$
ΔH is usually more important because it is usually much larger than $T\Delta S$.

8.80 A reaction can be spontaneous yet endothermic if ΔS is positive (more disorder) and the $T\Delta S$ term is larger than ΔH.

8.81 A reaction can be nonspontaneous yet exothermic if ΔS is negative (more order) and the temperature is high enough so that the $T\Delta S$ term is more negative than ΔH.

8.82 (a) positive (more disorder) (b) negative (more order)

8.83 (a) positive (more disorder) (b) negative (more order)
(c) positive (more disorder)

8.84 (a) zero (equilibrium) (b) zero (equilibrium)
(c) negative (spontaneous)

8.85 Because the mixing of gas molecules is spontaneous, ΔG is negative. The mixture of gas molecules is more disordered so ΔS is positive. For the diffusion of gases, ΔH is approximately zero.

8.86 ΔS is positive. The reaction increases the total number of molecules.

8.87 $\Delta S < 0$. The reaction decreases the number of gas molecules.

8.88 $\Delta G = \Delta H - T\Delta S$
(a) $\Delta G = -48\ kJ - (400\ K)(135 \times 10^{-3}\ kJ/K) = -102\ kJ$
$\Delta G < 0$, spontaneous; $\Delta H < 0$, exothermic.
(b) $\Delta G = -48\ kJ - (400\ K)(-135 \times 10^{-3}\ kJ/K) = +6\ kJ$
$\Delta G > 0$, nonspontaneous; $\Delta H < 0$, exothermic.
(c) $\Delta G = +48\ kJ - (400\ K)(135 \times 10^{-3}\ kJ/K) = -6\ kJ$
$\Delta G < 0$, spontaneous; $\Delta H > 0$, endothermic.
(d) $\Delta G = +48\ kJ - (400\ K)(-135 \times 10^{-3}\ kJ/K) = +102\ kJ$
$\Delta G > 0$, nonspontaneous; $\Delta H > 0$, endothermic.

8.89 $\Delta G = \Delta H - T\Delta S$
(a) $\Delta G = -128\ kJ - (500\ K)(35 \times 10^{-3}\ kJ/K) = -146\ kJ$
$\Delta G < 0$, spontaneous; $\Delta H < 0$, exothermic
(b) $\Delta G = +67\ kJ - (250\ K)(-140 \times 10^{-3}\ kJ/K) = +102\ kJ$
$\Delta G > 0$, nonspontaneous; $\Delta H > 0$, endothermic
(c) $\Delta G = +75\ kJ - (800\ K)(95 \times 10^{-3}\ kJ/K) = -1\ kJ$
$\Delta G < 0$, spontaneous; $\Delta H > 0$, endothermic

8.90 $\Delta G = \Delta H - T\Delta S$; Set $\Delta G = 0$ and solve for T (the crossover temperature).

$$T = \frac{\Delta H}{\Delta S} = \frac{-33\ kJ}{-0.058\ kJ/K} = 570\ K$$

8.91 Because $\Delta H > 0$ and $\Delta S < 0$, the reaction is nonspontaneous at all temperatures. There is no crossover temperature.

8.92 (a) $\Delta H < 0$ and $\Delta S > 0$; reaction is spontaneous at all temperatures.
(b) $\Delta H < 0$ and $\Delta S < 0$; reaction has a crossover temperature.
(c) $\Delta H > 0$ and $\Delta S > 0$; reaction has a crossover temperature.
(d) $\Delta H > 0$ and $\Delta S < 0$; reaction is nonspontaneous at all temperatures.

8.93 (a) $\Delta H < 0$ and $\Delta S < 0$. The reaction is favored by enthalpy but not by entropy.
$\Delta G^o = \Delta H^o - T\Delta S^o = -217.5$ kJ/mol - (298 K)[-233.9×10^{-3} kJ/(K · mol)] = -147.8 kJ
(b) The reaction has a crossover temperature. Set $\Delta G = 0$ and solve for T (the crossover temperature).
$\Delta G^o = 0 = \Delta H^o - T\Delta S^o$

$$T = \frac{\Delta H^o}{\Delta S^o} = \frac{217.5 \text{ kJ/mol}}{233.9 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}} = 929.9 \text{ K}$$

8.94 $T = -114.1^oC = 273.15 + (-114.1) = 159.0$ K
$\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$; $\Delta G = 0$ at the melting point temperature.
Set $\Delta G = 0$ and solve for ΔS_{fus}.
$\Delta G = 0 = \Delta H_{fus} - T\Delta S_{fus}$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \frac{5.02 \text{ kJ/mol}}{159.0 \text{ K}} = 0.0316 \text{ kJ/(K·mol)} = 31.6 \text{ J/(K·mol)}$$

8.95 $T = 61.2^oC = 273.15 + (61.2) = 334.4$ K
$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$; $\Delta G = 0$ at the boiling point temperature.
Set $\Delta G = 0$ and solve for ΔS_{vap}.
$\Delta G = 0 = \Delta H_{vap} - T\Delta S_{vap}$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{29.2 \text{ kJ/mol}}{334.4 \text{ K}} = 0.0873 \text{ kJ/(K·mol)} = 87.3 \text{ J/(K·mol)}$$

General Problems

8.96 $Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

$$\text{mol Mg} = 1.50 \text{ g} \times \frac{1 \text{ mol}}{24.3 \text{ g}} = 0.0617 \text{ mol Mg}$$

$$\text{mol HCl} = 0.200 \text{ L} \times 6.00 \frac{\text{mol}}{\text{L}} = 1.20 \text{ mol HCl}$$

There is an excess of HCl. Mg is the limiting reactant.

$$q = \left(4.18 \frac{\text{J}}{\text{g} \bullet {}^o\text{C}}\right)(200 \text{ g})(42.9 {}^o\text{C} - 25.0 {}^{oC}) + \left(776 \frac{\text{J}}{{}^o\text{C}}\right)(42.9 {}^o\text{C} - 25.0 {}^o\text{C}) =$$

2.89×10^4 J

$$q = 2.89 \times 10^4 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 28.9 \text{ kJ}$$

$$\text{Heat evolved per mole of Mg} = \frac{28.9 \text{ kJ}}{0.0617 \text{ mol}} = 468 \text{ kJ / mol}$$

Because the reaction evolves heat, the sign for ΔH is negative. ΔH = - 468 kJ

8.97 (a) $C(s) + CO_2(g) \rightarrow 2\ CO(g)$

$\Delta H^o_{rxn} = [2\ \Delta H^o_f(CO)] - \Delta H^o_f(CO_2)$

$\Delta H^o_{rxn} = [(2\ mol)(-110.5\ kJ/mol)] - [(1\ mol)(-393.5\ kJ/mol)] = +172.5\ kJ$

(b) $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

$\Delta H^o_{rxn} = [2\ \Delta H^o_f(H_2O)] - [2\ \Delta H^o_f(H_2O_2)]$

$\Delta H^o_{rxn} = [(2\ mol)(-285.8\ kJ/mol)] - [(2\ mol)(-191.2\ kJ/mol)] = -189.2\ kJ$

(c) $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

$\Delta H^o_{rxn} = [3\ \Delta H^o_f(CO_2)] - [\Delta H^o_f(Fe_2O_3) + 3\ \Delta H^o_f(CO)]$

$\Delta H^o_{rxn} = [(3\ mol)(-393.5\ kJ/mol)]$

$- [(1\ mol)(-824.2\ kJ/mol) + (3\ mol)(-110.5\ kJ/mol)] = -24.8\ kJ$

8.98

	$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$	$\Delta H^o_1 = 2(-57.0\ kJ)$
	$2\ NO_2(g) \rightarrow N_2O_4(g)$	$\Delta H^o_2 = -57.2\ kJ$
Sum	$2\ NO(g) + O_2(g) \rightarrow N_2O_4(g)$	

$\Delta H^o = \Delta H^o_1 + \Delta H^o_2 = -171.2\ kJ$

8.99 ΔG = ΔH - TΔS; at equilibrium ΔG = 0. Set ΔG = 0 and solve for T.

$\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{30.91\ kJ/mol}{93.2\ \times 10^{-3}\ kJ/(K \bullet mol)} = 332\ K = 59^oC$$

8.100 $\Delta G_{fus} = \Delta H_{fus} - T\Delta S_{fus}$; at the melting point ΔG = 0. Set ΔG = 0 and solve for T (the melting point).

$\Delta G = 0 = \Delta H_{fus} - T\Delta S_{fus}$

$$T = \frac{\Delta H_{fus}}{\Delta S_{fus}} = \frac{9.95\ kJ}{0.0357\ kJ/K} = 279\ K$$

8.101 $HgS(s) + O_2(g) \rightarrow Hg(l) + SO_2(g)$

(a) $\Delta H^o_{rxn} = \Delta H^o_f(SO_2) - \Delta H^o_f(HgS)$

$\Delta H^o_{rxn} = [(1\ mol)(-296.8\ kJ/mol)] - [(1\ mol)(-58.2\ kJ/mol)] = -238.6\ kJ$

(b) and (c) Because ΔH < 0 and ΔS > 0, the reaction is spontaneous at <u>all</u> temperatures.

8.102 $\Delta H^o_{rxn} = D$ (Reactant bonds) - D (Product bonds)

(a) $2\ CH_4(g) \rightarrow C_2H_6(g) + H_2(g)$

$\Delta H^o_{rxn} = (8\ D_{C\text{-}H}) - (D_{C\text{-}C} + 6\ D_{C\text{-}H} + D_{H\text{-}H})$

$\Delta H^o_{rxn} = [(8\ mol)(410\ kJ/mol)] - [(1\ mol)(350\ kJ/mol) + (6\ mol)(410\ kJ/mol)$

$+ (1\ mol)(436\ kJ/mol)] = +34\ kJ$

(b) $C_2H_6(g) + F_2(g) \rightarrow C_2H_5F(g) + HF(g)$

$\Delta H^o_{rxn} = (6\ D_{C\text{-}H} + D_{C\text{-}C} + D_{F\text{-}F}) - (5\ D_{C\text{-}H} + D_{C\text{-}C} + D_{C\text{-}F} + D_{H\text{-}F})$

$\Delta H^o_{rxn} = [(6\ mol)(410\ kJ/mol) + (1\ mol)(350\ kJ/mol) + (1\ mol)(159\ kJ/mol)]$

- [(5 mol)(410 kJ/mol) + (1 mol)(350 kJ/mol) + (1 mol)(450 kJ/mol) + (1 mol)(570 kJ/mol)] = - 451 kJ

(c) $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

The bond dissociation energy for N_2 is 945 kJ/mol.

$\Delta H^o_{rxn} = (D_{N_2} + 3\ D_{H\text{-}H}) - (6\ D_{N\text{-}H})$

ΔH^o_{rxn} = [(1 mol)(945 kJ/mol) + (3 mol)(436 kJ/mol)] - [(6 mol)(390 kJ/mol)] = -87 kJ

8.103 (a) $\Delta H^o_{rxn} = \Delta H^o_f(CH_3OH) - \Delta H^o_f(CO)$

ΔH^o_{rxn} = [(1 mol)(-238.7 kJ/mol)] - [(1 mol)(-110.5 kJ/mol)] = -128.2 kJ

(b) $\Delta G^o = \Delta H^o - T\Delta S^o$ = -128.2 kJ - (298 K)(-332 x 10^{-3} kJ/K) = -29.3 kJ

(c) Step 1 is spontaneous since $\Delta G^o < 0$.

(d) ΔH^o, because it is larger than $T\Delta S^o$.

(e) Set $\Delta G = 0$ and solve for T.

$\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{128.2\ kJ}{332 \times 10^{-3}\ kJ/K} = 386\ K;$$ The reaction is spontaneous below 386 K.

(f) $\Delta H^o_{rxn} = \Delta H^o_f(CH_4) - \Delta H^o_f(CH_3OH)$

ΔH^o_{rxn} = [(1 mol)(-74.8 kJ/mol)] - [(1 mol)(-238.7 kJ/mol)] = +163.9 kJ

(g) $\Delta G^o = \Delta H^o - T\Delta S^o$ = +163.9 kJ - (298 K)(162 x 10^{-3} kJ/K) = +115.6 kJ

(h) Step 2 is nonspontaneous since $\Delta G^o > 0$.

(i) ΔH^o, because it is larger than $T\Delta S^o$.

(j) Set $\Delta G = 0$ and solve for T.

$\Delta G = 0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{163.9\ kJ}{162 \times 10^{-3}\ kJ/K} = 1012\ K;$$ The reaction is spontaneous above 1012 K.

(k) $\Delta G^o_{overall} = \Delta G^o_1 + \Delta G^o_2$ = -29.3 kJ + 115.6 kJ = +86.3 kJ

$\Delta H^o_{overall} = \Delta H^o_1 + \Delta H^o_2$ = -128.2 kJ + 163.9 kJ = +35.7 kJ

$\Delta S^o_{overall} = \Delta S^o_1 + \Delta S^o_2$ = -332 J/K + 162 J/K = -170 J/K

(l) The overall reaction is nonspontaneous since $\Delta G^o_{overall} > 0$.

(m) The two reactions should be run separately. Run step 1 below 386 K and run step 2 above 1012 K.

8.104 (a) $2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(g)$

(b) $C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(g)$

$\Delta H^o_{rxn} = \Delta H^o_c$ = -5456.6 kJ

$\Delta H^o_{rxn} = [8\ \Delta H^o_f(CO_2) + 9\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_8H_{18})$

-5456.6 kJ = [(8 mol)(-393.5 kJ/mol) +(9 mol)(-241.8 kJ/mol)] - [(1 mol)($\Delta H^o_f(C_8H_{18})$)]

Solve for $\Delta H^o_f(C_8H_{18})$.

-5456.6 kJ = -5324 kJ - [(1 mol)($\Delta H^o_f(C_8H_{18})$)]

-132.4 kJ = -(1 mol)($\Delta H^o_f(C_8H_{18})$)

$\Delta H^o_f(C_8H_{18})$ = +132.4 kJ/mol

8.105 Assume 1.00 kg of H_2O; 1 kg·m^2/s^2 = 1 J

E_p = (1.00 kg)(9.81 m/s^2)(739 m) = 7250 kg·m^2/s^2 = 7250 J

q = specific heat x m x ΔT

$$\Delta T = \frac{q}{\text{m x specific heat}} = \frac{7250\ \text{J}}{(1000\ \text{g})(4.18\ \text{J/(g} \bullet\ ^{o}\text{C})} = 1.73^{o}\text{C (temperature rise)}$$

8.106 (a) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$ and $\Delta S_{surr} = -\Delta H/T$

$\Delta S_{total} = \Delta S_{system} + (-\Delta H/T) = \Delta S_{system} - \Delta H/T$

$\Delta S_{system} = \Delta S_{total} + \Delta H/T$

$\Delta G = \Delta H - T\Delta S$ (substitute ΔS_{system} for ΔS in this equation)

$\Delta G = \Delta H - T(\Delta S_{total} + \Delta H/T) = -T\Delta S_{total}$

$\Delta G = -T\Delta S_{total}$ For a spontaneous reaction, if $\Delta S_{total} > 0$ then $\Delta G < 0$.

(b) $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$

$\Delta H^{o} = \Delta G^{o} + T\Delta S^{o}$

$$\Delta S_{surr} = -\frac{\Delta H^{o}}{T} = -\frac{[\Delta G^{o} + T\Delta S^{o}]}{T} = -\frac{[2879\ \text{x}\ 10^{3}\ \text{J/mol} + (298\ \text{K})(-210\ \text{J/(K} \bullet\ \text{mol}))]}{298\ \text{K}}$$

$\Delta S_{surr} = -9451\ \text{J/(K} \cdot\ \text{mol)}$

8.107

	$3/2\ NO_2(g) + 1/2\ H_2O(l) \rightarrow HNO_3(aq) + 1/2\ NO(g)$	$\Delta H^{o}_1 = \frac{-138.4\ \text{kJ}}{2}$
	$3/2\ NO(g) + 3/4\ O_2(g) \rightarrow 3/2\ NO_2(g)$	$\Delta H^{o}_2 = \frac{(3)(-114.0\ \text{kJ})}{4}$
	$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$	$\Delta H^{o}_3 = -46.1\ \text{kJ}$
	$NH_3(g) + 5/4\ O_2(g) \rightarrow NO(g) + 6/4\ H_2O(l)$	$\Delta H^{o}_4 = \frac{-1169.6\ \text{kJ}}{4}$
	$H_2O(l) \rightarrow 1/2\ O_2(g) + H_2(g)$	$\Delta H^{o}_5 = +285.8\ \text{kJ}$
Sum	$1/2\ H_2(g) + 1/2\ N_2(g) + 3/2\ O_2(g) \rightarrow HNO_3(aq)$	$\Delta H^{o} = -207.4\ \text{kJ}$

8.108

	$2\ CH_4(g) + 4\ O_2(g) \rightarrow 2\ CO_2(g) + 4\ H_2O(l)$	$\Delta H^{o}_1 = 2(-890.3\ \text{kJ})$
	$C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g)$	$\Delta H^{o}_2 = +137.0\ \text{kJ}$
	$2\ CO_2(g) + 3\ H_2O(l) \rightarrow C_2H_6(g) + 7/2\ O_2(g)$	$\Delta H^{o}_3 = \frac{3119.4\ \text{kJ}}{2}$
	$H_2O(l) \rightarrow H_2(g) + 1/2\ O_2(g)$	$\Delta H^{o}_4 = +285.8\ \text{kJ}$
Sum	$2\ CH_4(g) \rightarrow C_2H_4(g) + 2\ H_2(g)$	$\Delta H^{o} = +201.9\ \text{kJ}$

8.109 $q_{Mo} = (110.0\ \text{g})(\text{specific heat Mo})(28.0^{o}\text{C} - 100.0^{o}\text{C})$

$q_{H_2O} = (150.0\ \text{g})[4.184\ \text{J/(g} \cdot\ ^{o}\text{C})](28.0^{o}\text{C} - 24.6^{o}\text{C})$

$q_{Mo} = -q_{H_2O}$

$(110.0\ \text{g})(\text{specific heat Mo})(28.0^{o}\text{C} - 100.0^{o}\text{C}) = -(150.0\ \text{g})[4.184\ \text{J/(g} \cdot\ ^{o}\text{C})](28.0^{o}\text{C} - 24.6^{o}\text{C})$

$$\text{specific heat Mo} = \frac{-(150.0\ \text{g})[4.184\ \text{J/(g} \bullet\ ^{o}\text{C})](28.0^{o}\text{C} - 24.6^{o}\text{C})}{(110.0\ \text{g})(28.0^{o}\text{C} - 100.0^{o}\text{C})} = 0.27\ \text{J/(g} \cdot\ ^{o}\text{C})$$

8.110 $q_{ice\ tea} = -q_{ice}$

$q_{ice\ tea} = (4.18\ \frac{J}{g \bullet\ ^oC})(400.0\ g)(10.0\ ^oC - 80.0\ ^oC) = -1.17 \times 10^5\ J$

H_2O, 18.02 amu

$$q_{ice} = 1.17 \times 10^5\ J = (6.01\ kJ/mol)\left(\frac{1000\ J}{1\ kJ}\right)\left(m_{ice} \times \frac{1\ mol\ H_2O}{18.02\ g\ H_2O}\right) + \left(4.18\ \frac{J}{(g \bullet\ ^oC)}\right)(m_{ice})(10.0^oC - 0.0^oC)$$

Solve for the mass of ice, m_{ice}.

$1.17 \times 10^5\ J = (3.34 \times 10^2\ J/g)(m_{ice}) + (41.8\ J/g)(m_{ice}) = (3.76 \times 10^2\ J/g)(m_{ice})$

$$m_{ice} = \frac{1.17 \times 10^5\ J}{3.76 \times 10^2\ J/g} = 311\ g\ of\ ice$$

8.111 There is a large excess of NaOH.

5.00 mL = 0.005 00 L

mol citric acid = (0.005 00 L)(0.64 mol/L) = 0.0032 mol citric acid

$q_{H_2O} = (51.6\ g)[4.0\ J/(g \cdot\ ^oC)](27.9^oC - 26.0^oC) = 392\ J$

$q_{rxn} = -q_{H_2O} = -392\ J$

$$\Delta H = -\frac{392\ J}{0.0032\ mol} \times \frac{1\ kJ}{1000\ J} = -123\ kJ/mol = -120\ kJ/mol\ citric\ acid$$

8.112 $CsOH(aq) + HCl(aq) \rightarrow CsCl(aq) + H_2O(l)$

$$mol\ CsOH = 0.100\ L \times \frac{0.200\ mol\ CsOH}{1.00\ L} = 0.0200\ mol\ CsOH$$

$$mol\ HCl = 0.050\ L \times \frac{0.400\ mol\ HCl}{1.00\ L} = 0.0200\ mol\ HCl$$

The reactants were mixed in equal mole amounts.

Total volume = 150 mL and has a mass of 150 g

$$q_{solution} = \left(4.2\ \frac{J}{(g \bullet\ ^oC)}\right)(150\ g)(24.28^oC - 22.50^oC) = 1121\ J$$

$q_{reaction} = -q_{solution} = -1121\ J$

$$\Delta H = \frac{q_{reaction}}{mol\ CsOH} = \frac{-1121\ J}{0.0200\ mol\ CsOH} \times \frac{1\ kJ}{1000\ J} = -56\ kJ/mol\ CsOH$$

8.113 $NaNO_3$, 84.99 amu; KF, 58.10 amu

$$For\ NaNO_3(s) \rightarrow NaNO_3(aq),\ q = 20.5\ kJ/mol \times \frac{1\ mol\ NaNO_3}{84.99\ g\ NaNO_3} = 0.241\ kJ/g$$

$$For\ KF(s) \rightarrow KF(aq),\ q = -17.7\ kJ/mol \times \frac{1\ mol\ KF}{58.10\ g\ KF} = -0.305\ kJ/g$$

$q_{soln} = (110.0\ g)[4.18\ J/(g \cdot\ ^oC)](2.22^oC) = 1021\ J = 1.02\ kJ$

$q_{rxn} = -q_{soln} = -1.02\ kJ$

Let X = mass of $NaNO_3$ and Y = mass of KF

X + Y = 10.0 g, so Y = 10.0 g - X

q_{rxn} = -1.02 kJ = X(0.241 kJ/g) + Y(- 0.305 kJ/g) (substitute for Y and solve for X)

-1.02 kJ = X(0.241 kJ/g) + (10.0 g - X)(- 0.305 kJ/g)

-1.02 kJ = (0.241 kJ)X - 3.05 kJ + (0.305 kJ)X

2.03 kJ = (0.546 kJ)X

$$X = \frac{2.03\ kJ}{0.546\ kJ} = 3.72\ g\ NaNO_3$$

Y = 10.0 g - X = 10.0 g - 3.72 g = 6.28 g KF = 6.3 g KF

8.114

	ΔH
$4\ CO(g) + 2\ O_2(g) \rightarrow 4\ CO_2(g)$	2(-566.0 kJ)
$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$	+114.0 kJ
$2\ NO(g) \rightarrow O_2(g) + N_2(g)$	2(- 90.2 kJ)
$4\ CO(g) + 2\ NO_2(g) \rightarrow 4\ CO_2(g) + N_2(g)$	- 1198.4 kJ

Multi-Concept Problems

8.115 (a) Each S has 2 bonding pairs and 2 lone pairs of electrons. Each S is sp^3 hybridized and the geometry around each S is bent.

(b) ΔH = *D*(reactant bonds) - *D*(product bonds)

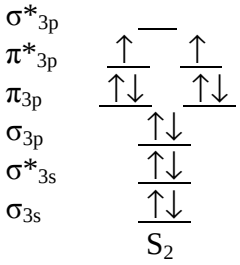
ΔH = (8 D_{S-S}) - (4 $D_{S=S}$) = +99 kJ

ΔH = [(8 mol)(225 kJ/mol) - [(4 mol)($D_{S=S}$)] = +99 kJ

- (4 mol)($D_{S=S}$) = 99 kJ - 1800 kJ = -1701 kJ

$D_{S=S}$ = (1701 kJ)/(4 mol) = 425 kJ/mol

(c)



S_2 should be paramagnetic with two unpaired electrons in the π^*_{3p} MOs.

8.116 (a)

(b) $C(g) + \frac{1}{2}\ O_2(g) + Cl_2(g) \rightarrow COCl_2(g)$

$\Delta H^o_f = \Delta H^o_f(C(g)) + (\frac{1}{2}\ D_{O=O} + D_{Cl-Cl}) - (D_{C=O} + 2\ D_{C-Cl})$

ΔH^o_f = (716.7 kJ) + [(½ mol)(498 kJ/mol) + (1 mol)(243 kJ/mol)]
- [(1 mol)(732 kJ/mol) + (2 mol)(330 kJ/mol)]

ΔH^o_{rxn} = - 183 kJ per mol $COCl_2$

From Appendix B, $\Delta H^o_f(COCl_2)$ = -219.1 kJ/mol

The calculation of ΔH^o_f from bond energies is only an estimate because the bond energies

are average values derived from many different compounds.

8.117 (a) (1) $2\ CH_3CO_2H(l) + Na_2CO_3(s) \rightarrow 2\ CH_3CO_2Na(aq) + CO_2(g) + H_2O(l)$
(2) $CH_3CO_2H(l) + NaHCO_3(s) \rightarrow CH_3CO_2Na(aq) + CO_2(g) + H_2O(l)$

(b) CH_3CO_2H, 60.05 amu; Na_2CO_3, 105.99 amu; $NaHCO_3$, 84.01 amu

$$1\ gal \times \frac{3.7854\ L}{1\ gal} \times \frac{1000\ mL}{1\ L} \times \frac{1.049\ g\ CH_3CO_2H}{1\ mL} = 3971\ g\ CH_3CO_2H$$

$$3971\ g\ CH_3CO_2H \times \frac{1\ mol\ CH_3CO_2H}{60.05\ g\ CH_3CO_2H} = 66.13\ mol\ CH_3CO_2H$$

For reaction (1)

$$66.13\ mol\ CH_3CO_2H \times \frac{1\ mol\ Na_2CO_3}{2\ mol\ CH_3CO_2H} \times \frac{105.99\ g\ Na_2CO_3}{1\ mol\ Na_2CO_3} \times \frac{1\ kg}{1000\ g} = 3.505\ kg\ Na_2CO_3$$

For reaction (2)

$$66.13\ mol\ CH_3CO_2H \times \frac{1\ mol\ NaHCO_3}{1\ mol\ CH_3CO_2H} \times \frac{84.01\ g\ NaHCO_3}{1\ mol\ NaHCO_3} \times \frac{1\ kg}{1000\ g} = 5.556\ kg\ NaHCO_3$$

(c) $2\ CH_3CO_2H(l) + Na_2CO_3(s) \rightarrow 2\ CH_3CO_2Na(aq) + CO_2(g) + H_2O(l)$

$\Delta H^o_{rxn} = [2\ \Delta H^o_f(CH_3CO_2Na) + \Delta H^o_f(CO_2) + \Delta H^o_f(H_2O)]$
$- [2\ \Delta H^o_f(CH_3CO_2H) + \Delta H^o_f(Na_2CO_3)]$

$\Delta H^o_{rxn} = [(2\ mol)(-726.1\ kJ/mol) + (1\ mol)(-393.5\ kJ/mol) + (1\ mol)(-285.8\ kJ/mol)]$
$- [(2\ mol)(-484.5\ kJ/mol) + (1\ mol)(-1130.7\ kJ/mol)]$

$\Delta H^o_{rxn} = -31.8\ kJ$ for 2 mol CH_3CO_2H

$$Heat = -\frac{31.8\ kJ}{2\ mol\ CH_3CO_2H} \times 66.13\ mol\ CH_3CO_2H = -1050\ kJ\ (liberated)$$

$CH_3CO_2H(l) + NaHCO_3(s) \rightarrow CH_3CO_2Na(aq) + CO_2(g) + H_2O(l)$

$\Delta H^o_{rxn} = [\Delta H^o_f(CH_3CO_2Na) + \Delta H^o_f(CO_2) + \Delta H^o_f(H_2O)]$
$- [\Delta H^o_f(CH_3CO_2H) + \Delta H^o_f(NaHCO_3)]$

$\Delta H^o_{rxn} = [(1\ mol)(-726.1\ kJ/mol) + (1\ mol)(-393.5\ kJ/mol) + (1\ mol)(-285.8\ kJ/mol)]$
$- [(1\ mol)(-484.5\ kJ/mol) + (1\ mol)(-950.8\ kJ/mol)]$

$\Delta H^o_{rxn} = +29.9\ kJ$ for 1 mol CH_3CO_2H

$$q = \frac{29.9\ kJ}{1\ mol\ CH_3CO_2H} \times 66.13\ mol\ CH_3CO_2H = +1980\ kJ\ (absorbed)$$

8.118 (a) $2\ K(s) + 2\ H_2O(l) \rightarrow 2\ KOH(aq) + H_2(g)$

(b) $\Delta H^o_{rxn} = [2\ \Delta H^o_f(KOH)] - [2\ \Delta H^o_f(H_2O)]$
$\Delta H^o_{rxn} = [(2\ mol)(-482.4\ kJ/mol)] - [(2\ mol)(-285.8\ kJ/mol)] = -393.2\ kJ$

(c) The reaction produces 393.2 kJ/ 2 mol K = 196.6 kJ/ mol K. Assume that the mass of the water does not change and that the specific heat = 4.18 J/(g·°C) for the solution that is produced.

$$q = 7.55\ g\ K \times \frac{1\ mol\ K}{39.10\ g\ K} \times \frac{196.6\ kJ}{1\ mol\ K} \times \frac{1000\ J}{1\ kJ} = 3.80 \times 10^4\ J$$

q = (specific heat) x m x ΔT

$$\Delta T = \frac{q}{(\text{specific heat}) \times m} = \frac{3.80 \times 10^4\ J}{[4.18\ J/(g \bullet {}^oC)](400.0\ g)} = 22.7^oC$$

$\Delta T = T_{final} - T_{initial}$

$T_{final} = \Delta T + T_{initial} = 22.7^oC + 25.0^oC = 47.7^oC$

(d) $$7.55\ g\ K \times \frac{1\ mol\ K}{39.10\ g\ K} \times \frac{2\ mol\ KOH}{2\ mol\ K} = 0.193\ mol\ KOH$$

Assume that the mass of the solution does not change during the reaction and that the solution has a density of 1.00 g/mL.

$$\text{solution volume} = 400.0\ g \times \frac{1.00\ mL}{1\ g} \times \frac{1\ L}{1000\ mL} = 0.400\ L$$

$$\text{molarity} = \frac{0.193\ mol\ KOH}{0.400\ L} = 0.483\ M$$

$2\ KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2\ H_2O(l)$

$$0.193\ mol\ KOH \times \frac{1\ mol\ H_2SO_4}{2\ mol\ KOH} \times \frac{1000\ mL}{0.554\ mol\ H_2SO_4} = 174\ mL\ \text{of}\ 0.554\ M\ H_2SO_4$$

8.119 (a) Each N is sp^3 hybridized and the geometry about each N is trigonal pyramidal.

(b)

$2/4\ NH_3(g) + 3/4\ N_2O(g) \rightarrow N_2(g) + 3/4\ H_2O(l)$ $\quad \Delta H^o_1 = \frac{-1011.2\ kJ}{4}$

$1/4\ H_2O(l) + 1/4\ N_2H_4(l) \rightarrow 1/8\ O_2(g) + 1/2\ NH_3(g)$ $\quad \Delta H^o_2 = \frac{+286\ kJ}{8}$

$3/4\ N_2H_4(l) + 3/4\ H_2O(l) \rightarrow 3/4\ N_2O(g) + 9/4\ H_2(g)$ $\quad \Delta H^o_3 = \frac{(3)(+314\ kJ)}{4}$

$9/4\ H_2(g) + 9/8\ O_2(g) \rightarrow 9/4\ H_2O(l)$ $\quad \Delta H^o_4 = \frac{(9)(-285.8\ kJ)}{4}$

Sum $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(l)$

$\Delta H^o = -622\ kJ$

(c) N_2H_4, 32.045 amu

$$\text{mol}\ N_2H_4 = 100.0\ g\ N_2H_4 \times \frac{1\ mol\ N_2H_4}{32.045\ g\ N_2H_4} = 3.12\ mol\ N_2H_4$$

$q = (3.12\ mol\ N_2H_4)(622\ kJ/mol) = 1940\ kJ$

8.120 Assume 100.0 g of Y.

$$\text{mol F} = 61.7 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 3.25 \text{ mol F}$$

$$\text{mol Cl} = 38.3 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 1.08 \text{ mol Cl}$$

$Cl_{1.08}F_{3.25}$, divide each subscript by the smaller of the two, 1.08.

$Cl_{1.08 / 1.08}F_{3.25 / 1.08}$

ClF_3

(a) Y is ClF_3 and X is ClF

(b)

There are five electron clouds around the Cl (3 bonding and 2 lone pairs). The geometry is T-shaped.

(c)

	ΔH
$Cl_2O(g) + 3\ OF_2(g) \rightarrow 2\ O_2(g) + 2\ ClF_3(g)$	-533.4 kJ
$2\ ClF(g) + O_2(g) \rightarrow Cl_2O(g) + OF_2(g)$	+205.6 kJ
$O_2(g) + 2\ F_2(g) \rightarrow 2\ OF_2(g)$	2(24.7 kJ)
$2\ ClF(g) + 2\ F_2(g) \rightarrow 2\ ClF_3(g)$	-278.4 kJ

Divide reaction coefficients and ΔH by 2.

$ClF(g) + F_2(g) \rightarrow ClF_3(g)$ $\quad \Delta H = -278.4 \text{ kJ}/2 = -139.2 \text{ kJ/mol } ClF_3$

(d) ClF, 54.45 amu

$$q = 25.0 \text{ g ClF} \times \frac{1 \text{ mol ClF}}{54.45 \text{ g ClF}} \times \frac{-139.2 \text{ kJ}}{1 \text{ mol ClF}} \times 0.875 = -55.9 \text{ kJ}$$

55.9 kJ is released in this reaction.

9 Gases: Their Properties and Behavior

9.1 1.00 atm = 14.7 psi

$$1.00 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} \times \frac{14.7 \text{ psi}}{1 \text{ atm}} = 1.93 \times 10^{-2} \text{ psi}$$

9.2 1.00 atmosphere pressure can support a column of Hg 0.760 m high. Because the density of H_2O is 1.00 g/mL and that of Hg is 13.6 g/mL, 1.00 atmosphere pressure can support a column of H_2O 13.6 times higher than that of Hg. The column of H_2O supported by 1.00 atmosphere will be (0.760 m)(13.6) = 10.3 m.

9.3 The pressure in the flask is less than 0.975 atm because the liquid level is higher on the side connected to the flask. The 24.7 cm of Hg is the difference between the two pressures.

$$\text{Pressure difference} = 24.7 \text{ cm Hg} \times \frac{1 \text{ atm}}{76.0 \text{ cm Hg}} = 0.325 \text{ atm}$$

Pressure in flask = 0.975 atm - 0.325 atm = 0.650 atm

9.4 The pressure in the flask is greater than 750 mm Hg because the liquid level is lower on the side connected to the flask.

$$\text{Pressure difference} = 25 \text{ cm Hg} \times \frac{10 \text{ mm Hg}}{1 \text{ cm Hg}} = 250 \text{ mm Hg}$$

Pressure in flask = 750 mm Hg + 250 mm Hg = 1000 mm Hg

9.5 (a) Assume an initial volume of 1.00 L.

First consider the volume change resulting from a change in the number of moles with the pressure and temperature constant.

$$\frac{V_i}{n_i} = \frac{V_f}{n_f}; \quad V_f = \frac{V_i \, n_f}{n_i} = \frac{(1.00 \text{ L})(0.225 \text{ mol})}{0.3 \text{ mol}} = 0.75 \text{ L}$$

Now consider the volume change from 0.75 L as a result of a change in temperature with the number of moles and the pressure constant.

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}; \quad V_f = \frac{V_i \, T_f}{T_i} = \frac{(0.75 \text{ L})(400 \text{ K})}{300 \text{ K}} = 1.0 \text{ L}$$

There is no net change in the volume as a result of the decrease in the number of moles of gas and a temperature increase.

(b) Assume an initial volume of 1.00 L.
First consider the volume change resulting from a change in the number of moles with the pressure and temperature constant.

$$\frac{V_i}{n_i} = \frac{V_f}{n_f};\ V_f = \frac{V_i\ n_f}{n_i} = \frac{(1.00\ \text{L})(0.225\ \text{mol})}{0.3\ \text{mol}} = 0.75\ \text{L}$$

Now consider the volume change from 0.75 L as a result of a change in temperature with the number of moles and the pressure constant.

$$\frac{V_i}{T_i} = \frac{V_f}{T_f};\ V_f = \frac{V_i\ T_f}{T_i} = \frac{(0.75\ \text{L})(200\ \text{K})}{300\ \text{K}} = 0.5\ \text{L}$$

The volume would be cut in half as a result of the decrease in the number of moles of gas and a temperature decrease.

9.6 $$n = \frac{PV}{RT} = \frac{(1.000\ \text{atm})(1.000\ \text{x}\ 10^5\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(273.15\ \text{K})} = 4.461\ \text{x}\ 10^3\ \text{mol}\ CH_4$$

CH_4, 16.04 amu; mass $CH_4 = (4.461\ \text{x}\ 10^3\ \text{mol})\left(\frac{16.04\ \text{g}}{1\ \text{mol}}\right) = 7.155\ \text{x}\ 10^4\ \text{g}\ CH_4$

9.7 C_3H_8, 44.10 amu; V = 350 mL = 0.350 L; T = 20°C = 293 K

$$n = 3.2\ \text{g}\ \text{x}\ \frac{1\ \text{mol}\ C_3H_8}{44.10\ \text{g}\ C_3H_8} = 0.073\ \text{mol}\ C_3H_8$$

$$P = \frac{nRT}{V} = \frac{(0.073\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(293\ \text{K})}{0.350\ \text{L}} = 5.0\ \text{atm}$$

9.8 $$P = 1.51\ \text{x}\ 10^4\ \text{kPa}\ \text{x}\ \frac{1\ \text{atm}}{101.325\ \text{kPa}} = 149\ \text{atm};$$ T = 25.0°C = 298 K

$$n = \frac{PV}{RT} = \frac{(149\ \text{atm})(43.8\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(298\ \text{K})} = 267\ \text{mol He}$$

9.9 The volume and number of moles of gas remain constant.

$$\frac{nR}{V} = \frac{P_i}{T_i} = \frac{P_f}{T_f};\qquad T_f = \frac{P_f\ T_i}{P_i} = \frac{(2.37\ \text{atm})(273\ \text{K})}{2.15\ \text{atm}} = 301\ \text{K} = 28^\text{o}\text{C}$$

9.10 (a) The temperature has increased by about 10% (from 300 K to 325 K) while the

amount and the pressure are unchanged. Thus, the volume should increase by about 10%.

(b) The temperature has increased by a factor of 1.5 (from 300 K to 450 K) and the pressure has increased by a factor of 3 (from 0.9 atm to 2.7 atm) while the amount is unchanged. Thus, the volume should decrease by half (1.5/3 = 0.5).

(c) Both the amount and the pressure have increased by a factor of 3 (from 0.075 mol to 0.22 mol and from 0.9 atm to 2.7 atm) while the temperature is unchanged. Thus, the volume is unchanged.

9.11 $CaCO_3(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

$CaCO_3$, 100.1 amu; CO_2, 44.01 amu

$$\text{mole } CO_2 = 33.7 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g } CaCO_3} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3} = 0.337 \text{ mol } CO_2$$

$$\text{mass } CO_2 = 0.337 \text{ mol } CO_2 \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 14.8 \text{ g } CO_2$$

$$V = \frac{nRT}{P} = \frac{(0.337 \text{ mol})\left(0.082\,06 \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273 \text{ K})}{1.00 \text{ atm}} = 7.55 \text{ L}$$

9.12 $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

$$n_{propane} = \frac{PV}{RT} = \frac{(4.5\ atm)(15.0\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 2.76\ mol\ C_3H_8$$

$$2.76\ mol\ C_3H_8 \times \frac{3\ mol\ CO_2}{1\ mol\ C_3H_8} = 8.28\ mol\ CO_2$$

$$V = \frac{nRT}{P} = \frac{(8.28\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(273\ K)}{1.00\ \ atm} = 186\ L = 190\ L$$

9.13 $$n = \frac{PV}{RT} = \frac{(1.00\ atm)(1.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(273\ K)} = 0.0446\ mol$$

$$\text{molar mass} = \frac{1.52\ g}{0.0446\ mol} = 34.1\ g/mol;\ \text{molecular mass} = 34.1\ amu$$

$Na_2S(aq) + 2\ HCl(aq) \rightarrow H_2S(g) + 2\ NaCl(aq)$

The foul-smelling gas is H_2S, hydrogen sulfide.

9.14 $$12.45\ g\ H_2 \times \frac{1\ mol\ H_2}{2.016\ g\ H_2} = 6.176\ mol\ H_2$$

$$60.67\ g\ N_2 \times \frac{1\ mol\ N_2}{28.01\ g\ N_2} = 2.166\ mol\ N_2$$

$$2.38\ g\ NH_3 \times \frac{1\ mol\ NH_3}{17.03\ g\ NH_3} = 0.140\ mol\ NH_3$$

$$n_{total} = n_{H_2} + n_{N_2} + n_{NH_3} = 6.176\ mol + 2.166\ mol + 0.140\ mol = 8.482\ mol$$

$$X_{H_2} = \frac{6.176\ mol}{8.482\ mol} = 0.7281; \quad X_{N_2} = \frac{2.166\ mol}{8.482\ mol} = 0.2554; \quad X_{NH_3} = \frac{0.140\ mol}{8.482\ mol} = 0.0165$$

9.15 $n_{total} = 8.482\ mol$ (from Problem 9.14). $T = 90^oC = 363\ K$

$$P_{total} = \frac{n_{total}RT}{V} = \frac{(8.482\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(363\ K)}{10.00\ L} = 25.27\ atm$$

$$P_{H_2} = X_{H_2} \bullet P_{total} = (0.7281)(25.27\ atm) = 18.4\ atm$$

$$P_{N_2} = X_{N_2} \bullet P_{total} = (0.2554)(25.27\ atm) = 6.45\ atm$$

$$P_{NH_3} = X_{NH_3} \bullet P_{total} = (0.0165)(25.27\ atm) = 0.417\ atm$$

9.16 $$P_{H_2O} = X_{H_2O} \cdot P_{Total} = (0.0287)(0.977\ atm) = 0.0280\ atm$$

9.17 The number of moles of each gas is proportional to the number of each of the different gas molecules in the container.

$$n_{total} = n_{red} + n_{yellow} + n_{green} = 6 + 2 + 4 = 12$$

$X_{red} = \frac{n_{red}}{n_{total}} = \frac{6}{12} = 0.500$; $X_{yellow} = \frac{n_{yellow}}{n_{total}} = \frac{2}{12} = 0.167$; $X_{green} = \frac{n_{green}}{n_{total}} = \frac{4}{12} = 0.333$

$P_{red} = X_{red} \cdot P_{total} = (0.500)(600 \text{ mm Hg}) = 300 \text{ mm Hg}$
$P_{yellow} = X_{yellow} \cdot P_{total} = (0.167)(600 \text{ mm Hg}) = 100 \text{ mm Hg}$
$P_{green} = X_{green} \cdot P_{total} = (0.333)(600 \text{ mm Hg}) = 200 \text{ mm Hg}$

9.18 $u = \sqrt{\frac{3RT}{M}}$, M = molar mass, R = 8.314 J/(K · mol), 1 J = 1 kg · m^2/s^2

at 37°C = 310 K, $u = \sqrt{\frac{3 \text{ x } 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \text{ x } 310 \text{ K}}{28.01 \text{ x } 10^{-3} \text{ kg/mol}}} = 525 \text{ m/s}$

at -25°C = 248 K, $u = \sqrt{\frac{3 \text{ x } 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \text{ x } 248 \text{ K}}{28.01 \text{ x } 10^{-3} \text{ kg/mol}}} = 470 \text{ m/s}$

9.19 $u = \sqrt{\frac{3RT}{M}}$, M = molar mass, R = 8.314 J/(K · mol), 1 J = 1 kg · m^2/s^2

O_2, 32.00 amu, 32.00 x 10^{-3} kg/mol

$u = 580 \text{ mi/h} \times \frac{1.6093 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 259 \text{ m/s}$

$u = \sqrt{\frac{3RT}{M}}$; $u^2 = \frac{3RT}{M}$

$T = \frac{u^2 M}{3R} = \frac{(259 \text{ m/s})^2 (32.00 \text{ x } 10^{-3} \text{ kg/mol})}{(3)(8.314 \text{ kg} \bullet \text{m}^2/\text{s}^2 \bullet \text{K} \bullet \text{mol})} = 86.1 \text{ K}$

$T = 86.1 - 273.15 = -187.0^{\circ}C$

9.20 (a) $\frac{\text{rate } O_2}{\text{rate Kr}} = \sqrt{\frac{M_{Kr}}{M_{O_2}}} = \sqrt{\frac{83.8}{32.0}}$; $\frac{\text{rate } O_2}{\text{rate Kr}} = 1.62$

O_2 diffuses 1.62 times faster than Kr.

(b) $\frac{\text{rate } C_2H_2}{\text{rate } N_2} = \sqrt{\frac{M_{N_2}}{M_{C_2H_2}}} = \sqrt{\frac{28.0}{26.0}}$; $\frac{\text{rate } C_2H_2}{\text{rate } N_2} = 1.04$

C_2H_2 diffuses 1.04 times faster than N_2.

9.21 $\frac{\text{rate } {}^{20}\text{Ne}}{\text{rate } {}^{22}\text{Ne}} = \sqrt{\frac{M\ {}^{22}\text{Ne}}{M\ {}^{20}\text{Ne}}} = \sqrt{\frac{22}{20}} = 1.05$; $\frac{\text{rate } {}^{21}\text{Ne}}{\text{rate } {}^{22}\text{Ne}} = \sqrt{\frac{M\ {}^{22}\text{Ne}}{M\ {}^{21}\text{Ne}}} = \sqrt{\frac{22}{21}} = 1.02$

Thus, the relative rates of diffusion are ${}^{20}\text{Ne}(1.05) > {}^{21}\text{Ne}(1.02) > {}^{22}\text{Ne}(1.00)$.

9.22 $P = \frac{nRT}{V} = \frac{(0.500 \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(300 \text{ K})}{(0.600 \text{ L})} = 20.5 \text{ atm}$

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$P = \frac{(0.500\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(300\ \text{K})}{[(0.600\ \text{L}) - (0.500\ \text{mol})(0.0387\ \text{L/mol})]} - \frac{\left(1.35\ \frac{\text{L}^2\bullet\text{atm}}{\text{mol}^2}\right)(0.500\ \text{mol})^2}{(0.600\ \text{L})^2} = 20.3\ \text{atm}$$

9.23 The amount of ozone is assumed to be constant.

Therefore $nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$

Because $V \propto h$, then $\frac{P_i h_i}{T_i} = \frac{P_f h_f}{T_f}$ where h is the thickness of the O_3 layer.

$$h_f = \frac{P_i}{P_f} \times \frac{T_f}{T_i} \times h_i = \left(\frac{1.6 \times 10^{-9}\ \text{atm}}{1\ \text{atm}}\right)\left(\frac{273\ \text{K}}{230\ \text{K}}\right)(20 \times 10^3\ \text{m}) = 3.8 \times 10^{-5}\ \text{m}$$

(Actually, $V = 4\pi r^2 h$, where r = the radius of the earth. When you go out ~30 km to get to the ozone layer, the change in r^2 is less than 1%. Therefore you can neglect the change in r^2 and assume that V is proportional to h.)

9.24 For ether, the MAC $= \frac{15\ \text{mm Hg}}{760\ \text{mm Hg}} \times 100\% = 2.0\%$

9.25 (a) Let X = partial pressure of chloroform.

$$\text{MAC} = \frac{X}{760\ \text{mm Hg}} \times 100\% = 0.77\%$$

Solve for X. $X = 760\ \text{mm Hg} \times \frac{0.77\%}{100\%} = 5.9\ \text{mm Hg}$

(b) $CHCl_3$, 119.4 amu

$$PV = nRT;\ n = \frac{PV}{RT} = \frac{(5.9\ \text{mm Hg})(10.0\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(273\ \text{K})} = 0.00347\ \text{mol } CHCl_3$$

$$\text{mass } CHCl_3 = 0.00347\ \text{mol } CHCl_3 \times \frac{119.4\ \text{g } CHCl_3}{1\ \text{mol } CHCl_3} = 0.41\ \text{g } CHCl_3$$

Understanding Key Concepts

9.26 (a) The volume of a gas is proportional to the kelvin temperature at constant pressure. As the temperature increases from 300 K to 450 K, the volume will increase by a factor of 1.5.

(b) The volume of a gas is inversely proportional to pressure at constant temperature. As the pressure increases from 1 atm to 2 atm, the volume will decrease by a factor of 2.

(c) $PV = nRT$; The amount of gas (n) is constant.

Therefore $nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$.

Assume $V_i = 1$ L and solve for V_f.

$$\frac{P_i V_i T_f}{T_i P_f} = \frac{(3\ \text{atm})(1\ \text{L})(200\ \text{K})}{(300\ \text{K})(2\ \text{atm})} = V_f = 1\ \text{L}$$

There is no change in volume.

9.27 If the sample remains a gas at 150 K, then drawing (c) represents the gas at this temperature. The gas molecules still fill the container.

9.28 The two gases should mix randomly and homogeneously and this is best represented by drawing (c).

9.29 The two gases will be equally distributed among the three flasks.

9.30 The gas pressure in the bulb in mm Hg is equal to the difference in the height of the Hg in the two arms of the manometer.

9.31 A

When stopcock A is opened, the pressure in the flask will equal the external pressure, and the level of mercury will be the same in both arms of the manometer.

9.32 (a) Because there are more yellow gas molecules than there are blue, the yellow gas molecules have the higher average speed.

(b) Each rate is proportional to the number of effused gas molecules of each type.

$M_{yellow} = 25$ amu

$$\frac{rate_{blue}}{rate_{yellow}} = \sqrt{\frac{M_{yellow}}{M_{blue}}}; \quad \frac{5}{6} = \sqrt{\frac{25\ amu}{M_{blue}}}; \quad \left(\frac{5}{6}\right)^2 = \frac{25\ amu}{M_{blue}}; \quad M_{blue} = \frac{25\ amu}{\left(\frac{5}{6}\right)^2} = 36$$

amu

9.33

(a) $\frac{P_2}{T_2} = \frac{P_1}{T_1}; \quad P_2 = \frac{(T_2)(P_1)}{T_1} = \frac{(248\ K)(760\ mm\ Hg)}{298\ K} = 632$ mm Hg

The column of Hg will rise to ~130 mm Hg inside the tube (drawing 1). The pressure inside the tube (632 mm Hg) plus the pressure of 130 mm Hg equals the external pressure, ~760 mm Hg.

(b) The column of Hg will rise to ~760 mm (drawing 2), which is equal to the external pressure, ~760 mm Hg.

(c) The pressure inside the tube is equal to the external pressure and the Hg level inside the tube will be the same as in the dish (drawing 3).

Additional Problems
Gases and Gas Pressure

9.34 Temperature is a measure of the average kinetic energy of gas particles.

9.35 Gases are much more compressible than solids or liquids because there is a large amount of empty space between individual gas molecules.

9.36 $P = 480 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}} = 0.632 \text{ atm}$

$P = 480 \text{ mm Hg} \times \frac{101{,}325 \text{ Pa}}{760 \text{ mm Hg}} = 6.40 \times 10^4 \text{ Pa}$

9.37 $P = 352 \text{ torr} \times \frac{101{,}325 \text{ Pa}}{760 \text{ torr}} \times \frac{1 \text{ kPa}}{1000 \text{ Pa}} = 46.9 \text{ kPa}$

$P = 0.255 \text{ atm} \times \frac{760 \text{ mm Hg}}{1.00 \text{ atm}} = 194 \text{ mm Hg}$

$P = 0.0382 \text{ mm Hg} \times \frac{101{,}325 \text{ Pa}}{760 \text{ mm Hg}} = 5.09 \text{ Pa}$

9.38 $P_{flask} > 754.3$ mm Hg; $P_{flask} = 754.3 \text{ mm Hg} + 176 \text{ mm Hg} = 930 \text{ mm Hg}$

9.39 $P_{flask} < 1.021$ atm (see Figure 9.4)

$P_{difference} = 28.3 \text{ cm Hg} \times \frac{1.00 \text{ atm}}{76.0 \text{ cm Hg}} = 0.372 \text{ atm}$

$P_{flask} = 1.021 \text{ atm} - P_{difference} = 1.021 \text{ atm} - 0.372 \text{ atm} = 0.649 \text{ atm}$

9.40 $P_{flask} > 752.3$ mm Hg (see Figure 9.4)
If the pressure in the flask can support a column of ethyl alcohol (d = 0.7893 g/mL) 55.1 cm high, then it can only support a column of Hg that is much shorter because of the higher density of Hg.

$55.1 \text{ cm} \times \frac{0.7893 \text{ g/mL}}{13.546 \text{ g/mL}} = 3.21 \text{ cm Hg} = 32.1 \text{ mm Hg}$

$P_{flask} = 752.3 \text{ mm Hg} + 32.1 \text{ mm Hg} = 784.4 \text{ mm Hg}$

$P_{flask} = 784.4 \text{ mm Hg} \times \frac{101{,}325 \text{ Pa}}{760 \text{ mm Hg}} = 1.046 \times 10^5 \text{ Pa}$

9.41 Compute the height of a column of $CHCl_3$ that 1.00 atm can support.

$760 \text{ mm Hg} \times \frac{13.546 \text{ g/mL}}{1.4832 \text{ g/mL}} = 6941 \text{ mm } CHCl_3$; therefore 1.00 atm = 6941 mm $CHCl_3$

The pressure in the flask is less than atmospheric pressure.

$P_{atm} - P_{flask} = 0.849 \text{ atm} - 0.788 \text{ atm} = 0.061 \text{ atm}$

$$0.061 \text{ atm} \times \frac{6941 \text{ mm } CHCl_3}{1.00 \text{ atm}} = 423 \text{ mm } CHCl_3$$

The chloroform will be 423 mm higher in the manometer arm connected to the flask.

9.42

	% Volume
N_2	78.08
O_2	20.95
Ar	0.93
CO_2	0.037

The % volume for a particular gas is proportional to the number of molecules of that gas in a mixture of gases.

Average molecular mass of air

= (0.7808)(mol. mass N_2) + (0.2095)(mol. mass O_2)
+ (0.0093)(at. mass Ar) + (0.000 37)(mol. mass CO_2)

= (0.7808)(28.01 amu) + (0.2095)(32.00 amu)
+ (0.0093)(39.95 amu) + (0.000 37)(44.01 amu) = 28.96 amu

9.43 The % volume for a particular gas is proportional to the number of molecules of that gas in a mixture of gases.

Average molecular mass of a diving-gas = (0.020)(mol. mass O_2) + (0.980)(at. mass He)
= (0.020)(32.00 amu) + (0.980)(4.00 amu) = 4.56 amu

The Gas Laws

9.44 (a) $\frac{nR}{V} = \frac{P_i}{T_i} = \frac{P_f}{T_f}$; $\frac{P_i T_f}{T_i} = P_f$

Let $P_i = 1$ atm, $T_i = 100$ K, $T_f = 300$ K

$$P_f = \frac{P_i T_f}{T_i} = \frac{(1 \text{ atm})(300 \text{ K})}{(100 \text{ K})} = 3 \text{ atm}$$

The pressure would triple.

(b) $\frac{RT}{V} = \frac{P_i}{n_i} = \frac{P_f}{n_f}$; $\frac{P_i n_f}{n_i} = P_f$

Let $P_i = 1$ atm, $n_i = 3$ mol, $n_f = 1$ mol

$$P_f = \frac{P_i n_f}{n_i} = \frac{(1 \text{ atm})(1 \text{ mol})}{(3 \text{ mol})} = \frac{1}{3} \text{ atm}$$

The pressure would be $\frac{1}{3}$ the initial pressure.

(c) $nRT = P_iV_i = P_fV_f$; $\frac{P_i V_i}{V_f} = P_f$

Let $P_i = 1$ atm, $V_i = 1$ L, $V_f = 1 - 0.45$ L $= 0.55$ L

$$P_f = \frac{P_i V_i}{V_f} = \frac{(1\ \text{atm})(1\ \text{L})}{(0.55\ \text{L})} = 1.8\ \text{atm}$$

The pressure would increase by 1.8 times.

(d) $nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$; $\frac{P_i V_i T_f}{T_i V_f} = P_f$

Let $P_i = 1$ atm, $V_i = 1$ L, $T_i = 200$ K, $V_f = 3$ L, $T_i = 100$ K

$$P_f = \frac{P_i V_i T_f}{T_i V_f} = \frac{(1\ \text{atm})(1\ \text{L})(100\ \text{K})}{(200\ \text{K})(3\ \text{L})} = 0.17\ \text{atm}$$

The pressure would be 0.17 times the initial pressure.

9.45 (a) $\frac{nR}{P} = \frac{V_i}{T_i} = \frac{V_f}{T_f}$; $\frac{V_i T_f}{T_i} = V_f$

Let $V_i = 1$ L, $T_i = 400$ K, $T_f = 200$ K

$$V_f = \frac{V_i T_f}{T_i} = \frac{(1\ \text{L})(200\ \text{K})}{(400\ \text{K})} = 0.5\ \text{L}$$

The volume would be halved.

(b) $\frac{RT}{P} = \frac{V_i}{n_i} = \frac{V_f}{n_f}$; $\frac{V_i n_f}{n_i} = V_f$

Let $V_i = 1$ L, $n_i = 4$ mol, $n_f = 5$ mol

$$V_f = \frac{V_i n_f}{n_i} = \frac{(1\ \text{L})(5\ \text{mol})}{(4\ \text{mol})} = 1.25\ \text{L}$$

The volume would increase by 1/4.

(c) $nRT = P_i V_i = P_f V_f$; $\frac{P_i V_i}{P_f} = V_f$

Let $V_i = 1$ L, $P_i = 4$ atm, $P_f = 1$ atm

$$V_f = \frac{P_i V_i}{P_f} = \frac{(4\ \text{atm})(1\ \text{L})}{(1\ \text{atm})} = 4\ \text{L}$$

The volume would increase by a factor of 4.

(d) $nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$; $\frac{P_i V_i T_f}{P_f T_i} = V_f$

Let $V_i = 1$ L, $T_i = 200$ K, $T_f = 400$ K, $P_i = 1$ atm, $P_f = 2$atm

$$V_f = \frac{P_i V_i T_f}{P_f T_i} = \frac{(1\ \text{atm})(1\ \text{L})(400\ \text{K})}{(2\ \text{atm})(200\ \text{K})} = 1\ \text{L}$$

There is no volume change.

9.46 They all contain the same number of gas molecules.

9.47 For air, $T = 50^{\circ}\text{C} = 323$ K.

$$n = \frac{PV}{RT} = \frac{\left(750\ \text{mm Hg}\ \text{x}\ \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(2.50\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(323\ \text{K})} = 0.0931\ \text{mol air}$$

For CO_2, T = -10°C = 263 K

$$n = \frac{PV}{RT} = \frac{\left(765\ \text{mm Hg}\ \text{x}\ \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(2.16\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(263\ \text{K})} = 0.101\ \text{mol CO}_2$$

Because the number of moles of CO_2 is larger than the number of moles of air, the CO_2 sample contains more molecules.

9.48 n and T are constant; therefore $nRT = P_i V_i = P_f V_f$

$$V_f = \frac{P_i V_i}{P_f} = \frac{(150\ \text{atm})(49.0\ \text{L})}{(1.02\ \text{atm})} = 7210\ \text{L}$$

n and P are constant; therefore $\frac{nR}{P} = \frac{V_i}{T_i} = \frac{V_f}{T_f}$

$$V_f = \frac{V_i T_f}{T_i} = \frac{(49.0\ \text{L})(308\ \text{K})}{(293\ \text{K})} = 51.5\ \text{L}$$

9.49 $T_i = 20°C = 293\ \text{K}$; $nR = \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$

$$V_f = \frac{P_i V_i T_f}{T_i P_f} = \frac{(140\ \text{atm})(8.0\ \text{L})(273\ \text{K})}{(293\ \text{K})(1.00\ \text{atm})} = 1.0 \times 10^3\ \text{L}$$

9.50 $15.0\ \text{g CO}_2\ \text{x}\ \frac{1\ \text{mol CO}_2}{44.0\ \text{g CO}_2} = 0.341\ \text{mol CO}_2$

$$P = \frac{nRT}{V} = \frac{(0.341\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(300\ \text{K})}{(0.30\ \text{L})} = 27.98\ \text{atm}$$

$$27.98\ \text{atm}\ \text{x}\ \frac{760\ \text{mm Hg}}{1\ \text{atm}} = 2.1 \times 10^4\ \text{mm Hg}$$

9.51 $20.0\ \text{g N}_2\ \text{x}\ \frac{1\ \text{mol N}_2}{28.0\ \text{g N}_2} = 0.714\ \text{mol N}_2$

$$T = \frac{PV}{nR} = \frac{(6.0\ \text{atm})(0.40\ \text{L})}{(0.714\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)} = 41\ \text{K}$$

9.52 $\frac{1\,\text{H atom}}{\text{cm}^3} \times \frac{1\,\text{mol H}}{6.02 \times 10^{23}\,\text{atoms}} \times \frac{1000\ \text{cm}^3}{1\ \text{L}} = 1.7 \times 10^{-21}\ \text{mol H/L}$

$$P = \frac{nRT}{V} = \frac{(1.7 \times 10^{-21}\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(100\ \text{K})}{(1\ \text{L})} = 1.4 \times 10^{-20}\ \text{atm}$$

$$P = 1.4 \times 10^{-20}\ \text{atm} \times \frac{760\ \text{mm Hg}}{1.0\ \text{atm}} = 1 \times 10^{-17}\ \text{mm Hg}$$

9.53 CH_4, 16.04 amu; $5.54\ \text{kg} = 5.54 \times 10^3\ \text{g}$; $T = 20^oC = 293\ \text{K}$

$$P = \frac{nRT}{V} = \frac{\left(5.54 \times 10^3\ \text{g} \times \frac{1\ \text{mol}}{16.04\ \text{g}}\right)\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293\ \text{K})}{(43.8\ \text{L})} = 189.6\ \text{atm}$$

$$P = 189.6\ \text{atm} \times \frac{101{,}325\ \text{Pa}}{1\ \text{atm}} \times \frac{1\ \text{k Pa}}{1000\ \text{Pa}} = 1.92 \times 10^4\ \text{kPa}$$

9.54 $$n = \frac{PV}{RT} = \frac{\left(17{,}180\ \text{kPa} \times \frac{1000\ \text{Pa}}{1\ \text{k Pa}} \times \frac{1\ \text{atm}}{101{,}325\ \text{Pa}}\right)(43.8\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293\,\text{K})} = 308.9\ \text{mol}$$

$$\text{mass Ar} = 308.9\ \text{mol} \times \frac{39.948\ \text{g}}{1\ \text{mol}} = 12340\ \text{g} = 1.23 \times 10^4\ \text{g}$$

9.55 $$P = 13{,}800\ \text{kPa} \times \frac{1000\ \text{Pa}}{1\ \text{kPa}} \times \frac{1\ \text{atm}}{101{,}325\ \text{Pa}} = 136.2\ \text{atm}$$

n and T are constant; therefore $nRT = P_iV_i = P_fV_f$

$$V_f = \frac{P_i V_i}{P_f} = \frac{(136.2\ \text{atm})(2.30\ \text{L})}{(1.25\ \text{atm})} = 250.6\ \text{L}$$

$$250.6\ \text{L} \times \frac{1\ \text{balloon}}{1.5\ \text{L}} = 167\ \text{balloons}$$

Gas Stoichiometry

9.56 For steam, $T = 123.0^oC = 396\ \text{K}$

$$n = \frac{PV}{RT} = \frac{(0.93\ \text{atm})(15.0\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(396\ \text{K})} = 0.43\ \text{mol steam}$$

For ice, H_2O, 18.02 amu; $n = 10.5\ \text{g} \times \frac{1\ \text{mol}}{18.02\ \text{g}} = 0.583\ \text{mol ice}$

Because the number of moles of ice is larger than the number of moles of steam, the ice contains more H_2O molecules.

9.57 $T = 85.0^oC = 358\ \text{K}$

$$n_{Ar} = \frac{PV}{RT} = \frac{\left(1111\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(3.14\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(358\ \text{K})} = 0.156\ \text{mol Ar}$$

Cl_2, 70.91 amu; $n_{Cl_2} = 11.07\ \text{g } Cl_2 \times \frac{1\,\text{mol } Cl_2}{70.91\ \text{g } Cl_2} = 0.156\ \text{mol } Cl_2$

There are equal numbers of Ar atoms and Cl_2 molecules in their respective samples.

9.58 The containers are identical. Both containers contain the same number of gas molecules. Weigh the containers. Because the molecular mass for O_2 is greater than the molecular mass for H_2, the heavier container contains O_2.

9.59 Assuming that you can see through the flask, Cl_2 gas is greenish and He is colorless.

9.60 room volume = 4.0 m x 5.0 m x 2.5 m x $\frac{1\ \text{L}}{10^{-3}\ \text{m}^3} = 5.0 \times 10^4\ \text{L}$

$$n_{total} = \frac{PV}{RT} = \frac{(1.0\ \text{atm})(5.0 \times 10^4\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273\ \text{K})} = 2.23 \times 10^3\ \text{mol}$$

$n_{O_2} = (0.2095)n_{total} = (0.2095)(2.23 \times 10^3\ \text{mol}) = 467\ \text{mol } O_2$

mass O_2 = 467 mol x $\frac{32.0\ \text{g}}{1\ \text{mol}} = 1.5 \times 10^4\ \text{g } O_2$

9.61 0.25 g O_2 x $\frac{1\ \text{mol } O_2}{32.0\ \text{g } O_2} = 7.8 \times 10^{-3}\ \text{mol } O_2$

$$V = \frac{nRT}{P} = \frac{(7.8 \times 10^{-3}\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(310\ \text{K})}{1.0\ \text{atm}} = 0.198\ \text{L} = 0.200\ \text{L} = 200\ \text{mL } O_2$$

9.62 (a) CH_4, 16.04 amu; $d = \frac{16.04\ \text{g}}{22.4\ \text{L}} = 0.716\ \text{g/L}$

(b) CO_2, 44.01 amu; $d = \frac{44.01\ \text{g}}{22.4\ \text{L}} = 1.96\ \text{g/L}$

(c) O_2, 32.00 amu; $d = \frac{32.00\ \text{g}}{22.4\ \text{L}} = 1.43\ \text{g/L}$

(d) UF_6, 352.0 amu; $d = \frac{352.0\ \text{g}}{22.4\ \text{L}} = 15.7\ \text{g/L}$

9.63 Average molar mass = (0.270)(molar mass F_2) + (0.730)(molar mass He)
= (0.270)(38.00 g/mol) + (0.730)(4.003 g/mol) = 13.18 g/mol
Assume 1.00 mole of the gas mixture. T = 27.5°C = 300.6 K

$$V = \frac{nRT}{P} = \frac{(1.00\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(300.6\ \text{K})}{\left(714\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)} = 26.3\ \text{L}$$

$$d = \frac{13.18\ \text{g}}{26.3\ \text{L}} = 0.501\ \text{g/L}$$

9.64 $$n = \frac{PV}{RT} = \frac{\left(356\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.500\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(295.5\ \text{K})} = 0.0290\ \text{mol}$$

$$\text{molar mass} = \frac{0.9847\ \text{g}}{0.0290\ \text{mol}} = 34.0\ \text{g/mol};\quad \text{molecular mass} = 34.0\ \text{amu}$$

9.65 (a) Assume 1.000 L gas sample

$$n = \frac{PV}{RT} = \frac{(1.00\ \text{atm})(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(273\ \text{K})} = 0.0446\ \text{mol}$$

$$\text{molar mass} = \frac{1.342\ \text{g}}{0.0446\ \text{mol}} = 30.1\ \text{g/mol};\quad \text{molecular mass} = 30.1\ \text{amu}$$

(b) Assume 1.000 L gas sample

$$n = \frac{PV}{RT} = \frac{\left(752\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(298\ \text{K})} = 0.0405\ \text{mol}$$

$$\text{molar mass} = \frac{1.053\ \text{g}}{0.0405\ \text{mol}} = 26.0\ \text{g/mol};\quad \text{molecular mass} = 26.0\ \text{amu}$$

9.66 $2\ HgO(s) \rightarrow 2\ Hg(l) + O_2(g)$; HgO, 216.59 amu

$$10.57\ \text{g HgO} \times \frac{1\ \text{mol HgO}}{216.59\ \text{g HgO}} \times \frac{1\ \text{mol } O_2}{2\ \text{mol HgO}} = 0.024\,40\ \text{mol } O_2$$

$$V = \frac{nRT}{P} = \frac{(0.024\,40\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(273.15\ \text{K})}{1.000\ \text{atm}} = 0.5469\ \text{L}$$

9.67 $2\ HgO(s) \rightarrow 2\ Hg(l) + O_2(g)$; HgO, 216.59 amu

$$\text{mass HgO} = 0.0155\ \text{mol } O_2 \times \frac{2\ \text{mol HgO}}{1\ \text{mol } O_2} \times \frac{216.59\ \text{g HgO}}{1\ \text{mol HgO}} = 6.71\ \text{g HgO}$$

9.68 $Zn(s) + 2\ HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

(a) $25.5\ g\ Zn \times \frac{1\ mol\ Zn}{65.39\ g\ Zn} \times \frac{1\ mol\ H_2}{1\ mol\ Zn} = 0.390\ mol\ H_2$

$$V = \frac{nRT}{P} = \frac{(0.390\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(288\ K)}{\left(742\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)} = 9.44\ L$$

(b) $$n = \frac{PV}{RT} = \frac{\left(350\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(5.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(303.15\ K)} = 0.092\,56\ mol\ H_2$$

$$0.092\,56\ mol\ H_2 \times \frac{1\ mol\ Zn}{1\ mol\ H_2} \times \frac{65.39\ g\ Zn}{1\ mol\ Zn} = 6.05\ g\ Zn$$

9.69 $2\ NH_4NO_3(s) \rightarrow 2\ N_2(g) + 4\ H_2O(g) + O_2(g)$; NH_4NO_3, 80.04 amu

Total moles of gas = $450\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.04\ g\ NH_4NO_3} \times \frac{7\ mol\ gas}{2\ mol\ NH_4NO_3} = 19.68$ mol

$T = 450^oC = 723\ K$

$$V = \frac{nRT}{P} = \frac{(19.68\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(723\ K)}{(1.00\ atm)} = 1.17 \times 10^3\ L$$

9.70 (a) $V_{24h} = (4.50\ L/min)(60\ min/h)(24\ h/day) = 6480\ L$

$V_{CO_2} = (0.034)V_{24h} = (0.034)(6480\ L) = 220\ L$

$$n = \frac{PV}{RT} = \frac{\left(735\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(220\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 8.70\ mol\ CO_2$$

$$8.70\ mol\ CO_2 \times \frac{44.01\ g\ CO_2}{1\ mol\ CO_2} = 383\ g = 380\ g\ CO_2$$

(b) $2\ Na_2O_2(s) + 2\ CO_2(g) \rightarrow 2\ Na_2CO_3(s) + O_2(g)$; Na_2O_2, 77.98 amu

$3.65\ kg = 3650\ g$

$$3650\ g\ Na_2O_2 \times \frac{1\ mol\ Na_2O_2}{77.98\ g\ Na_2O_2} \times \frac{2\ mol\ CO_2}{2\ mol\ Na_2O_2} \times \frac{1\ day}{8.70\ mol\ CO_2} = 5.4\ days$$

9.71 $2\ TiCl_4(g) + H_2(g) \rightarrow 2\ TiCl_3(s) + 2\ HCl(g)$; $TiCl_4$, 189.69 amu

(a) $T = 435^oC = 708\ K$

$$n_{H_2} = \frac{PV}{RT} = \frac{\left(795\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(155\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(708\ \text{K})} = 2.79\ \text{mol } H_2$$

$$2.79\ \text{mol } H_2 \times \frac{2\ \text{mol } TiCl_4}{1\ \text{mol } H_2} \times \frac{189.69\ \text{g } TiCl_4}{1\ \text{mol } TiCl_4} = 1058\ \text{g} = 1060\ \text{g } TiCl_4$$

(b) $n_{HCl} = 2.79\ \text{mol } H_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol } H_2} = 5.58\ \text{mol HCl}$

$$V = \frac{n_{HCl}RT}{P} = \frac{(5.58\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273\ \text{K})}{(1.00\ \text{atm})} = 125\ \text{L HCl}$$

Dalton's Law and Mole Fraction

9.72 Because of Avogadro's Law ($V \propto n$), the % volumes are also % moles.

	% mole
N_2	78.08
O_2	20.95
Ar	0.93
CO_2	0.037 In decimal form, % mole = mole fraction.

$P_{N_2} = X_{N_2} \bullet P_{total} = (0.7808)(1.000\ \text{atm}) = 0.7808\ \text{atm}$

$P_{O_2} = X_{O_2} \bullet P_{total} = (0.2095)(1.000\ \text{atm}) = 0.2095\ \text{atm}$

$P_{Ar} = X_{Ar} \bullet P_{total} = (0.0093)(1.000\ \text{atm}) = 0.0093\ \text{atm}$

$P_{CO_2} = X_{CO_2} \bullet P_{total} = (0.000\,37)(1.000\ \text{atm}) = 0.000\,37\ \text{atm}$

Pressures of the rest are negligible.

9.73 $X_{CH_4} = \frac{94\ \text{mol}}{100\ \text{mol}} = 0.94$; $P_{CH_4} = X_{CH_4} \bullet P_{total} = (0.94)(1.48\ \text{atm}) = 1.4\ \text{atm}$

$X_{C_2H_6} = \frac{4\ \text{mol}}{100\ \text{mol}} = 0.040$; $P_{C_2H_6} = X_{C_2H_6} \bullet P_{total} = (0.040)(1.48\ \text{atm}) = 0.059\ \text{atm}$

$X_{C_3H_8} = \frac{1.5\ \text{mol}}{100\ \text{mol}} = 0.015$; $P_{C_3H_8} = X_{C_3H_8} \bullet P_{total} = (0.015)(1.48\ \text{atm}) = 0.022\ \text{atm}$

$X_{C_4H_{10}} = \frac{0.5\ \text{mol}}{100\ \text{mol}} = 0.0050$; $P_{C_4H_{10}} = X_{C_4H_{10}} \bullet P_{total} = (0.0050)(1.48\ \text{atm}) = 0.0074\ \text{atm}$

9.74 Assume a 100.0 g sample. g CO_2 = 1.00 g and g O_2 = 99.0 g

mol $CO_2 = 1.00\ \text{g } CO_2 \times \frac{1\ \text{mol } CO_2}{44.01\ \text{g } CO_2} = 0.0227\ \text{mol } CO_2$

mol O_2 = 99.0 g O_2 x $\frac{1\ mol\ O_2}{32.00\ g\ O_2}$ = 3.094 mol O_2

n_{total} = 3.094 mol + 0.0227 mol = 3.117 mol

$X_{O_2} = \frac{3.094\ mol}{3.117\ mol}$ = 0.993; $X_{CO_2} = \frac{0.0227\ mol}{3.117\ mol}$ = 0.007 28

$P_{O_2} = X_{O_2} \bullet P_{total}$ = (0.993)(0.977 atm) = 0.970 atm

$P_{CO_2} = X_{CO_2} \bullet P_{total}$ = (0.007 28)(0.977 atm) = 0.007 11 atm

9.75 From Problem 9.76: X_{HCl} = 0.026, X_{H_2} = 0.094, X_{Ne} = 0.88

$P_{HCl} = X_{HCl} \cdot P_{total}$ = (0.026)(13,800 kPa) = 3.6 x 10^2 kPa

$P_{H_2} = X_{H_2} \bullet P_{total}$ = (0.094)(13,800 kPa) = 1.3 x 10^3 kPa

$P_{Ne} = X_{Ne} \cdot P_{total}$ = (0.88)(13,800) kPa) = 1.2 x 10^4 kPa

9.76 Assume a 100.0 g sample.

g HCl = (0.0500)(100.0 g) = 5.00 g; 5.00 g HCl x $\frac{1\ mol\ HCl}{36.5\ g\ HCl}$ = 0.137 mol HCl

g H_2 = (0.0100)(100.0 g) = 1.00 g; 1.00 g H_2 x $\frac{1\ mol\ H_2}{2.016\ g\ H_2}$ = 0.496 mol H_2

g Ne = (0.94)(100.0 g) = 94 g; 94 g Ne x $\frac{1\ mol\ Ne}{20.18\ g\ Ne}$ = 4.66 mol Ne

n_{total} = 0.137 + 0.496 + 4.66 = 5.3 mol

$X_{HCl} = \frac{0.137\ mol}{5.3\ mol}$ = 0.026; $X_{H_2} = \frac{0.496\ mol}{5.3\ mol}$ = 0.094; $X_{Ne} = \frac{4.66\ mol}{5.3\ mol}$ = 0.88

9.77 Assume a 1.000 L gas sample.

$n = \frac{PV}{RT} = \frac{(1.000\ atm)(1.000\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(273.15\ K)}$ = 0.044 61 mol

average molar mass = $\frac{1.413\ g}{0.044\,61\ mol}$ = 31.67 g/mol

31.67 = x $\bullet$ M_{Ar} + (1 _ x) $\bullet$ M_{N_2}

31.67 = (x)(39.948) + (1 - x)(28.013)

Solve for x: x = 0.3064, 1 - x = 0.6936

The mixture contains 30.64% Ar and 69.36% N_2.

Assume 100 moles of gas.

$X_{Ar} = \frac{30.64\ mol}{100\ mol}$ = 0.3064; $X_{N_2} = \frac{69.36\ mol}{100\ mol}$ = 0.6936

9.78 $P_{total} = P_{H_2} + P_{H_2O}$; $P_{H_2} = P_{total} - P_{H_2O}$ = 747 mm Hg - 23.8 mm Hg = 723 mm Hg

$$n = \frac{PV}{RT} = \frac{\left(723\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(3.557\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.1384\ mol\ H_2$$

$$0.1384\ mol\ H_2 \times \frac{1\ mol\ Mg}{1\ mol\ H_2} \times \frac{24.3\ g\ Mg}{1\ mol\ Mg} = 3.36\ g\ Mg$$

9.79 $P_{total} = P_{Cl_2} + P_{H_2O}$ = 755 mm Hg

$P_{Cl_2} = P_{total} - P_{H_2O}$ = 755 mm Hg - 28.7 mm Hg = 726.3 mm Hg

(a) $X_{Cl_2} = \frac{P_{Cl_2}}{P_{total}} = \frac{726.3\ mm\ Hg}{755\ mm\ Hg} = 0.962$

(b) NaCl, 58.44 amu

$$n_{Cl_2} = \frac{p_{Cl_2}V}{RT} = \frac{(726.3 mm Hg / 760 mm Hg\ atm^{-1})(0.597\ L)}{0.082\ L\ atm\ K^{-1} mol^{-1}(27+273)K} = 0.0232 mol\ Cl_{2(g)}$$

$$0.0232\ mol\ Cl_2 \times \frac{2\ mol\ NaCl}{1 mol\ Cl_2} \times \frac{58.44\ g\ NaCl}{1 mol\ NaCl} = 2.71\ g\ NaCl$$

Kinetic-Molecular Theory and Graham's Law

9.80 The kinetic-molecular theory is based on the following assumptions:
1. A gas consists of tiny particles, either atoms or molecules, moving about at random.
2. The volume of the particles themselves is negligible compared with the total volume of the gas; most of the volume of a gas is empty space.
3. The gas particles act independently; there are no attractive or repulsive forces between particles.
4. Collisions of the gas particles, either with other particles or with the walls of the container, are elastic; that is, the total kinetic energy of the gas particles is constant at constant T.
5. The average kinetic energy of the gas particles is proportional to the Kelvin temperature of the sample.

9.81 Diffusion – The mixing of different gases by random molecular motion and with frequent collisions.
Effusion – The process in which gas molecules escape through a tiny hole in a membrane without collisions.

9.82 Heat is the energy transferred from one object to another as the result of a temperature difference between them.

Temperature is a measure of the kinetic energy of molecular motion.

9.83 The atomic mass of He is much less than the molecular mass of the major components of air (N_2 and O_2). The rate of effusion of He through the balloon skin is much faster.

9.84 $$u = \sqrt{\frac{3\ RT}{M}} = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times 220\ K}{28.0 \times 10^{-3}\ kg/mol}} = 443\ m/s$$

9.85 For Br_2: $$u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times 293\ K}{159.8 \times 10^{-3}\ kg/mol}} = 214\ m/s$$

For Xe: $$u = 214\ m/s = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times T}{131.3 \times 10^{-3}\ kg/mol}}$$

Square both sides of the equation and solve for T.

$$45796\ m^2/s^2 = \frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times T}{131.3 \times 10^{-3}\ kg/mol}$$

$T = 241\ K = -32^oC$

9.86 For H_2, $$u = \sqrt{\frac{3\ RT}{M}} = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times 150\ K}{2.02\ \times 10^{-3}\ kg/mol}} = 1360\ m/s$$

For He, $$u = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times 648\ K}{4.00 \times 10^{-3}\ kg/mol}} = 2010\ m/s$$

He at 375^oC has the higher average speed.

9.87 UF_6, 352.02 amu; $T = 25^oC = 298\ K$

$$u = \sqrt{\frac{3\ RT}{M}} = \sqrt{\frac{3 \times 8.314\ kg\ m^2/(s^2\ K\ mol) \times 298\ K}{352.02\ \times 10^{-3}\ kg/mol}} = 145\ m/s$$

Ferrari

$$145\ \frac{mi}{hr} \times \frac{1.6093\ km}{1\ mi} \times \frac{1000\ m}{1\ km} \times \frac{1\ hr}{3600\ s} = 64.8\ m/s$$

The UF_6 molecule has the higher average speed.

9.88 $$\frac{rate_{H_2}}{rate_X} = \sqrt{\frac{M_X}{M_{H_2}}}; \qquad \frac{2.92}{1} = \frac{\sqrt{M_X}}{\sqrt{2.02}}; \qquad 2.92\ \sqrt{2.02} = \sqrt{M_X}$$

$M_X = (2.92\ \sqrt{2.02}\ )^2 = 17.2$ g/mol; molecular mass = 17.2 amu

9.89 $\frac{\text{rate Xe}}{\text{rate Z}} = \sqrt{\frac{M_Z}{M_{Xe}}}$; $\frac{1}{1.86} = \frac{\sqrt{M_Z}}{\sqrt{131.29}}$; $\frac{\sqrt{131.29}}{1.86} = \sqrt{M_Z}$; $\frac{131.29}{(1.86)^2} = M_Z$

M_Z = 37.9 g/mol; molecular mass = 37.9 amu; The gas could be F_2.

9.90 HCl, 36.5 amu; F_2, 38.0 amu; Ar, 39.9 amu

$\frac{\text{rate HCl}}{\text{rate Ar}} = \sqrt{\frac{M_{Ar}}{M_{HCl}}} = \sqrt{\frac{39.9}{36.5}} = 1.05$ $\frac{\text{rate } F_2}{\text{rate Ar}} = \sqrt{\frac{M_{Ar}}{M_{F_2}}} = \sqrt{\frac{39.9}{38.0}} = 1.02$

The relative rates of diffusion are HCl(1.05) > F_2(1.02) > Ar(1.00).

9.91 Because CO and N_2 have the same mass, they will have the same diffusion rates.

9.92 $u = 45 \text{ m/s} = \sqrt{\frac{3 \times 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \times T}{4.00 \times 10^{-3} \text{ kg/mol}}}$

Square both sides of the equation and solve for T.

$2025 \text{ m}^2/\text{s}^2 = \frac{3 \times 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \times T}{4.00 \times 10^{-3} \text{ kg/mol}}$

T = 0.325 K = -272.83°C (near absolute zero)

9.93 $230 \text{ km/h} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 63.9 \text{ m/s}$

$u = 63.9 \text{ m/s} = \sqrt{\frac{3 \times 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \times T}{32.0 \times 10^{-3} \text{ kg/mol}}}$

Square both sides of the equation and solve for T.

$4083 \text{ m}^2/\text{s}^2 = \frac{3 \times 8.314 \text{ kg m}^2/(\text{s}^2 \text{ K mol}) \times T}{32.0 \times 10^{-3} \text{ kg/mol}}$

T = 5.24 K = -268°C

General Problems

9.94 $\frac{\text{rate } {}^{35}Cl_2}{\text{rate } {}^{37}Cl_2} = \sqrt{\frac{M\ {}^{37}Cl_2}{M\ {}^{35}Cl_2}} = \sqrt{\frac{74.0}{70.0}} = 1.03$

$\frac{\text{rate } {}^{35}Cl\ {}^{37}Cl}{\text{rate } {}^{37}Cl_2} = \sqrt{\frac{M\ {}^{37}Cl_2}{M\ {}^{35}Cl\ {}^{37}Cl}} = \sqrt{\frac{74.0}{72.0}} = 1.01$

The relative rates of diffusion are ${}^{35}Cl_2(1.03) > {}^{35}Cl\ {}^{37}Cl(1.01) > {}^{37}Cl_2(1.00)$.

9.95 Average molecular mass of air = 28.96 amu; CO_2, 44.01 amu

$P = 760 \text{ mm Hg} \times \frac{44.01 \text{ g/mol}}{28.96 \text{ g/mol}} = 1155 \text{ mm Hg}$

9.96 $$V = \frac{nRT}{P} = \frac{(1.00\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1050\ \text{K})}{(75\ \text{atm})} = 1.1\ \text{L}$$

9.97 1 atm = 1033.228 g/cm^2
column height = (1033.228 g/cm^2)(1 cm^3/0.89g) = 1200 cm = 12 m

9.98 $$n = \frac{PV}{RT} = \frac{(2.15\ \text{atm})(7.35\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(293\ \text{K})} = 0.657\ \text{mol Ar}$$

$$0.657\ \text{mol Ar} \times \frac{39.948\ \text{g Ar}}{1\ \text{mol Ar}} = 26.2\ \text{g Ar}$$

m_{total} = 478.1 g + 26.2 g = 504.3 g

9.99 This is initially a Boyle's Law problem, because only P and V are changing while n and T remain fixed. The initial volume for each gas is the volume of their individual bulbs. The final volume for each gas is the total volume of the three bulbs.
$nRT = P_iV_i = P_fV_f$; $V_f = 1.50 + 1.00 + 2.00 = 4.50$ L

For CO_2: $$P_f = \frac{P_i V_i}{V_f} = \frac{(2.13\ \text{atm})(1.50\ \text{L})}{(4.50\ \text{L})} = 0.710\ \text{atm}$$

For H_2: $$P_f = \frac{P_i V_i}{V_f} = \frac{(0.861\ \text{atm})(1.00\ \text{L})}{(4.50\ \text{L})} = 0.191\ \text{atm}$$

For Ar: $$P_f = \frac{P_i V_i}{V_f} = \frac{(1.15\ \text{atm})(2.00\ \text{L})}{(4.50\ \text{L})} = 0.511\ \text{atm}$$

From Dalton's Law, $P_{total} = P_{CO_2} + P_{H_2} + P_{Ar}$

P_{total} = 0.710 atm + 0.191 atm + 0.511 atm = 1.412 atm

9.100 (a) Bulb A contains CO_2(g) and N_2(g); Bulb B contains CO_2(g), N_2(g), and H_2O(s).

(b) Initial moles of gas = $$n = \frac{PV}{RT} = \frac{\left(564\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(298\ \text{K})}$$

Initial moles of gas = 0.030 35 mol

mol gas in Bulb A = $$n = \frac{PV}{RT} = \frac{\left(219\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(298\ \text{K})} = 0.011\ 78\ \text{mol}$$

$$\text{mol gas in Bulb B} = n = \frac{PV}{RT} = \frac{\left(219\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(203\ \text{K})} = 0.017\,29\ \text{mol}$$

$n_{H_2O} = n_{initial} - n_A - n_B = 0.030\,35 - 0.011\,78 - 0.017\,29 = 0.001\,28\ \text{mol} = 0.0013\ \text{mol}\ H_2O$

(c) Bulb A contains $N_2(g)$.
Bulb B contains $N_2(g)$ and $H_2O(s)$.
Bulb C contains $N_2(g)$ and $CO_2(s)$.

(d) $$n_A = \frac{PV}{RT} = \frac{\left(33.5\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298\ \text{K})} = 0.001\,803\ \text{mol}$$

$$n_B = \frac{PV}{RT} = \frac{\left(33.5\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(203\ \text{K})} = 0.002\,646\ \text{mol}$$

$$n_C = \frac{PV}{RT} = \frac{\left(33.5\ \text{mm Hg} \times \frac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(83\ \text{K})} = 0.006\,472\ \text{mol}$$

$n_{N_2} = n_A + n_B + n_C = 0.001\,803 + 0.002\,646 + 0.006\,472 = 0.010\,92\ \text{mol}\ N_2$

(e) $n_{CO_2} = n_{initial} - n_{H_2O} - n_{N_2} = 0.030\,35 - 0.0013 - 0.010\,92 = 0.0181\ \text{mol}\ CO_2$

9.101 $C_3H_5N_3O_9$, 227.1 amu

(a) $$\text{moles } C_3H_5N_3O_9 = 1.00\ \text{g} \times \frac{1\ \text{mol}}{227.1\ \text{g}} = 0.004\,40\ \text{mol}$$

$$n_{air} = \frac{PV}{RT} = \frac{(1.00\ \text{atm})(0.500\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293\ \text{K})} = 0.0208\ \text{mol air}$$

(b) $$\text{moles gas from } C_3H_5N_3O_9 = 0.004\,40\ \text{mol} \times \frac{29\ \text{mol gas}}{4\ \text{mol nitro}}$$

moles gas from $C_3H_5N_3O_9 = 0.0319$ mol gas from $C_3H_5N_3O_9$
$n_{total} = 0.0319\ \text{mol} + 0.0208\ \text{mol} = 0.0527\ \text{mol}$

(c) $P = \frac{nRT}{V} = \frac{(0.0527\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(698\ \text{K})}{(0.500\ \text{L})} = 6.04\ \text{atm}$

9.102 NH_3, 17.03 amu; $\text{mol } NH_3 = 45.0\ \text{g} \times \frac{1\ \text{mol}}{17.03\ \text{g}} = 2.64\ \text{mol}$

$P = \frac{nRT}{V}$ or $P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$

(a) At $T = 0^oC = 273\ K$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273\ \text{K})}{(1.000\ \text{L})} = 59.1\ \text{atm}$$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273\ \text{K})}{[(1.000\ \text{L}) - (2.64\ \text{mol})(0.0371\ \text{L/mol})]} - \frac{\left(4.17\ \frac{\text{L}^2 \bullet \text{atm}}{\text{mol}^2}\right)(2.64\ \text{mol})^2}{(1.000\ \text{L})^2}$$

$P = 65.6\ \text{atm} - 29.1\ \text{atm} = 36.5\ \text{atm}$

(b) At $T = 50^oC = 323\ K$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(323\ \text{K})}{(1.000\ \text{L})} = 70.0\ \text{atm}$$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(323\ \text{K})}{[(1.000\ \text{L}) - (2.64\ \text{mol})(0.0371\ \text{L/mol})]} - \frac{\left(4.17\ \frac{\text{L}^2 \bullet \text{atm}}{\text{mol}^2}\right)(2.64\ \text{mol})^2}{(1.000\ \text{L})^2}$$

$P = 77.6\ \text{atm} - 29.1\ \text{atm} = 48.5\ \text{atm}$

(c) At $T = 100^oC = 373\ K$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(373\ \text{K})}{(1.000\ \text{L})} = 80.8\ \text{atm}$$

$$P = \frac{(2.64\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(373\ \text{K})}{[(1.000\ \text{L}) - (2.64\ \text{mol})(0.0371\ \text{L/mol})]} - \frac{\left(4.17\ \frac{\text{L}^2 \bullet \text{atm}}{\text{mol}^2}\right)(2.64\ \text{mol})^2}{(1.000\ \text{L})^2}$$

$P = 89.6\ \text{atm} - 29.1\ \text{atm} = 60.5\ \text{atm}$

At the three temperatures, the van der Waals equation predicts a much lower pressure than does the ideal gas law. This is likely due to the fact that NH_3 can hydrogen bond leading to strong intermolecular forces.

9.103 (a) $n_{total} = \dfrac{PV}{RT} = \dfrac{\left(258\ \text{mm Hg} \times \dfrac{1.00\ \text{atm}}{760\ \text{mm Hg}}\right)(0.500\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293\ \text{K})} = 0.007\,06\ \text{mol}$

(b) $n_B = \dfrac{PV}{RT} = \dfrac{\left(344\ \text{mm Hg} \times \dfrac{1\ \text{atm}}{760\ \text{mm Hg}}\right)(0.250\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293\ \text{K})} = 0.004\,71\ \text{moles}$

(c) $d = \dfrac{0.218\ \text{g}}{0.250\ \text{L}} = 0.872\ \text{g/L}$

(d) molar mass = $\dfrac{0.218\ \text{g}}{0.004\,71\ \text{mol}} = 46.3\ \text{g/mol}$, NO_2; mol. mass = 46.3 amu

(e) $Hg_2CO_3(s) + 6\ HNO_3(aq) \rightarrow 2\ Hg(NO_3)_2(aq) + 3\ H_2O(l) + CO_2(g) + 2\ NO_2(g)$

9.104 CO_2, 44.01 amu

mol CO_2 = 500.0 g $CO_2 \times \dfrac{1\ \text{mol}\ CO_2}{44.01\ \text{g}\ CO_2} = 11.36\ \text{mol}\ CO_2$

$PV = nRT$

$$P = \frac{nRT}{V} = \frac{(11.36\ \text{mol})\left(0.082\,06\ \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(700\ \text{K})}{(0.800\ \text{L})} = 816\ \text{atm}$$

9.105 (a) Let x = mol C_nH_{2n+2} in reaction mixture.

Combustion of $C_nH_{2n+2} \rightarrow nCO_2 + (n+1)H_2O$ needs $n + \left(\dfrac{n+1}{2}\right) = \dfrac{3n+1}{2}$ mol O_2

Balanced equation is: $C_nH_{2n+2}(g) + \left(\dfrac{3n+1}{2}\right)O_2(g) \rightarrow nCO_2(g) + (n+1)H_2O(g)$

In going from reactants to products, the increase in the number of moles is

$[n + (n+1)] - \left[1 + \dfrac{3n+1}{2}\right] = \dfrac{n-1}{2}$ per mol of C_nH_{2n+2} reacted.

Before reaction: total mol = $\dfrac{PV}{RT} = \dfrac{(2.000\ \text{atm})(0.4000\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298.15\ \text{K})} = 0.032\,70\ \text{mol}$

After reaction: total mol = $\dfrac{PV}{RT} = \dfrac{(2.983\ \text{atm})(0.4000\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(398.15\ \text{K})} = 0.036\,52\ \text{mol}$

Difference = 0.032 70 mol - 0.036 52 mol = 0.003 82 mol

Increase in number of mol = $\left(\frac{n\_1}{2}\right)x = 0.003\ 82$ mol; $x = \frac{2(0.003\ 82)}{n\_1}$

Also $x = \frac{g\ \ C_nH_{2n+2}}{\text{molar mass}} = \frac{0.148\ g}{[12.01n\ +\ 1.008(2n+2)]\ g/mol}$

So $\frac{2(0.003\ 82)}{n\_1} = \frac{0.148}{14.026n\ +\ 2.016}$; $0.148\ n - 0.148 = 0.107\ n + 0.0154$

$0.041\ n = 0.163$; $n = \frac{0.163}{0.041} = 4.0$

C_nH_{2n+2} is C_4H_{10} (butane); molar mass = (4)(12.01) + (10)(1.008) = 58.12 g/mol

(b) $0.148\ g\ C_4H_{10} \times \frac{1\ mol\ C_4H_{10}}{58.12\ g\ C_4H_{10}} = 0.002\ 55\ mol\ C_4H_{10}$

mol O_2 initially = total mol - mol C_4H_{10} = 0.032 70 mol - 0.002 55 mol = 0.030 15 mol O_2

$P_{C_4H_{10}} = \left(\frac{n_{C_4H_{10}}}{n_{total}}\right)P_{initial} = \left(\frac{0.002\ 55\ mol}{0.032\ 70\ mol}\right)(2.000\ atm) = 0.156\ atm$

$P_{O_2} = \left(\frac{n_{O_2}}{n_{total}}\right)P_{initial} = \left(\frac{0.030\ 15\ mol}{0.032\ 70\ mol}\right)(2.000\ atm) = 1.844\ atm$

(c) $C_4H_{10}(g) + \frac{13}{2}\ O_2 \rightarrow 4\ CO_2(g) + 5\ H_2O(g)$

$0.002\ 55\ mol\ C_4H_{10} \times \frac{4\ mol\ CO_2}{1\ mol\ C_4H_{10}} = 0.0102\ mol\ CO_2$

$0.002\ 55\ mol\ C_4H_{10} \times \frac{5\ mol\ H_2O}{1\ mol\ C_4H_{10}} = 0.012\ 75\ mol\ H_2O$

mol O_2 unreacted = total mol after reaction - mol CO_2 - mol H_2O

= 0.03652 mol - 0.0102 mol - 0.01275 = 0.01357 mol O_2

$P_{CO_2} = \left(\frac{n_{CO_2}}{n_{total}}\right)P_{final} = \left(\frac{0.0102\ mol}{0.036\ 52\ mol}\right)(2.983\ atm) = 0.833\ atm$

$P_{H_2O} = \left(\frac{n_{H_2O}}{n_{total}}\right)P_{final} = \left(\frac{0.012\ 75\ mol}{0.036\ 52\ mol}\right)(2.983\ atm) = 1.041\ atm$

$P_{O_2} = \left(\frac{n_{O_2}}{n_{total}}\right)P_{final} = \left(\frac{0.013\ 57\ mol}{0.036\ 52\ mol}\right)(2.983\ atm) = 1.108\ atm$

9.106 (a) average molecular mass for natural gas

= (0.915)(16.04 amu) + (0.085)(30.07 amu) = 17.2 amu

total moles of gas = $15.50\ g \times \frac{1\ mol\ gas}{17.2\ g\ gas} = 0.901\ mol\ gas$

(b) $P = \dfrac{(0.901\ \text{mol})\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(293\ \text{K})}{(15.00\ \text{L})} = 1.44\ \text{atm}$

(c) $P_{CH_4} = X_{CH_4} \bullet P_{total} = (1.44\ \text{atm})(0.915) = 1.32\ \text{atm}$

$P_{C_2H_6} = X_{C_2H_6} \bullet P_{total} = (1.44\ \text{atm})(0.085) = 0.12\ \text{atm}$

(d) $\Delta H_{combustion}(CH_4) = -802.3\ \text{kJ/mol}$ and $\Delta H_{combustion}(C_2H_6) = -1427.7\ \text{kJ/mol}$

Heat liberated = (0.915)(0.901 mol)(-802.3 kJ/mol)

+ (0.085)(0.901)(-1427.7 kJ/mol) = -771 kJ

9.107 PV = nRT

$n_{total\,(initial)} = \dfrac{PV}{RT} = \dfrac{(3.00\ \text{atm})(10.0\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(373.1\ \text{K})} = 0.980\ \text{mol}$

$n_{total\,(final)} = \dfrac{PV}{RT} = \dfrac{(2.40\ \text{atm})(10.0\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(373.1\ \text{K})} = 0.784\ \text{mol}$

	$CS_2(g)$	+ $3\ O_2(g)$	→ $CO_2(g)$	+ $2\ SO_2(g)$
before reaction (mol)	y	0.980 - y	0	0
change (mol)	-x	-3x	+x	+2x
after reaction (mol)	y - x = 0	0.980 - y - 3x	x	2x

$n_{total\,(final)} = (y - x) + (0.980 - y - 3x) + x + 2x = 0.784\ \text{mol}$

0.980 mol - 4x + 3x = 0.784 mol

x = 0.980 mol - 0.784 mol = 0.196 mol

mol CO_2 = x = 0.196 mol

$P_{CO_2} = \dfrac{nRT}{V} = \dfrac{(0.196\ \text{mol})\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(373.1\ \text{K})}{(10.0\ \text{L})} = 0.600\ \text{atm}$

mol SO_2 = 2x = 2(0.196 mol) = 0.392 mol

$P_{SO_2} = \dfrac{nRT}{V} = \dfrac{(0.392\ \text{mol})\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(373.1\ \text{K})}{(10.0\ \text{L})} = 1.20\ \text{atm}$

mol O_2 = 0.980 mol - y - 3x = 0.980 mol - x - 3x = 0.980 - 4(0.196 mol) = 0.196 mol

$P_{O_2} = P_{CO_2} = 0.600\ \text{atm}$

9.108 (a) $T = 0^oC = 273\ \text{K}$; PV = nRT

$n_Q = \dfrac{PV}{RT} = \dfrac{(0.229\ \text{atm})(0.0500\ \text{L})}{\left(0.082\,06\ \dfrac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(273\ \text{K})} = 5.11 \times 10^{-4}\ \text{mol Q}$

Q molar mass = $\frac{0.100\ \text{g Q}}{5.11\ \text{x}\ 10^{-4}\ \text{mol Q}} = 196\ \text{g/mol}$

Xe molar mass = 131.3 g/mol

O_n molar mass = 196 g/mol - 131.3 g/mol = 65 g/mol

So, n = 4 and XeO_4 is the likely formula for Q.

(b) $XeO_4(g) \rightarrow Xe(g) + 2\ O_2(g)$

After decomposition, $P_{Total} = P_{Xe} + P_{O_2}$.

Because of the stoichiometry of the decomposition reaction, the partial pressure of O_2 is twice the partial pressure of Xe.

Let x = P_{Xe} and 2x = P_{O_2}. $P_{Total} = P_{Xe} + P_{O_2} = x + 2x = 3x = 0.941$ atm

$x = \frac{0.941\ \text{atm}}{3} = 0.314\ \text{atm}$

$P_{Xe} = x = 0.314$ atm; $P_{O_2} = P_{Total} - P_{Xe} = 0.941$ atm - 0.314 atm = 0.627 atm

9.109 $Ca(ClO_3)_2$, 206.98 amu; $Ca(ClO)_2$, 142.98 amu

(a) $Ca(ClO_3)_2(s) \rightarrow CaCl_2(s) + 3\ O_2(g)$

$Ca(ClO)_2(s) \rightarrow CaCl_2(s) + O_2(g)$

(b) T = 700°C = 700 + 273 = 973 K

PV = nRT

$n_{O_2} = \frac{PV}{RT} = \frac{(1.00\ \text{atm})(10.0\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(973\ \text{K})} = 0.125\ \text{mol}\ O_2$

Let X = mol $Ca(ClO_3)_2$ and let Y = mol $Ca(ClO)_2$

X(206.98 g/mol) + Y(142.98 g/mol) = 10.0 g

3X + Y = 0.125 mol, so Y = 0.125 mol - 3X (substitute for Y and solve for X)

X(206.98 g/mol) + (0.125 mol - 3X)(142.98 g/mol) = 10.0 g

X(206.98 g/mol) + 17.9 g - X(428.94 g/mol) = 10.0 g

X(206.98 g/mol) - X(428.94 g/mol) = 10.0 g - 17.9 g = -7.9 g

X(-221.96 g/mol) = -7.9 g

X = (-7.9 g)/(-221.96 g/mol) = 0.0356 mol $Ca(ClO_3)_2$

Y = 0.125 mol - 3X; Y = 0.125 mol - 3(0.0356 mol) = 0.0182 mol $Ca(ClO)_2$

mass $Ca(ClO_3)_2$ = 0.0356 mol $Ca(ClO_3)_2$ x $\frac{206.98\ \text{g Ca(ClO}_3)_2}{1\ \text{mol Ca(ClO}_3)_2} = 7.4\ \text{g Ca(ClO}_3)_2$

mass $Ca(ClO)_2$ = 10.0 g - 7.4 g = 2.6 g $Ca(ClO)_2$

9.110 PCl_3, 137.3 amu; O_2, 32.00 amu; $POCl_3$, 153.3 amu

$2\ PCl_3(g) + O_2(g) \rightarrow 2\ POCl_3(g)$

mol PCl_3 = 25.0 g x $\frac{1\ \text{mol PCl}_3}{137.3\ \text{g PCl}_3} = 0.182\ \text{mol}\ PCl_3$

mol O_2 = 3.00 g x $\frac{1\ \text{mol O}_2}{32.00\ \text{g O}_2} = 0.0937\ \text{mol}\ O_2$

Check for limiting reactant.

mol O_2 needed = 0.182 mol PCl_3 x $\frac{1 \text{ mol } O_2}{2 \text{ mol } PCl_3}$ = 0.0910 mol O_2 needed

There is a slight excess of O_2. PCl_3 is the limiting reactant.

mol $POCl_3$ = 0.182 mol PCl_3 x $\frac{2 \text{ mol } POCl_3}{2 \text{ mol } PCl_3}$ = 0.182 mol $POCl_3$

mol O_2 left over = 0.0937 mol - 0.0910 mol = 0.0027 mol O_2 left over

T = 200.0°C = 200.0 + 273.15 = 473.1 K; PV = nRT

$$P = \frac{nRT}{V} = \frac{(0.182 \text{ mol} + 0.0027 \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(473.1 \text{ K})}{(5.00 \text{ L})} = 1.43 \text{ atm}$$

9.111 (a) T = 225°C = 225 + 273 = 498 K

PV = nRT

$$P^{\circ}_{NOCl} = \frac{nRT}{V} = \frac{(2.00 \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(498 \text{ K})}{(400.0 \text{ L})} = 0.204 \text{ atm}$$

	2 NOCl(g)	→	2 NO(g)	+	Cl_2(g)
initial (atm)	0.204		0		0
change (atm)	-2x		+2x		+x
equil (atm)	0.204 - 2x		2x		x

P_{total} (after rxn) = (0.204 atm - 2x) + 2x + x = 0.246 atm

x = 0.246 atm - 0.204 atm = 0.042 atm

P_{NO} = 2x = 2(0.042) = 0.084 atm

P_{Cl_2} = x = 0.042 atm

P_{NOCl} = 0.204 - 2x = 0.204 - 2(0.042) = 0.120 atm

(b) % NOCl decomposed = $\frac{2x}{P^{\circ}_{NOCl}} \times 100\,\% = \frac{0.084 \text{ atm}}{0.204 \text{ atm}} \times 100\,\% = 41\%$

9.112 O_2, 32.00 amu; O_3, 48.00 amu

	3 O_2(g)	→	2 O_3(g)
initial (atm)	32.00		0
change (atm)	-3x		+2x
after rxn (atm)	32.00 - 3x		2x

$P_{Total} = P_{O_2} + P_{O_3}$ = 30.64 atm = 32.00 atm - 3x + 2x = 32.00 atm - x

x = 32.00 atm - 30.64 atm = 1.36 atm

P_{O_2} = 32.00 - 3x = 32.00 - 3(1.36 atm) = 27.92 atm

P_{O_3} = 2x = 2(1.36 atm) = 2.72 atm

$T = 25^oC = 25 + 273 = 298\ K;\ PV = nRT$

$$n_{O_2} = \frac{PV}{RT} = \frac{(27.92\ atm)(10.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 11.42\ mol\ O_2$$

$$n_{O_3} = \frac{PV}{RT} = \frac{(2.72\ atm)(10.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 1.11\ mol\ O_3$$

$$\text{mass } O_2 = 11.42\ mol\ O_2 \times \frac{32.00\ g\ O_2}{1\ mol\ O_2} = 365.4\ g\ O_2$$

$$\text{mass } O_3 = 1.11\ mol\ O_3 \times \frac{48.00\ g\ O_3}{1\ mol\ O_3} = 53.3\ g\ O_3$$

$\text{total mass} = 365.4\ g + 53.3\ g = 418.7\ g$

$$\text{mass \% } O_3 = \frac{\text{mass } O_3}{\text{total mass}} = \frac{53.3\ g}{418.7\ g} \times 100\% = 12.7\ \%$$

9.113 $CaCO_3$, 100.09 amu; CaO, 56.08 amu

$$\text{mol CaO (or } CO_2) = 25.0\ g\ CaCO_3 \times \frac{1\ mol\ CaCO_3}{100.09\ g\ CaCO_3} \times \frac{1\ mol\ CaO\ or\ CO_2}{1\ mol\ CaCO_3} = 0.250\ \text{mol}$$

$$\text{mass CaO} = 0.250\ mol\ CaO \times \frac{56.08\ g\ CaO}{1\ mol\ CaO} = 14.02\ g\ CaO$$

(a) 500.0 mL = 0.5000 L

$PV = nRT;\quad n_{CO_2} = 0.250\ mol$

$$P_{CO_2} = \frac{nRT}{V} = \frac{(0.250\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(1500\ K)}{(0.5000\ L)} = 61.5\ atm$$

(b) $V_{CaO} = (14.02\ g)(3.34\ g/mL) = 4.20\ mL$

$V = 500.0\ mL - 4.20\ mL = 495.8\ mL = 0.4958\ L$

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$P = \frac{(0.250\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(1500\ K)}{[(0.4958\ L) - (0.250\ mol)(0.0427\ L/mol)]} - \frac{\left(3.59\ \frac{L^2 \bullet atm}{mol^2}\right)(0.250\ mol)^2}{(0.4958\ L)^2} = 62.5\ atm$$

Multi-Concept Problems

9.114 CO_2, 44.01 amu

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g) \qquad \Delta H^o = -802\ kJ$

(a) 1.00 atm of CH_4 only requires 2.00 atm O_2, therefore O_2 is in excess.

$T = 300^oC = 300 + 273 = 573\ K;\ PV = nRT$

$$n_{CH_4} = \frac{PV}{RT} = \frac{(1.00\ atm)(4.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(573\ K)} = 0.0851\ mol\ CH_4$$

$$n_{O_2} = \frac{PV}{RT} = \frac{(4.00\ atm)(4.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(573\ K)} = 0.340\ mol\ O_2$$

$$\text{mass } CO_2 = 0.0851\ mol\ CH_4 \times \frac{1\ mol\ CO_2}{1\ mol\ CH_4} \times \frac{44.01\ g\ CO_2}{1\ mol\ CO_2} = 3.75\ g\ CO_2$$

(b) $q_{rxn} = 0.0851\ mol\ CH_4 \times \frac{-802\ kJ}{1\ mol\ CH_4} = -68.3\ kJ$

	$CH_4(g)$	+ $2\ O_2(g)$	→ $CO_2(g)$	+ $2\ H_2O(g)$
initial (mol)	0.0851	0.340	0	0
change (mol)	-0.0851	-2(0.0851)	+0.0851	+2(0.0851)
after rxn (mol)	0	0.340 - 2(0.0851)	0.0851	0.170

total moles of gas = 0.340 ml - 2(0.0851) mol + 0.0851 mol + 0.170 mol = 0.425 mol gas

$$q_{rxn} = -68.3\ kJ \times \frac{1000\ J}{1\ kJ} = -68{,}300\ J$$

$q_{vessel} = -q_{rxn} = 68{,}300\ J = (0.425\ mol)(21\ J/(mol \cdot {}^oC))(t_f - 300^oC) +$
$(14.500\ kg)\left(\frac{1000\ g}{1\ kg}\right)(0.449\ J/(g \bullet {}^oC))(t_f - 300^oC)$

Solve for t_f.

$68{,}300\ J = (8.925\ J/^oC + 6510\ J/^oC)(t_f - 300^oC) = (6519\ J/^oC)(t_f - 300^oC)$

$$\frac{68{,}300\ J}{6519\ J/^oC} = 10.5^oC = (t_f - 300^oC)$$

$300^oC + 10.5^oC = t_f$

$t_f = 310^oC$

(c) $T = 310^oC = 310 + 273 = 583\ K$

$$P_{CO_2} = \frac{nRT}{V} = \frac{(0.0851\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(583\ K)}{(4.00\ L)} = 1.02\ atm$$

9.115 $X + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

(a) $X = C_2H_6O$

$C_2H_6O + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

(b) It is an empirical formula because it is the smallest whole number ratio of atoms. It is also a molecular formula because any higher multiple such as $C_4H_{12}O_2$ does not correspond to a stable electron-dot structure.

(c)

(d) C_2H_6O, 46.07 amu

$$\text{mol } C_2H_6O = 5.000 \text{ g } C_2H_6O \times \frac{1 \text{ mol } C_2H_6O}{46.07 \text{ g } C_2H_6O} = 0.1085 \text{ mol } C_2H_6O$$

$$\Delta H_{combustion} = \frac{-144.2 \text{ kJ}}{0.1085 \text{ mol}} = -1328.6 \text{ kJ/mol}$$

$$\Delta H_{combustion} = [2\ \Delta H^o_f(CO_2) + 3\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_2H_6O)$$

$$\Delta H^o_f(C_2H_6O) = [2\ \Delta H^o_f(CO_2) + 3\ \Delta H^o_f(H_2O)] - \Delta H_{combustion}$$
$$= [(2\text{mol})(-393.5 \text{ kJ/mol}) + (3 \text{ mol})(-241.8 \text{ kJ/mol})] - (-1328.6 \text{ kJ})$$
$$= -183.8 \text{ kJ/mol}$$

9.116 (a) $2\ C_8H_{18}(l) + 25\ O_2(g) \rightarrow 16\ CO_2(g) + 18\ H_2O(g)$

(b) $$4.6 \times 10^{10} \text{ L } C_8H_{18} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.792 \text{ g}}{1 \text{ mL}} = 3.64 \times 10^{13} \text{ g } C_8H_{18}$$

$$3.64 \times 10^{13} \text{ g } C_8H_{18} \times \frac{1 \text{ mol } C_8H_{18}}{114.2 \text{ g } C_8H_{18}} \times \frac{16 \text{ mol } CO_2}{2 \text{ mol } C_8H_{18}} = 2.55 \times 10^{12} \text{ mol } CO_2$$

$$2.55 \times 10^{12} \text{ mol } CO_2 \times \frac{44.0 \text{ g } CO_2}{1 \text{ mol } CO_2} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.1 \times 10^{11} \text{ kg } CO_2$$

(c) $$V = \frac{nRT}{P} = \frac{(2.55 \times 10^{12} \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273 \text{ K})}{(1.00 \text{ atm})} = 5.7 \times 10^{13} \text{ L of } CO_2$$

(d) 12.5 moles of O_2 are needed for each mole of isooctane (from part a).

$$12.5 \text{ mol } O_2 = (0.210)(n_{air}); \qquad n_{air} = \frac{12.5 \text{ mol}}{0.210} = 59.5 \text{ mol air}$$

$$V = \frac{nRT}{P} = \frac{(59.5 \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273 \text{ K})}{(1.00 \text{ atm})} = 1.33 \times 10^3 \text{ L}$$

9.117 (a) Freezing point of H_2O on the Rankine scale is (9/5)(273.15) = 492°R.

(b) $$R = \frac{PV}{nT} = \frac{(1.00 \text{ atm})(22.414 \text{ L})}{(1.00 \text{ mol})(492^{\circ})} = 0.0456 \frac{\text{L} \bullet \text{atm}}{^{\circ}\text{R} \bullet \text{mol}}$$

(c) $$P = \frac{(2.50 \text{ mol})\left(0.0456 \frac{\text{L} \bullet \text{atm}}{^{\circ}\text{R} \bullet \text{mol}}\right)(525\ ^{\circ}\text{R})}{[(0.4000 \text{ L}) - (2.50 \text{ mol})(0.04278 \text{ L/mol})]} - \frac{\left(2.253 \frac{\text{L}^2 \bullet \text{atm}}{\text{mol}^2}\right)(2.50 \text{ mol})^2}{(0.4000 \text{ L})^2}$$

P = 204.2 atm - 88.0 atm = 116 atm

9.118 $n = \frac{PV}{RT} = \frac{(1\ atm)(1323\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(2223\ K)} = 7.25$ mol of all gases

(a) 0.004 00 mol "nitro" x $\frac{7.25\ mol\ gases}{1\ mol\ \_nitro\_} = 0.0290$ mol hot gases

(b) $n = \frac{PV}{RT} = \frac{\left(623\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(0.500\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(263\ K)} = 0.0190$ mol B + C + D

$n_A = n_{total} - n_{(B+C+D)} = 0.0290 - 0.0190 = 0.0100$ mol A; A = H_2O

(c) $n = \frac{PV}{RT} = \frac{\left(260\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(0.500\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.007\,00$ mol C + D

$n_B = n_{(B+C+D)} - n_{(C+D)} = 0.0190 - 0.007\,00 = 0.0120$ mol B; B = CO_2

(d) $n = \frac{PV}{RT} = \frac{\left(223\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(0.500\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.006\,00$ mol D

$n_C = n_{(C+D)} - n_D = 0.007\,00 - 0.006\,00 = 0.001\,00$ mol C; C = O_2

molar mass D = $\frac{0.168\ g}{0.006\,00\ mol} = 28.0$ g/mol; D = N_2

(e) 0.004 $C_3H_5N_3O_9(l) \rightarrow$ 0.0100 $H_2O(g)$ + 0.012 $CO_2(g)$ + 0.001 $O_2(g)$ + 0.006 $N_2(g)$
Multiply each coefficient by 1000 to obtain integers.
4 $C_3H_5N_3O_9(l) \rightarrow$ 10 $H_2O(g)$ + 12 $CO_2(g)$ + $O_2(g)$ + 6 $N_2(g)$

9.119 CO_2, 44.01 amu; H_2O, 18.02 amu

(a) mol C = 0.3744 g CO_2 x $\frac{1\ mol\ CO_2}{44.01\ g\ CO_2}$ x $\frac{1\ mol\ C}{1\ mol\ CO_2} = 0.008\,507$ mol C

mass C = 0.008 507 mol C x $\frac{12.011\ g\ C}{1\ mol\ C} = 0.1022$ g C

mol H = 0.1838 g H_2O x $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$ x $\frac{2\ mol\ H}{1\ mol\ H_2O} = 0.020\,400$ mol H

mass H = 0.020 400 mol H x $\frac{1.008\ g\ H}{1\ mol\ H}$ = 0.02056 g H

mass O = 0.1500 g - 0.1022 g - 0.02056 g = 0.0272 g O

mol O = 0.0272 g O x $\frac{1\ mol\ O}{16.00\ g\ O}$ = 0.001 70 mol O

$C_{0.008\ 507}H_{0.020\ 400}O_{0.001\ 70}$ Divide each subscript by the smallest, 0.001 70.

$C_{0.008\ 507\ /\ 0.001\ 70}H_{0.020\ 400\ /\ 0.001\ 70}O_{0.001\ 70\ /\ 0.001\ 70}$

The empirical formula is $C_5H_{12}O$. The empirical formula mass is 88 g/mol.

(b) 1 atm = 101,325 Pa; T = 54.8°C = 54.8 + 273.15 = 327.9 K

PV = nRT

$$n = \frac{PV}{RT} = \frac{\left(100.0\ kPa\ x \frac{1.00\ atm}{101.325\ kPa}\right)(1.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(327.9\ K)} = 0.0367 \text{ mol methyl } \textit{tert}\text{-butyl ether}$$

methyl *tert*-butyl ether molar mass = $\frac{3.233\ g}{0.0367\ mol}$ = 88.1 g/mol

The empirical formula mass and the molar mass are the same, so the molecular formula and empirical formula are the same. $C_5H_{12}O$ is the molecular formula and 88.15 amu is the molecular mass for methyl *tert*-butyl ether.

(c) $C_5H_{12}O(l) + 15/2\ O_2(g) \rightarrow 5\ CO_2(g) + 6\ H_2O(l)$

(d) $\Delta H^o_{combustion} = [5\ \Delta H^o_f\ (CO_2) + 6\ \Delta H^o_f\ (H_2O(l))] - \Delta H^o_f\ (C_5H_{12}O) = -3368.7$ kJ

-3368.7 kJ = [(5 mol)(-393.5 kJ/mol) + (6 mol)(-285.8 kJ/mol)] - (1 mol)$\Delta H^o_f\ (C_5H_{12}O)$

(1 mol)$\Delta H^o_f\ (C_5H_{12}O)$ = [(5 mol)(-393.5 kJ/mol) + (6 mol)(-285.8 kJ/mol)] + 3368.7 kJ

$\Delta H^o_f\ (C_5H_{12}O)$ = -313.6 kJ/mol

10 Liquids, Solids, and Changes of State

10.1 $\mu = Q \times r = (1.60 \times 10^{-19}\ C)(92 \times 10^{-12}\ m)\left(\frac{1\ D}{3.336 \times 10^{-30}\ C \bullet m}\right) = 4.41\ D$

$\%\ \text{ionic character for HF} = \frac{1.82\ D}{4.41\ D} \times 100\% = 41\%$

HF has more ionic character than HCl. HCl has only 17% ionic character.

10.2 (a) SF_6 has polar covalent bonds but the molecule is symmetrical (octahedral). The individual bond polarities cancel, and the molecule has no dipole moment.
(b) $H_2C{=}CH_2$ can be assumed to have nonpolar C–H bonds. In addition, the molecule is symmetrical. The molecule has no dipole moment.

(c) The C–Cl bonds in $CHCl_3$ are polar covalent bonds, and the molecule is polar.

(d) The C–Cl bonds in CH_2Cl_2 are polar covalent bonds, and the molecule is polar.

10.3

10.4 The N atom is electron rich (red) because of its high electronegativity. The H atoms are electron poor (blue) because they are less electronegative.

10.5 (a) Of the four substances, only HNO_3 has a net dipole moment.
(b) Only HNO_3 can hydrogen bond.
(c) Ar has fewer electrons than Cl_2 and CCl_4, and has the smallest dispersion forces.

10.6 H_2S dipole-dipole, dispersion

CH_3OH hydrogen bonding, dipole-dipole, dispersion
C_2H_6 dispersion
Ar dispersion
$Ar < C_2H_6 < H_2S < CH_3OH$

10.7 (a) $CO_2(s) \rightarrow CO_2(g)$, ΔS is positive.
(b) $H_2O(g) \rightarrow H_2O(l)$, ΔS is negative.
(c) ΔS is positive (more disorder).

10.8 $\Delta G = \Delta H - T\Delta S$; at the boiling point (phase change), $\Delta G = 0$.

$$\Delta H = T\Delta S; \quad T = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{29.2 \text{ kJ/mol}}{87.5 \text{ x } 10^{-3} \text{ kJ/(K•mol)}} = 334 \text{ K}$$

10.9 The boiling point is the temperature where the vapor pressure of a liquid equals the external pressure.
$P_1 = 760$ mm Hg; $P_2 = 260$ mm Hg; $T_1 = 80.1^oC$
$\Delta H_{vap} = 30.8$ kJ/mol

$$\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$(\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_1} - \frac{1}{T_2}$$

Solve for T_2 (the boiling point for benzene at 260 mm Hg).

$$\frac{1}{T_1} - (\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_2}$$

$$\frac{1}{353.2 \text{ K}} - [\ln(260) - \ln(760)]\left(\frac{8.3145 \frac{\text{J}}{\text{K•mol}}}{30{,}800 \text{ J/mol}}\right) = \frac{1}{T_2}$$

$\frac{1}{T_2} = 0.003\,121\ K^{-1}$; $T_2 = 320$ K = 47^oC (boiling point is lower at lower pressure)

10.10 $$\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$P_1 = 400$ mm Hg; $T_1 = 41.0\ ^oC = 314.2$ K
$P_2 = 760$ mm Hg; $T_2 = 331.9$ K

$$\Delta H_{vap} = \frac{[\ln (760) - \ln (400)]\left(8.3145 \frac{\text{J}}{\text{K•mol}}\right)}{\left(\frac{1}{314.2 \text{ K}} - \frac{1}{331.9 \text{ K}}\right)} = 31{,}442 \text{ J/mol} = 31.4 \text{ kJ/mol}$$

10.11 (a) 1/8 atom at 8 corners and 1 atom at body center = 2 atoms

(b) 1/8 atom at 8 corners and 1/2 atom at 6 faces = 4 atoms

10.12 For a simple cube, d = 2r; $r = \frac{d}{2} = \frac{334\ pm}{2} = 167\ pm$

10.13 For a simple cube, there is one atom per unit cell.

$$\text{mass of one Po atom} = 209\ \text{g/mol} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} = 3.4706 \times 10^{-22}\ \text{g/atom}$$

unit cell edge = d = 334 pm = 334×10^{-12} m = 3.34×10^{-8} cm

unit cell volume = $d^3 = (3.34 \times 10^{-8}\ \text{cm})^3 = 3.7260 \times 10^{-23}\ \text{cm}^3$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{3.4706 \times 10^{-22}\ \text{g}}{3.7260 \times 10^{-23}\ \text{cm}^3} = 9.31\ \text{g/cm}^3$$

10.14 There are several possibilities. Here's one.

10.15 For CuCl:
1/8 Cl^- at 8 corners and 1/2 Cl^- at 6 faces = 4 Cl^- (4 minuses)
4 Cu^+ inside (4 pluses)
For $BaCl_2$:
1/8 Ba^{2+} at 8 corners and 1/2 Ba^{2+} at 6 faces = 4 Ba^{2+} (8 pluses)
8 Cl^- inside (8 minuses)

10.16 (a) In the unit cell there is a rhenium atom at each corner of the cube. The number of rhenium atoms in the unit cell = 1/8 Re at 8 corners = 1 Re atom.
In the unit cell there is an oxygen atom in the center of each edge of the cube. The number of oxygen atoms in the unit cell = 1/4 O on 12 edges = 3 O atoms.
(b) ReO_3
(c) Each oxide has a -2 charge and there are three of them for a total charge of -6. The charge (oxidation state) of rhenium must be +6 to balance the negative charge of the oxides.
(d) Each oxygen atom is surrounded by two rhenium atoms. The geometry is linear.
(e) Each rhenium atom is surrounded by six oxygen atoms. The geometry is octahedral.

10.17 The minimum pressure at which liquid CO_2 can exist is its triple point pressure of 5.11 atm.

10.18 (a) $CO_2(s) \rightarrow CO_2(g)$
(b) $CO_2(l) \rightarrow CO_2(g)$
(c) $CO_2(g) \rightarrow CO_2(l) \rightarrow$ supercritical CO_2

10.19 (a)

(b) Gallium has two triple points. The one below 1 atm is a solid, liquid, vapor triple point. The one at 10^4 atm is a solid(1), solid(2), liquid triple point.
(c) Increasing the pressure favors the liquid phase, giving the solid/liquid boundary a negative slope. At 1 atm pressure the liquid phase is more dense than the solid phase.

10.20 The molecules in a liquid crystal can move around, as in viscous liquids, but they have a restricted range of motion, as in solids.

10.21 Liquid crystal molecules have a rigid rodlike shape with a length four to eight times greater than their diameter.

Understanding Key Concepts

10.22 The electronegative O atoms are electron rich (red), while the rest of the molecule is electron poor (blue).

10.23 (a) cubic closest-packed (b) simple cubic
(c) hexagonal closest-packed (d) body-centered cubic

10.24 (a) cubic closest-packed
(b) 1/8 S^{2-} at 8 corners and 1/2 S^{2-} at 6 faces = 4 S^{2-}; 4 Zn^{2+} inside

10.25 (a) 1/8 Ca^{2+} at 8 corners = 1 Ca^{2+}; 1/2 O^{2-} at 6 faces = 3 O^{2-}; 1 Ti^{4+} inside
The formula for perovskite is $CaTiO_3$.
(b) The oxidation number of Ti is +4 to maintain charge neutrality in the unit cell.

10.26 (a) normal boiling point ≈ 300 K; normal melting point ≈ 180 K
(b) (i) solid (ii) gas (iii) supercritical fluid

10.27

10.28 Here are two possibilities.

10.29 (a), (c), (d)

(b) There are three triple points.
(e) The solid phase that is stable at the higher pressure is more dense. The more dense phase is diamond.

Additional Problems
Dipole Moments and Intermolecular Forces

10.30 If a molecule has polar covalent bonds, the molecular shape (and location of lone pairs of electrons) determines whether a molecule has a dipole moment or not. The molecular shape will determine whether the bond dipoles cancel or not.

10.31 Dipole-dipole forces arise between molecules that have permanent dipole moments. London dispersion forces arise between molecules as a result of induced temporary dipoles.

10.32 (a) $CHCl_3$ has a permanent dipole moment. Dipole-dipole intermolecular forces are important. London dispersion forces are also present.
(b) O_2 has no dipole moment. London dispersion intermolecular forces are important.
(c) polyethylene, C_nH_{2n+2}. London dispersion intermolecular forces are important.
(d) CH_3OH has a permanent dipole moment. Dipole-dipole intermolecular forces and hydrogen bonding are important. London dispersion forces are also present.

10.33 (a) Xe has no dipole-dipole forces (b) HF has the largest hydrogen bond forces
(c) Xe has the largest dispersion forces

10.34 For CH_3OH and CH_4, dispersion forces are small. CH_3OH can hydrogen bond; CH_4 cannot. This accounts for the large difference in boiling points.
For 1-decanol and decane, dispersion forces are comparable and relatively large along the C–H chain. 1-decanol can hydrogen bond; decane cannot. This accounts for the 55°C higher boiling point for 1-decanol.

10.35 (a) C_8H_{18} has the larger dispersion forces because of its longer hydrocarbon chain.
(b) HI has the larger dispersion forces because of the larger, more polarizable iodine.
(c) H_2Se has the larger dispersion forces because of the more polarizable and less electronegative Se.

10.36 (a) (b)

(c) (d)

10.37 (a) (b)

(c) (d)

10.38

SO_2 is bent and the individual bond dipole moments add to give the molecule a net dipole moment.
CO_2 is linear and the individual bond dipole moments point in opposite directions to cancel each other out. CO_2 has no net dipole moment.

10.39

In both PCl_3 and PCl_5 the P–Cl bond is polar covalent. PCl_3 is trigonal pyramidal and the bond dipoles add to give the molecule a net dipole moment. PCl_5 is trigonal bipyramidal and the bond dipoles cancel. PCl_5 has no dipole moment.

10.40

10.41

Vapor Pressure and Changes of State

10.42 ΔH_{vap} is usually larger than ΔH_{fusion} because ΔH_{vap} is the heat required to overcome all intermolecular forces.

10.43 Sublimation is the direct conversion of a solid to a gas. A solid can also be converted to a gas in two steps; melting followed by vaporization. The energy to convert a solid to a gas must be the same regardless of the path. Therefore $\Delta H_{subl} = \Delta H_{fusion} + \Delta H_{vap}$.

10.44 (a) $Hg(l) \rightarrow Hg(g)$
(b) no change of state, Hg remains a liquid
(c) $Hg(g) \rightarrow Hg(l) \rightarrow Hg(s)$

10.45 (a) solid I_2 melts to form liquid I_2 (b) no change of state, I_2 remains a liquid

10.46 As the pressure over the liquid H_2O is lowered, H_2O vapor is removed by the pump. As H_2O vapor is removed, more of the liquid H_2O is converted to H_2O vapor. This conversion is an endothermic process and the temperature decreases. The combination of both a decrease in pressure and temperature takes the system across the liquid/solid boundary in the phase diagram so the H_2O that remains turns to ice.

10.47 The normal boiling point for ether is relatively low (34.6°C). As the pressure is reduced by the pump, the relatively high vapor pressure of the ether equals the external pressure produced by the pump and the liquid boils.

10.48 H_2O, 18.02 amu; $5.00 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.2775 \text{ mol } H_2O$

$q_1 = (0.2775 \text{ mol})[36.6 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](273 \text{ K} - 263 \text{ K}) = 0.1016 \text{ kJ}$
$q_2 = (0.2775 \text{ mol})(6.01 \text{ kJ/mol}) = 1.668 \text{ kJ}$
$q_3 = (0.2775 \text{ mol})(75.3 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](303 \text{ K} - 273 \text{ K}) = 0.6269 \text{ kJ}$
$q_{total} = q_1 + q_2 + q_3 = 2.40 \text{ kJ}$; 2.40 kJ of heat is required.

10.49 H_2O, 18.02 amu; $15.3 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.8491 \text{ mol } H_2O$

$q_1 = (0.8491 \text{ mol})[33.6 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](373 \text{ K} - 388 \text{ K}) = -0.4279 \text{ kJ}$
$q_2 = -(0.8491 \text{ mol})(40.67 \text{ kJ/mol}) = -34.53 \text{ kJ}$
$q_3 = (0.8491 \text{ mol})[75.3 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](348 \text{ K} - 373 \text{ K}) = -1.598 \text{ kJ}$
$q_{total} = q_1 + q_2 + q_3 = -36.6 \text{ kJ}$; 36.6 kJ of heat is released.

10.50 H_2O, 18.02 amu; $7.55 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 0.4190 \text{ mol } H_2O$

$q_1 = (0.4190 \text{ mol})[75.3 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](273.15 \text{ K} - 306.65 \text{ K}) = -1.057 \text{ kJ}$
$q_2 = -(0.4190 \text{ mol})(6.01 \text{ kJ/mol}) = -2.518 \text{ kJ}$
$q_3 = (0.4190 \text{ mol})[36.6 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](263.15 \text{ K} - 273.15 \text{ K}) = -0.1534 \text{ kJ}$
$q_{total} = q_1 + q_2 + q_3 = -3.73 \text{ kJ}$; 3.73 kJ of heat is released.

10.51 C_2H_5OH, 46.07 amu; $25.0 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 0.543 \text{ mol } C_2H_5OH$

$q_1 = (0.543 \text{ mol})[65.7 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](351.55 \text{ K} - 366.15 \text{ K}) = -0.521 \text{ kJ}$

q_2 = -(0.543 mol)(38.56 kJ/mol) = -20.94 kJ
q_3 = (0.543 mol)[113 x 10^{-3} kJ/(K · mol)](263.15 K - 351.55 K) = -5.42 kJ
$q_{total} = q_1 + q_2 + q_3$ = -26.9 kJ; 26.9 kJ of heat is released.

10.52

10.53

10.54 boiling point = 218°C = 491 K
$\Delta G = \Delta H_{vap} - T\Delta S_{vap}$; At the boiling point (phase change), $\Delta G = 0$

$$\Delta H_{vap} = T\Delta S_{vap}; \quad \Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{43.3 \text{ kJ/mol}}{491 \text{ K}} = 0.0882 \text{ kJ/(K· mol)} = 88.2 \text{ J/(K· mol)}$$

10.55 $$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \frac{2.64 \text{ kJ/mol}}{371 \text{ K}} = 0.007\,12 \text{ kJ/(K· mol)} = 7.12 \text{ J/(K· mol)}$$

10.56 $$\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

T_1 = -5.1°C = 268.0 K; P_1 = 100 mm Hg
T_2 = 46.5°C = 319.6 K; P_2 = 760 mm Hg

$$\Delta H_{vap} = \frac{[\ln (760) - \ln (100)][8.3145 \text{ x } 10^{-3} \text{ kJ/(K• mol)}]}{\left(\frac{1}{268.0 \text{ K}} - \frac{1}{319.6 \text{ K}}\right)} = 28.0 \text{ kJ/mol}$$

10.57 $$\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$P_1 = 100$ mm Hg; $T_1 = 5.4^oC = 278.6$ K
$P_2 = 760$ mm Hg; $T_2 = 56.8^oC = 330.0$ K

$$\Delta H_{vap} = \frac{[\ln(760) - \ln(100)][8.3145 \text{ x } 10^{-3} \text{ kJ/(K • mol)}]}{\left(\frac{1}{278.6 \text{ K}} - \frac{1}{330.0 \text{ K}}\right)} = 30.2 \text{ kJ/mol}$$

10.58 $$\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{vap} = 28.0$ kJ/mol
$P_1 = 100$ mm Hg; $T_1 = -5.1^oC = 268.0$ K; $T_2 = 20.0^oC = 293.2$ K
Solve for P_2.

$$\ln P_2 = \ln (100) + \frac{28.0 \text{ kJ/mol}}{[8.3145 \text{ x } 10^{-3} \text{ kJ/(K• mol)}]}\left(\frac{1}{268.0 \text{ K}} - \frac{1}{293.2 \text{ K}}\right)$$

$\ln P_2 = 5.6852$; $P_2 = e^{5.6852} = 294.5$ mm Hg = 294 mm Hg

10.59 $$\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{vap} = 30.2$ kJ/mol
$P_1 = 100$ mm Hg; $T_1 = 5.4^oC = 278.6$ K; $T_2 = 30.0^oC = 303.2$ K
Solve for P_2.

$$\ln P_2 = \ln (100) + \frac{30.2 \text{ kJ/mol}}{[8.3145 \text{ x } 10^{-3} \text{ kJ/(K• mol)}]}\left(\frac{1}{278.6 \text{ K}} - \frac{1}{303.2 \text{ K}}\right)$$

$\ln P_2 = 5.6630$; $P_2 = e^{5.6620} = 288.0$ mm Hg = 288 mm Hg

10.60

T(K)	P_{vap}(mm Hg)	ln P_{vap}	1/T
263	80.1	4.383	0.003 802
273	133.6	4.8949	0.003 663
283	213.3	5.3627	0.003 534
293	329.6	5.7979	0.003 413

303	495.4	6.2054	0.003 300
313	724.4	6.5853	0.003 195

$$\ln P_{vap} = \left(- \frac{\Delta H_{vap}}{R} \right) \frac{1}{T} + C; \quad C = 18.2$$

$$\text{slope} = -3628 \text{ K} = - \frac{\Delta H_{vap}}{R}$$

$$\Delta H_{vap} = (3628 \text{ K})(R) = (3628 \text{ K})[8.3145 \times 10^{-3} \text{ kJ/(K·mol)}] = 30.1 \text{ kJ/mol}$$

10.61

T(K)	P_{vap}(mm Hg)	ln P_{vap}	1/T
500	39.3	3.671	0.002 000
520	68.5	4.227	0.001 923
540	114.4	4.7397	0.001 852
560	191.6	5.2554	0.001 786
580	286.4	5.6574	0.001 724
600	432.3	6.0691	0.001 667

$$\ln P_{vap} = \left(- \frac{\Delta H_{vap}}{R} \right) \frac{1}{T} + C; \quad C = 18.1$$

$$\text{slope} = -7219 \text{ K} = - \frac{\Delta H_{vap}}{R}$$

$$\Delta H_{vap} = (7219 \text{ K})(R) = (7219 \text{ K})[8.3145 \times 10^{-3} \text{ kJ/(K·mol)}] = 60.0 \text{ kJ/mol}$$

10.62 $\Delta H_{vap} = 30.1$ kJ/mol

10.63 $\Delta H_{vap} = 60.0$ kJ/mol

10.64 $$\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$P_1 = 80.1$ mm Hg; $T_1 = 263$ K

$P_2 = 724.4$ mm Hg; $T_2 = 313$ K

$$\Delta H_{vap} = \frac{[\ln (724.4) - \ln (80.1)][8.3145 \text{ x } 10^{-3} \text{ kJ/(K•mol)}]}{\left(\frac{1}{263 \text{ K}} - \frac{1}{313 \text{ K}}\right)} = 30.1 \text{ kJ/mol}$$

The calculated ΔH_{vap} and that obtained from the plot in Problem 10.62 are the same.

10.65 $$\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$P_1 = 39.3$ mm Hg; $T_1 = 500$ K

$P_2 = 432.3$ mm Hg; $T_2 = 600$ K

$$\Delta H_{vap} = \frac{[\ln(432.3) - \ln(39.3)][8.3145 \text{ x } 10^{-3} \text{ kJ/(K•mol)}]}{\left(\frac{1}{500 \text{ K}} - \frac{1}{600 \text{ K}}\right)} = 59.8 \text{ kJ/mol}$$

The calculated ΔH_{vap} and that obtained from the plot in Problem 10.63 are consistent with each other. The value from the slope is 60.0 kJ/mol

Structures of Solids

10.66 molecular solid, CO_2, I_2; metallic solid, any metallic element; covalent network solid, diamond; ionic solid, NaCl

10.67 molecular solid, covalent molecules; metallic solid, metal atoms; covalent network solid, nonmetal atoms; ionic solid, cations and anions

10.68 The unit cell is the smallest repeating unit in a crystal.

10.69 From Table 10.10.
Hexagonal and cubic closest packing are the most efficient because 74% of the available space is used.
Simple cubic packing is the least efficient because only 52% of the available space is used.

10.70 Cu is face-centered cubic. d = 362 pm; $r = \sqrt{\frac{d^2}{8}} = \sqrt{\frac{(362 \text{ pm})^2}{8}} = 128$ pm

362 pm = 362 x 10^{-12} m = 3.62 x 10^{-8} cm

unit cell volume = (3.62 x 10^{-8} cm)^3 = 4.74 x 10^{-23} cm^3

mass of one Cu atom = 63.55 g/mol x $\frac{1 \text{ mol}}{6.022 \text{ x } 10^{23} \text{ atom}}$ = 1.055 x 10^{-22} g/atom

Cu is face-centered cubic; there are therefore four Cu atoms in the unit cell.

unit cell mass = (4 atoms)(1.055 x 10^{-22} g/atom) = 4.22 x 10^{-22} g

density = $\frac{\text{mass}}{\text{volume}} = \frac{4.22 \text{ x } 10^{-22} \text{ g}}{4.74 \text{ x } 10^{-23} \text{ cm}^3}$ = 8.90 g/cm^3

10.71 Pb is face-centered cubic. d = 495 pm = 4.95 x 10^{-8} cm

$$r = \sqrt{\frac{d^2}{8}} = \sqrt{\frac{(495\ pm)^2}{8}} = 175\ pm$$

unit cell volume = $(4.95 \times 10^{-8}\ cm)^3 = 1.2129 \times 10^{-22}\ cm^3$

$$\text{mass of one Pb atom} = 207.2\ \frac{g}{mol} \times \frac{1\ mol}{6.022 \times 10^{23}\ atoms} = 3.4407 \times 10^{-22}\ g/atom$$

Pb is face-centered cubic; there are therefore four Pb atoms in the unit cell.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4(3.4407 \times 10^{-22}\ g)}{1.2129 \times 10^{-22}\ cm^3} = 11.3\ g/cm^3$$

10.72 $$\text{mass of one Al atom} = 26.98\ \frac{g}{mol} \times \frac{1\ mol}{6.022 \times 10^{23}\ atom} = 4.480 \times 10^{-23}\ g/atom$$

Al is face-centered cubic; there are therefore four Al atoms in the unit cell.

unit cell mass = (4 atoms)(4.480 x 10^{-23} g/atom) = 1.792 x 10^{-22} g

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{unit cell volume} = \frac{\text{unit cell mass}}{\text{density}} = \frac{1.792 \times 10^{-22}\ g}{2.699\ g/cm^3} = 6.640 \times 10^{-23}\ cm^3$$

$$\text{unit cell edge} = d = \sqrt[3]{6.640 \times 10^{-23}\ cm^3} = 4.049 \times 10^{-8}\ cm$$

$$d = 4.049 \times 10^{-8}\ cm \times \frac{1m}{100\ cm} = 4.049 \times 10^{-10}\ m = 404.9 \times 10^{-12}\ m = 404.9\ pm$$

10.73 W is body-centered cubic. d = 317 pm

a = edge = d; b = face diagonal; c = body diagonal

$b^2 = 2a^2$

$c^2 = a^2 + b^2$

$c^2 = a^2 + 2a^2 = 3a^2$

$c = \sqrt{3}\ a$

unit cell body diagonal = $\sqrt{3}\ d = \sqrt{3}\ (317\ pm) = 549\ pm$

10.74 unit cell body diagonal = 4r = 549 pm

$$\text{For W, } r = \frac{549\ pm}{4} = 137\ pm$$

10.75 $$\text{mass of one Na atom} = 23.0\ \frac{g}{mol} \times \frac{1\ mol}{6.022 \times 10^{23}\ atoms} = 3.82 \times 10^{-23}\ g/atom$$

Because Na is body-centered cubic; there are two Na atoms in the unit cell.

unit cell mass = 2(3.82 x 10^{-23} g) = 7.64 x 10^{-23} g

$$\text{unit cell volume} = \frac{\text{unit cell mass}}{\text{density}} = \frac{7.64 \times 10^{-23}\ g}{0.971\ g/cm^3} = 7.87 \times 10^{-23}\ cm^3$$

$$\text{unit cell edge} = d = \sqrt[3]{7.87 \times 10^{-23}\ cm^3} = 4.29 \times 10^{-8}\ cm = 429\ pm$$

$4R = \sqrt{3}\ d$; $R = \dfrac{\sqrt{3}\ d}{4} = \dfrac{\sqrt{3}\ (429\ pm)}{4} = 186\ pm$

10.76 mass of one Ti atom = $47.88\ g/mol \times \dfrac{1\ mol}{6.022 \times 10^{23}\ atoms} = 7.951 \times 10^{-23}\ g/atom$

$r = 144.8\ pm = 144.8 \times 10^{-12}\ m$

$r = 144.8 \times 10^{-12}\ m \times \dfrac{100\ cm}{1\ m} = 1.448 \times 10^{-8}\ cm$

Calculate the volume and then the density for Ti assuming it is primitive cubic, body-centered cubic, and face-centered cubic. Compare the calculated density with the actual density to identify the unit cell.

For primitive cubic:

$d = 2r$; volume = $d^3 = [2(1.448 \times 10^{-8}\ cm)]^3 = 2.429 \times 10^{-23}\ cm^3$

$\text{density} = \dfrac{\text{unit cell mass}}{\text{volume}} = \dfrac{7.951 \times 10^{-23}\ g}{2.429 \times 10^{-23}\ cm^3} = 3.273\ g/cm^3$

For face-centered cubic:

$d = 2\sqrt{2}\ r$; volume = $d^3 = [2\sqrt{2}\ (1.448 \times 10^{-8}\ cm)]^3 = 6.870 \times 10^{-23}\ cm^3$

$\text{density} = \dfrac{4(7.951 \times 10^{-23}\ g)}{6.870 \times 10^{-23}\ cm^3} = 4.630\ g/cm^3$

For body-centered cubic:

From Problems 10.73 and 10.74,

$d = \dfrac{4r}{\sqrt{3}}$; volume = $d^3 = \left[\dfrac{4(1.448 \times 10^{-8}\ cm)}{\sqrt{3}}\right]^3 = 3.739 \times 10^{-23}\ cm^3$

$\text{density} = \dfrac{2(7.951 \times 10^{-23}\ g)}{3.739 \times 10^{-23}\ cm^3} = 4.253\ g/cm^3$

The calculated density for a face-centered cube ($4.630\ g/cm^3$) is closest to the actual density of $4.54\ g/cm^3$. Ti crystallizes in the face-centered cubic unit cell.

10.77 mass of one Ca = $40.08\ g/mol \times \dfrac{1\ mol}{6.022 \times 10^{23}\ atom} = 6.656 \times 10^{-23}\ g/atom$

unit cell edge = $d = 558.2\ pm = 5.582 \times 10^{-8}\ cm$

unit cell volume = $d^3 = (5.582 \times 10^{-8}\ cm)^3 = 1.739 \times 10^{-22}\ cm^3$

unit cell mass = $(1.739 \times 10^{-22}\ cm^3)(1.55\ g/cm^3) = 2.695 \times 10^{-22}\ g$

(a) number of Ca atoms in unit cell = $\dfrac{\text{unit cell mass}}{\text{mass of one Ca atom}}$

$= \dfrac{2.695 \times 10^{-22}\ g}{6.656 \times 10^{-23}\ g/atom} = 4.05 = 4\ Ca\ atoms$

(b) Because the unit cell contains 4 Ca atoms, the unit cell is face-centered cubic.

10.78 Six Na^+ ions touch each H^- ion and six H^- ions touch each Na^+ ion.

10.79 For CsCl: (1/8 x 8 corners), so 1 Cl^- and 1 minus per unit cell
1 Cs^+ inside, so 1 plus per unit cell

10.80 Na^+ H^- Na^+
$\leftarrow$ 488 pm $\rightarrow$ unit cell edge = d = 488 pm; Na–H bond = d/2 = 244 pm

10.81 See Problem 10.73.
body diagonal = $\sqrt{3}$ d = $\sqrt{3}$ (412.3 pm) = 714.12 pm
Cs–Cl bond = body diagonal/2 = (714.12 pm)/2 = 357.1 pm
Cs–Cl bond length = $r_{Cs^+} + r_{Cl^-}$
357.1 pm = $r_{Cs^+} + r_{Cl^-}$
357.1 pm = r_{Cs^+} + 181 pm
r_{Cs^+} = 357.1 pm - 181 pm = 176 pm

Phase Diagrams

10.82 (a) gas (b) liquid (c) solid

10.83 (a) $H_2O(l) \rightarrow H_2O(s)$
(b) 380°C is above the critical temperature; therefore, the water cannot be liquefied. At the higher pressure, it will behave as a supercritical fluid.

10.84

10.85

10.86 (a) $Br_2(s)$ (b) $Br_2(l)$

10.87 (a) $O_2(l)$ (b) O_2 - supercritical fluid

10.88 Solid O_2 does not melt when pressure is applied because the solid is denser than the liquid and the solid/liquid boundary in the phase diagram slopes to the right.

10.89 Ammonia can be liquefied at 25°C because this temperature is below T_c (132.5°C). Methane cannot be liquefied at 25°C because this temperature is above T_c (-82.1°C). Sulfur dioxide can be liquefied at 25°C because this temperature is below T_c (157.8°C).

10.90

The starting phase is benzene as a solid, and the final phase is benzene as a gas.

10.91

The starting phase is a gas, and the final phase is a liquid.

10.92 solid $\rightarrow$ liquid $\rightarrow$ supercritical fluid $\rightarrow$ liquid $\rightarrow$ solid $\rightarrow$ gas

10.93 gas $\rightarrow$ solid $\rightarrow$ liquid $\rightarrow$ gas $\rightarrow$ liquid

General Problems

10.94 Because chlorine is larger than fluorine, the charge separation is larger in CH_3Cl compared to CH_3F resulting in CH_3Cl having a slightly larger dipole moment.

10.95 Because Ar crystallizes in a face-centered cubic unit cell, there are four Ar atoms in the unit cell.

$$\text{mass of one Ar atom} = 39.95 \text{ g/mol} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atom}} = 6.634 \times 10^{-23} \text{ g/atom}$$

$$\text{unit cell mass} = 4 \text{ atoms} \times \text{mass of one Ar atom}$$

$$= 4 \text{ atoms} \times 6.634 \times 10^{-23} \text{ g/atom} = 2.654 \times 10^{-22} \text{ g}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{unit cell volume} = \frac{\text{unit cell mass}}{\text{density}} = \frac{2.654 \times 10^{-22} \text{ g}}{1.623 \text{ g/cm}^3} = 1.635 \times 10^{-22} \text{ cm}^3$$

$$\text{unit cell edge} = d = \sqrt[3]{1.635 \times 10^{-22} \text{ cm}^3} = 5.468 \times 10^{-8} \text{ cm}$$

$$d = 5.468 \times 10^{-8} \text{ cm} \times \frac{1\text{m}}{100 \text{ cm}} = 5.468 \times 10^{-10} \text{ m} = 546.8 \times 10^{-12} \text{ m} = 546.8 \text{ pm}$$

$$r = \sqrt{\frac{d^2}{8}} = \sqrt{\frac{(546.8\ \text{pm})^2}{8}} = 193.3\ \text{pm}$$

10.96 $7.50\ \text{g} \times \frac{1\ \text{mol}}{200.6\ \text{g}} = 0.037\ 39\ \text{mol Hg}$

$q_1 = (0.037\ 39\ \text{mol})[28.2 \times 10^{-3}\ \text{kJ/(K} \cdot \text{mol)}](234.2\ \text{K} - 223.2\ \text{K}) = 0.011\ 60\ \text{kJ}$

$q_2 = (0.037\ 39\ \text{mol})(2.33\ \text{kJ/mol}) = 0.087\ 12\ \text{kJ}$

$q_3 = (0.037\ 39\ \text{mol})[27.9 \times 10^{-3}\ \text{kJ/(K} \cdot \text{mol)}](323.2\ \text{K} - 234.2\ \text{K}) = 0.092\ 84\ \text{kJ}$

$q_{total} = q_1 + q_2 + q_3 = 0.192\ \text{kJ}$; 0.192 kJ of heat is required.

10.97

10.98 $\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\Delta H_{vap} = 40.67\ \text{kJ/mol}$

At 1 atm, H_2O boils at 100°C; therefore set

$T_1 = 100°\text{C} = 373\ \text{K}$, and $P_1 = 1.00\ \text{atm}$.

Let $T_2 = 95°\text{C} = 368\ \text{K}$, and solve for P_2. (P_2 is the atmospheric pressure in Denver.)

$$\ln P_2 = \ln(1) + \frac{40.67\ \text{kJ/mol}}{[8.3145 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}]}\left(\frac{1}{373\ \text{K}} - \frac{1}{368\ \text{K}}\right)$$

$\ln P_2 = -0.1782$; $P_2 = e^{-0.1782} = 0.837\ \text{atm}$

10.99

10.100 $\Delta G = \Delta H - T\Delta S$; at the melting point (phase change), $\Delta G = 0$.

$$\Delta H = T\Delta S; \quad T = \frac{\Delta H_{fus}}{\Delta S_{fus}} = \frac{9.037\ \text{kJ/mol}}{9.79 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}} = 923\ \text{K} = 650°\text{C}$$

10.101 melting point = -23.2°C = 250.0 K

$\Delta G = \Delta H_{fusion} - T\Delta S_{fusion}$

At the melting point (phase change), $\Delta G = 0$

$\Delta H_{fusion} = T\Delta S_{fusion}$

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T} = \frac{9.37\ \text{kJ/mol}}{250.0\ \text{K}} = 0.0375\ \text{kJ/(K} \cdot \text{mol)} = 37.5\ \text{J/(K} \cdot \text{mol)}$$

10.102 $\Delta H_{vap} = \dfrac{(\ln P_2 - \ln P_1)(R)}{\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)}$

$P_1 = 40.0$ mm Hg; $T_1 = -81.6^oC = 191.6$ K

$P_2 = 400$ mm Hg; $T_2 = -43.9^oC = 229.2$ K

$$\Delta H_{vap} = \frac{[\ln (400) - \ln (40.0)]\left(8.3145 \text{ x } 10^{-3}\dfrac{kJ}{K \bullet mol}\right)}{\left(\dfrac{1}{191.6 \text{ K}} - \dfrac{1}{229.2 \text{ K}}\right)} = 22.36 \text{ kJ/mol}$$

Using $\Delta H_{vap} = 22.36$ kJ/mol

$$\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$(\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_1} - \frac{1}{T_2}$$

$$\frac{1}{T_1} - (\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_2}$$

$P_1 = 40.0$ mm Hg; $T_1 = 191.6$ K

$P_2 = 760$ mm Hg

Solve for T_2 (the normal boiling point).

$$\frac{1}{191.6 \text{ K}} - [\ln(760) - \ln(40.0)]\left(\frac{8.3145 \text{ x } 10^{-3}\dfrac{kJ}{K \bullet mol}}{22.36 \text{ kJ/mol}}\right) = \frac{1}{T_2}$$

$\dfrac{1}{T_2} = 0.004\ 124\ 33$; $T_2 = 242.46$ K $= -30.7^oC$

10.103 (a) $\ln P_2 = \ln P_1 + \dfrac{\Delta H_{vap}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$$(\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_1} - \frac{1}{T_2}$$

$$\frac{1}{T_1} - (\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_2}$$

$P_1 = 100.0$ mm Hg; $T_1 = -23^oC = 250$ K

$P_2 = 760.0$ mm Hg

Solve for T_2, the normal boiling point for CCl_3F.

$$\frac{1}{250\ \text{K}} - [\ln(760.0) - \ln(100.0)]\left(\frac{8.3145\ \text{x}\ 10^{-3}\ \frac{\text{kJ}}{\text{K}\bullet\ \text{mol}}}{24.77\ \text{kJ/mol}}\right) = \frac{1}{T_2}$$

$\frac{1}{T_2} = 0.003\ 319;$ $\qquad T_2 = 301.3\ \text{K} = 28.1^{\circ}\text{C}$

(b) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{24.77\ \text{kJ/mol}}{301.3\ \text{K}} = 0.082\ 21\ \text{kJ/(K} \cdot \text{mol)} = 82.2\ \text{J/(K} \cdot \text{mol)}$

10.104 $\Delta H_{vap} = \frac{(\ln P_2 - \ln P_1)(R)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

$P_1 = 100$ mm Hg; $\qquad T_1 = -110.3^{\circ}\text{C} = 162.85\ \text{K}$
$P_2 = 760$ mm Hg; $\qquad T_2 = -88.5^{\circ}\text{C} = 184.65\ \text{K}$

$$\Delta H_{vap} = \frac{[\ln (760) - \ln (100)]\left(8.3145\ \text{x}\ 10^{-3}\ \frac{\text{kJ}}{\text{K}\bullet\ \text{mol}}\right)}{\left(\frac{1}{162.85\ \text{K}} - \frac{1}{184.65\ \text{K}}\right)} = 23.3\ \text{kJ/mol}$$

10.105 $\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$(\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_1} - \frac{1}{T_2}$$

$$\frac{1}{T_1} - (\ln P_2 - \ln P_1)\left(\frac{R}{\Delta H_{vap}}\right) = \frac{1}{T_2}$$

$P_1 = 760$ mm Hg; $\qquad T_1 = 56.2^{\circ}\text{C} = 329.4\ \text{K}$
$P_2 = 105$ mm Hg $\qquad$ Solve for T_2.

$$\frac{1}{329.4\ \text{K}} - [\ln(105) - \ln(760)]\left(\frac{8.3145\ \text{x}\ 10^{-3}\ \frac{\text{kJ}}{\text{K}\bullet\ \text{mol}}}{29.1\ \text{kJ/mol}}\right) = \frac{1}{T_2}$$

$\frac{1}{T_2} = 0.003\ 601;$ $\qquad T_2 = 277.7\ \text{K} = 4.5^{\circ}\text{C}$

10.106

Kr cannot be liquified at room temperature because room temperature is above T_c (-63°C).

10.107 (a) Kr(l) (b) supercritical Kr

10.108 For a body-centered cube

$4r = \sqrt{3}$ edge; edge = $\frac{4r}{\sqrt{3}}$

volume of sphere = $\frac{4}{3}\pi r^3$

volume of unit cell = $\left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64\ r^3}{3\sqrt{3}}$

volume of 2 spheres = $2\left(\frac{4}{3}\pi r^3\right) = \frac{8}{3}\pi r^3$

% volume occupied = $\frac{\left(\frac{8}{3}\pi r^3\right)}{\left(\frac{64\,r^3}{3\sqrt{3}}\right)}$ x 100% = 68%

10.109 From Problem 10.73, $4r = \sqrt{3}\,d$; $r = \frac{\sqrt{3}\ d}{4} = \frac{\sqrt{3}(287\ pm)}{4}$ = 124 pm

10.110 unit cell edge = d = 287 pm = 287 x 10^{-12} m = 2.87 x 10^{-8} cm
unit cell volume = d^3 = (2.87 x 10^{-8} cm)^3 = 2.364 x 10^{-23} cm^3
unit cell mass = (2.364 x 10^{-23} cm^3)(7.86 g/cm^3) = 1.858 x 10^{-22} g
Fe is body-centered cubic; therefore there are two Fe atoms per unit cell.

mass of one Fe atom = $\frac{1.858\ \text{x}\ 10^{-22}\ \text{g}}{2\ \text{Fe atoms}}$ = 9.290 x 10^{-23} g/atom

Avogadro's number = 55.85 g/mol x $\frac{1\ \text{atom}}{9.290\ \text{x}\ 10^{-23}\ \text{g}}$ = 6.01 x 10^{23} atoms/mol

10.111 unit cell edge = d = 408 pm = 408 x 10^{-12} m = 4.08 x 10^{-8} cm
unit cell volume = (4.08 x 10^{-8} cm)^3 = 6.792 x 10^{-23} cm^3
unit cell mass = (10.50 g/cm^3)(6.792 x 10^{-23} cm^3) = 7.132 x 10^{-22} g
Ag is face-centered cubic; therefore there are four Ag atoms in the unit cell.

$$\text{mass of one Ag atom} = \frac{7.132 \text{ x } 10^{-22}\text{ g}}{4 \text{ Ag atoms}} = 1.783 \text{ x } 10^{-22} \text{ g/atom}$$

$$\text{Avogadro's number} = 107.9 \text{ g/mol x } \frac{1 \text{ atom}}{1.783 \text{ x } 10^{-22} \text{ g}} = 6.05 \text{ x } 10^{23} \text{ atoms/mol}$$

10.112 (a) unit cell edge = $2r_{Cl^-} + 2r_{Na^+}$ = 2(181 pm) + 2(97 pm) = 556 pm
(b) unit cell edge = d = 556 pm = 556 x 10^{-12} m = 5.56 x 10^{-8} cm
unit cell volume = (5.56 x 10^{-8} cm)^3 = 1.719 x 10^{-22} cm^3
The unit cell contains 4 Na^+ ions and 4 Cl^- ions.

$$\text{mass of one } Na^+ \text{ ion} = 22.99 \text{ g/mol x } \frac{1 \text{ mol}}{6.022 \text{ x } 10^{23} \text{ ions}} = 3.818 \text{ x } 10^{-23} \text{ g/}Na^+$$

$$\text{mass of one } Cl^- \text{ ion} = 35.45 \text{ g/mol x } \frac{1 \text{ mol}}{6.022 \text{ x } 10^{23} \text{ ions}} = 5.887 \text{ x } 10^{-23} \text{ g/}Cl^-$$

unit cell mass = 4(3.818 x 10^{-23} g) + 4(5.887 x 10^{-23} g) = 3.882 x 10^{-22} g

$$\text{density} = \frac{\text{unit cell mass}}{\text{unit cell volume}} = \frac{3.882 \text{ x } 10^{-22} \text{ g}}{1.719 \text{ x } 10^{-22} \text{ cm}^3} = 2.26 \text{ g/cm}^3$$

10.113 (a) (1/2 Nb/face)(6 faces) = 3 Nb; (1/4 O/edge)(12 edges) = 3 O
(b) NbO
(c) The oxidation state of Nb is +2.

10.114 Al_2O_3, ionic (greater lattice energy than NaCl because of higher ion charges);
F_2, dispersion; H_2O, dipole-dipole, H–bonding; Br_2, dispersion (larger and more polarizable than F_2), ICl, dipole-dipole, NaCl, ionic

rank according to normal boiling points: $F_2 < Br_2 < ICl < H_2O < NaCl < Al_2O_3$

10.115 Ag_2Te, 343. 33 amu; 529 pm = 529 x 10^{-12} m = 529 x 10^{-10} cm
unit cell volume = (529 x 10^{-10} cm)^3 = 1.48 x 10^{-22} cm^3
unit cell mass = (1.48 x 10^{-22} cm^3)(7.70 g/cm^3) = 1.14 x 10^{-21} g

$$\text{mass of one } Ag_2Te = \frac{343.33 \text{ g } Ag_2Te / \text{mol}}{6.022 \text{ x } 10^{23} \text{ } Ag_2Te \text{ formula units / mol}} = 5.70 \text{ x } 10^{-22} \text{ g } Ag_2Te/\text{formula unit}$$

$$Ag_2Te \text{ formula units/unit cell} = \frac{1.14 \text{ x } 10^{-21} \text{ g/unit cell}}{5.70 \text{ x } 10^{-22} \text{ g/ } Ag_2Te} = 2 \text{ } Ag_2Te/\text{unit cell}$$

$$Ag/\text{unit cell} = \frac{2 \text{ } Ag_2Te}{\text{unit cell}} \text{ x } \frac{2 \text{ Ag}}{Ag_2Te} = 4 \text{ Ag/unit cell}$$

10.116 (a)

(b) (i) solid (ii) gas (iii) liquid (iv) liquid (v) solid

Multi-Concept Problems

10.117 $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

Calculate ΔH and ΔS for this process and assume they do not change as a function of temperature.

$\Delta H^o = \Delta H^o_f(C_2H_5OH(g)) - \Delta H^o_f(C_2H_5OH(l))$

$\Delta H^o = [(1\ mol)(-235.1\ kJ/mol)] - [(1\ mol)(-277.7\ kJ/mol)] = 42.6\ kJ$

$\Delta S^o = S^o(C_2H_5OH(g)) - S^o(C_2H_5OH(l))$

$\Delta S^o = [(1\ mol)(282.6\ J/(K \cdot mol))] - [(1\ mol)(161\ J/(K \cdot mol))] = 122\ J/K$

$\Delta S^o = 122 \times 10^{-3}\ kJ/K)$

$\Delta G^o = \Delta H^o - T\Delta S^o$ and at the boiling point, $\Delta G = 0$

$0 = \Delta H^o - T_{bp}\Delta S^o$

$T_{bp}\Delta S^o = \Delta H^o$

$$T_{bp} = \frac{\Delta H^o}{\Delta S^o} = \frac{42.6\ kJ}{122 \times 10^{-3}\ kJ/K} = 349\ K$$

$T_{bp} = 349 - 273 = 76^oC$

$$\ln P_2 = \ln P_1 + \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{vap} = 42.6\ kJ/mol$

At 1 atm, C_2H_5OH boils at 349 K; therefore set

$T_1 = 349\ K$, and $P_1 = 1.00\ atm$.

Let $T_2 = 25^oC = 298\ K$, and solve for P_2.

P_2 is the vapor pressure of C_2H_5OH at 25^oC.

$$\ln P_2 = \ln(1.00) + \frac{42.6\ kJ/mol}{[8.3145 \times 10^{-3}\ kJ/(K \bullet mol)]}\left(\frac{1}{349\ K} - \frac{1}{298\ K}\right)$$

$\ln P_2 = -2.512$; $P_2 = e^{-2.512} = 0.0811\ atm$

$$P_2 = 0.0811 \text{ atm} \times \frac{760 \text{ mm Hg}}{1.00 \text{ atm}} = 61.6 \text{ mm Hg}$$

10.118 (a) Let the formula of magnetite be Fe_xO_y, then $Fe_xO_y + y\,CO \rightarrow x\,Fe + y\,CO_2$

$$n_{CO_2} = y = \frac{PV}{RT} = \frac{\left(751 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)(1.136 \text{ L})}{\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298 \text{ K})} = 0.04590 \text{ mol } CO_2$$

0.04590 mol CO_2 = mol of O in Fe_xO_y

$$\text{mass of O in } Fe_xO_y = 0.04590 \text{ mol O} \times \frac{16.0 \text{ g O}}{1 \text{ mol O}} = 0.7345 \text{ g O}$$

mass of Fe in Fe_xO_y = 2.660 g - 0.7345 g = 1.926 g Fe

(b) mol Fe in magnetite = $1.926 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 0.0345 \text{ mol Fe}$

formula of magnetite: $Fe_{0.0345}O_{0.0459}$ (divide each subscript by the smaller)

$Fe_{0.0345 / 0.0345}O_{0.0459 / 0.0345}$

$FeO_{1.33}$ (multiply both subscripts by 3)

$Fe_{(1 \times 3)}O_{(1.33 \times 3)}$; Fe_3O_4

(c) unit cell edge = d = 839 pm = 839×10^{-12} m

$$d = 839 \times 10^{-12} \text{ m} \times \frac{100 \text{ cm}}{1 \text{ m}} = 8.39 \times 10^{-8} \text{ cm}$$

unit cell volume = $d^3 = (8.39 \times 10^{-8} \text{ cm})^3 = 5.91 \times 10^{-22} \text{ cm}^3$

unit cell mass = $(5.91 \times 10^{-22} \text{ cm}^3)(5.20 \text{ g/cm}^3) = 3.07 \times 10^{-21}$ g

$$\text{mass of Fe in unit cell} = \left(\frac{1.926 \text{ g Fe}}{2.660 \text{ g}}\right)(3.07 \times 10^{-21} \text{ g}) = 2.22 \times 10^{-21} \text{ g Fe}$$

$$\text{mass of O in unit cell} = \left(\frac{0.7345 \text{ g O}}{2.660 \text{ g}}\right)(3.07 \times 10^{-21} \text{ g}) = 8.47 \times 10^{-22} \text{ g O}$$

$$\text{Fe atoms in unit cell} = 2.22 \times 10^{-21} \text{ g} \times \frac{6.022 \times 10^{23} \text{ atoms/mol}}{55.847 \text{ g/mol}} = 24 \text{ Fe atoms}$$

$$\text{O atoms in unit cell} = 8.47 \times 10^{-22} \text{ g} \times \frac{6.022 \times 10^{23} \text{ atoms/mol}}{16.00 \text{ g/mol}} = 32 \text{ O atoms}$$

10.119 (a) $$n_{H_2} = \frac{PV}{RT} = \frac{\left(740 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)(4.00 \text{ L})}{\left(0.08206 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(296 \text{ K})} = 0.160 \text{ mol } H_2$$

M = Group 3A metal; $2\,M(s) + 6\,H^+(aq) \rightarrow 2\,M^{3+}(aq) + 3\,H_2(g)$

$n_M = 0.160 \text{ mol } H_2 \times \frac{2 \text{ mol M}}{3 \text{ mol } H_2} = 0.107 \text{ mol M}$

mass M = $1.07 \text{ cm}^3 \times 2.70 \text{ g/cm}^3 = 2.89 \text{ g M}$

molar mass M = $\frac{2.89 \text{ g M}}{0.107 \text{ mol M}} = 27.0 \text{ g/mol}$; The Group 3A metal is Al

(b) mass of one Al atom = $26.98 \text{ g/mol} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 4.48 \times 10^{-23} \text{ g/atom}$

unit cell edge = d = 404 pm = 404×10^{-12} m

$d = 404 \times 10^{-12} \text{ m} \times \frac{100 \text{ cm}}{1 \text{ m}} = 4.04 \times 10^{-8} \text{ cm}$

unit cell volume = $d^3 = (4.04 \times 10^{-8} \text{ cm})^3 = 6.59 \times 10^{-23} \text{ cm}^3$

Calculate the density of Al assuming it is primitive cubic, body-centered cubic, and face-centered cubic. Compare the calculated density with the actual density to identify the unit cell.

For primitive cubic:

$$\text{density} = \frac{\text{unit cell mass}}{\text{unit cell volume}} = \frac{(1 \text{ Al})(4.48 \times 10^{-23} \text{ g/Al atom})}{6.59 \times 10^{-23} \text{ cm}^3} = 0.680 \text{ g/cm}^3$$

For body-centered cubic:

$$\text{density} = \frac{\text{unit cell mass}}{\text{unit cell volume}} = \frac{(2 \text{ Al})(4.48 \times 10^{-23} \text{ g/Al atom})}{6.59 \times 10^{-23} \text{ cm}^3} = 1.36 \text{ g/cm}^3$$

For face-centered cubic:

$$\text{density} = \frac{\text{unit cell mass}}{\text{unit cell volume}} = \frac{(4 \text{ Al})(4.48 \times 10^{-23} \text{ g/Al atom})}{6.59 \times 10^{-23} \text{ cm}^3} = 2.72 \text{ g/cm}^3$$

The calculated density for a face-centered cube (2.72 g/cm^3) is closest to the actual density of 2.70 g/cm^3. Al crystallizes in the face-centered cubic unit cell.

(c) $r = \sqrt{\frac{d^2}{8}} = \sqrt{\frac{(404 \text{ pm})^2}{8}} = 143 \text{ pm}$

10.120 (a) M = alkali metal; 500.0 mL = 0.5000 L; 802°C = 1075 K

$$n_M = \frac{PV}{RT} = \frac{\left(12.5 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)(0.5000 \text{ L})}{\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(1075 \text{ K})} = 9.32 \times 10^{-5} \text{ mol M}$$

1.62 mm = 1.62×10^{-3} m; crystal volume = $(1.62 \times 10^{-3} \text{ m})^3 = 4.25 \times 10^{-9} \text{ m}^3$

M atoms in crystal = $(9.32 \times 10^{-5} \text{ mol})(6.022 \times 10^{23} \text{ atoms/mol}) = 5.61 \times 10^{19}$ M atoms

Because M is body-centered cubic, only 68% (Table 10.10) of the total volume is occupied by M atoms.

$$\text{volume of M atom} = \frac{(0.68)(4.25 \times 10^{-9} \text{ m})}{5.61 \times 10^{19} \text{ M atoms}} = 5.15 \times 10^{-29} \text{ m}^3\text{/M atom}$$

volume of a sphere = $\frac{4}{3}\pi r^3$

$r_M = \sqrt[3]{\frac{3(\text{volume})}{4\pi}} = \sqrt[3]{\frac{3(5.15 \text{ x } 10^{-29} \text{ m}^3)}{4\pi}} = 2.31 \text{ x } 10^{-10} \text{ m} = 231 \text{ x } 10^{-12} \text{ m} = 231 \text{ pm}$

(b) The radius of 231 pm is closest to that of K.

(c) 1.62 mm = 0.162 cm

density of solid = $\frac{(9.32 \text{ x } 10^{-5} \text{ mol})(39.1 \text{ g/mol})}{(0.162 \text{ cm})^3} = 0.857 \text{ g/cm}^3$

density of vapor = $\frac{(9.32 \text{ x } 10^{-5} \text{ mol})(39.1 \text{ g/mol})}{500.0 \text{ cm}^3} = 7.29 \text{ x } 10^{-6} \text{ g/cm}^3$

10.121 (a)

$$n_{X_2} = \frac{PV}{RT} = \frac{\left(755 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)(0.500 \text{ L})}{\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298 \text{ K})} = 0.0203 \text{ mol } X_2$$

$M(s) + 1/2\ X_2(g) \rightarrow MX(s)$

$\text{mol M} = 0.0203 \text{ mol } X_2 \times \frac{1 \text{ mol M}}{1/2 \text{ mol } X_2} = 0.0406 \text{ mol M}$

molar mass M = $\frac{1.588 \text{ g M}}{0.0406 \text{ mol M}} = 39.1 \text{ g/mol}$; atomic mass = 39.1 amu ; M = K

(b) From Figure 6.1, the radius for K^+ is ~140 pm.

unit cell edge = 535 pm = $2r_{K^+} + 2r_{X^-}$

$r_{X^-} = \frac{535 \text{ pm} - 2r_{K^+}}{2} = \frac{535 \text{ pm} - 2(140 \text{ pm})}{2} = 128 \text{ pm}$

From Figure 6.2, $X^- = F^-$

(c) Because the cation and anion are of comparable size, the anions are not in contact with each other.

(d) unit cell contents: 1/8 F^- at 8 corners and 1/2 F^- at 6 faces = 4 F^-
1/4 K^+ at 12 edges and 1 K^+ inside = 4 K^+

mass of one K^+ = $\frac{39.098 \text{ g/mol}}{6.022 \text{ x } 10^{23} \text{ K}^+/\text{mol}} = 6.493 \text{ x } 10^{-23} \text{ g/K}^+$

mass of one F^- = $\frac{18.998\ g/mol}{6.022\ x\ 10^{23}\ F^-/mol}$ = 3.155×10^{-23} g/F^-

unit cell mass = $(4\ K^+)(6.493 \times 10^{-23}\ g/K^+) + (4\ F^-)(3.155 \times 10^{-23}\ g/F^-) = 3.859 \times 10^{-22}$ g

unit cell volume = $[(535 \times 10^{-12}\ m)(100\ cm/m)]^3 = 1.531 \times 10^{-22}\ cm^3$

density = $\frac{mass\ of\ unit\ cell}{volume\ of\ unit\ cell} = \frac{3.859\ x\ 10^{-22}\ g}{1.531\ x\ 10^{-22}\ cm^3} = 2.52\ g/cm^3$

(e) $K(s) + 1/2\ F_2(g) \rightarrow KF(s)$ is a formation reaction.

$\Delta H^o_f(KF) = \frac{-22.83\ kJ}{0.0406\ mol} = -562$ kJ/mol

11 Solutions and Their Properties

11.1 Toluene is nonpolar and is insoluble in water.
Br_2 is nonpolar but because of its size is polarizable and is soluble in water.
KBr is an ionic compound and is very soluble in water.
toluene < Br_2 < KBr (solubility in H_2O)

11.2 (a) Na^+ has the larger (more negative) hydration energy because the Na^+ ion is smaller than the Cs^+ ion and water molecules can approach more closely and bind more tightly to the Na^+ ion.
(b) Ba^{2+} has the larger (more negative) hydration energy because of its higher charge.

11.3 NaCl, 58.44 amu; 1.00 mol NaCl = 58.44 g
1.00 L H_2O = 1000 mL = 1000 g (assuming a density of 1.00 g/mL)

$$\text{mass \% NaCl} = \frac{58.44\ \text{g}}{1000\ \text{g} + 58.44\ \text{g}} \times 100\% = 5.52 \text{ mass \%}$$

11.4 $$\text{ppm} = \frac{\text{mass of } CO_2}{\text{total mass of solution}} \times 10^6 \text{ ppm}$$

total mass of solution = density x volume = (1.3 g/L)(1.0 L) = 1.3 g

$$35 \text{ ppm} = \frac{\text{mass of } CO_2}{1.3\ \text{g}} \times 10^6 \text{ ppm}$$

$$\text{mass of } CO_2 = \frac{(35\ \text{ppm})(1.3\ \text{g})}{10^6\ \text{ppm}} = 4.6 \times 10^{-5} \text{ g } CO_2$$

11.5 Assume 1.00 L of sea water.
mass of 1.00 L = (1000 mL)(1.025 g/mL) = 1025 g

$$\frac{\text{mass NaCl}}{1025\ \text{g}} \times 100\% = 3.50 \text{ mass \%; mass NaCl} = \frac{1025\ \text{g} \times 3.50}{100} = 35.88 \text{ g}$$

There are 35.88 g NaCl per 1.00 L of solution.

$$M = \frac{\left(35.88\ \text{g NaCl} \times \frac{1\ \text{mol NaCl}}{58.44\ \text{g NaCl}}\right)}{1.00\ \text{L}} = 0.614\ M$$

11.6 $C_{27}H_{46}O$, 386.7 amu; $CHCl_3$, 119.4 amu; $40.0\ \text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 0.0400$ kg

$$\text{molality} = \frac{\text{mol } C_{27}H_{46}O}{\text{kg } CHCl_3} = \frac{\left(0.385\ \text{g} \times \frac{1\ \text{mol}}{386.7\ \text{g}}\right)}{0.0400\ \text{kg}} = 0.0249 \text{ mol/kg} = 0.0249\ m$$

$$X_{C_{27}H_{46}O} = \frac{\text{mol } C_{27}H_{46}O}{\text{mol } C_{27}H_{46}O + \text{mol } CHCl_3}$$

$$X_{C_{27}H_{46}O} = \frac{\left(0.385 \text{ g x } \frac{1 \text{ mol}}{386.7 \text{ g}}\right)}{\left[\left(0.385 \text{ g x } \frac{1 \text{ mol}}{386.7 \text{ g}}\right) + \left(40.0 \text{ g x } \frac{1 \text{ mol}}{119.4 \text{ g}}\right)\right]} = 2.96 \text{ x } 10^{-3}$$

11.7 CH_3CO_2Na, 82.03 amu

$$\text{kg } H_2O = (0.150 \text{ mol } CH_3CO_2Na)\left(\frac{1 \text{ kg } H_2O}{0.500 \text{ mol } CH_3CO_2Na}\right) = 0.300 \text{ kg } H_2O$$

$$\text{mass } CH_3CO_2Na = 0.150 \text{ mol } CH_3CO_2Na \text{ x } \frac{82.03 \text{ g } CH_3CO_2Na}{1 \text{ mol } CH_3CO_2Na} = 12.3 \text{ g } CH_3CO_2Na$$

mass of solution needed = 300 g + 12.3 g = 312 g

11.8 Assume you have a solution with 1.000 kg (1000 g) of H_2O. If this solution is 0.258 *m*, then it must also contain 0.258 mol glucose.

$$\text{mass of glucose} = 0.258 \text{ mol x } \frac{180.2 \text{ g}}{1 \text{ mol}} = 46.5 \text{ g glucose}$$

mass of solution = 1000 g + 46.5 g = 1046.5 g
density = 1.0173 g/mL

$$\text{volume of solution} = 1046.5 \text{ g x } \frac{1 \text{ mL}}{1.0173 \text{ g}} = 1028.7 \text{ mL}$$

$$\text{volume} = 1028.7 \text{ mL x } \frac{1 \text{ L}}{1000 \text{ mL}} = 1.029 \text{ L}; \qquad \text{molarity} = \frac{0.258 \text{ mol}}{1.029 \text{ L}} = 0.251 \text{ M}$$

11.9 Assume 1.00 L of solution.
mass of 1.00 L = (1.0042 g/mL)(1000 mL) = 1004.2 g of solution

$$0.500 \text{ mol } CH_3CO_2H \text{ x } \frac{60.05 \text{ g } CH_3CO_2H}{1 \text{ mol } CH_3CO_2H} = 30.02 \text{ g } CH_3CO_2H$$

$$1004.2 \text{ g} - 30.02 \text{ g} = 974.2 \text{ g} = 0.9742 \text{ kg of } H_2O; \qquad \text{molality} = \frac{0.500 \text{ mol}}{0.9742 \text{ kg}} = 0.513 \text{ } m$$

11.10 Assume you have 100.0 g of seawater.
mass NaCl = (0.0350)(100.0 g) = 3.50 g NaCl
mass H_2O = 100.0 g - 3.50 g = 96.5 g H_2O

NaCl, 58.44 amu; $\quad \text{mol NaCl} = 3.50 \text{ g x } \frac{1 \text{ mol}}{58.44 \text{ g}} = 0.0599 \text{ mol NaCl}$

$$\text{mass } H_2O = 96.5 \text{ g x } \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0965 \text{ kg } H_2O; \qquad \text{molality} = \frac{0.0599 \text{ mol}}{0.0965 \text{ kg}} = 0.621 \text{ } m$$

11.11 $M = k \cdot P$; $k = \frac{M}{P} = \frac{3.2 \times 10^{-2}\ M}{1.0\ atm} = 3.2 \times 10^{-2}\ mol/(L \cdot atm)$

11.12 (a) $M = k \cdot P = [3.2 \times 10^{-2}\ mol/(L \cdot atm)](2.5\ atm) = 0.080\ M$
(b) $M = k \cdot P = [3.2 \times 10^{-2}\ mol/(L \cdot atm)](4.0 \times 10^{-4}\ atm) = 1.3 \times 10^{-5}\ M$

11.13 $C_7H_6O_2$, 122.1 amu; C_2H_6O, 46.07 amu

$$X_{solv} = \frac{mol\ C_2H_6O}{mol\ C_2H_6O + mol\ C_7H_6O_2} = \frac{\left(100\ g \times \frac{1\ mol}{46.07\ g}\right)}{\left(100\ g \times \frac{1\ mol}{46.07\ g}\right) + \left(5.00\ g \times \frac{1\ mol}{122.1\ g}\right)} = 0.981$$

$P_{soln} = P_{solv} \cdot X_{solv} = (100.5\ mm\ Hg)(0.981) = 98.6\ mm\ Hg$

11.14 $P_{soln} = P_{solv} \cdot X_{solv}$; $X_{solv} = \frac{P_{soln}}{P_{solv}} = \frac{(55.3 - 1.30)\ mm\ Hg}{55.3\ mm\ Hg} = 0.976$

NaBr dissociates into two ions in aqueous solution.

$$X_{solv} = \frac{mol\ H_2O}{mol\ H_2O + mol\ Na^+ + mol\ Br^-}$$

$$X_{solv} = 0.976 = \frac{\left(250\ g \times \frac{1\ mol}{18.02\ g}\right)}{\left(250\ g \times \frac{1\ mol}{18.02\ g}\right) + x\ mol\ Na^+ + x\ mol\ Br^-}$$

$0.976 = \frac{13.9\ mol}{13.9\ mol + 2x\ mol}$; solve for x.

$0.976(13.9\ mol + 2x\ mol) = 13.9\ mol$
$13.566\ mol + 1.952\ x\ mol = 13.9\ mol$
$1.952\ x\ mol = 13.9\ mol - 13.566\ mol$

$$x\ mol = \frac{13.9\ mol - 13.566\ mol}{1.952} = 0.171\ mol$$

$x = 0.171\ mol\ Na^+ = 0.171\ mol\ Br^- = 0.171\ mol\ NaBr$

NaBr, 102.9 amu; mass NaBr = $0.171\ mol \times \frac{102.9\ g}{1\ mol} = 17.6\ g\ NaBr$

11.15 At any given temperature, the vapor pressure of a solution is lower than the vapor pressure of the pure solvent. The upper curve represents the vapor pressure of the pure solvent. The lower curve represents the vapor pressure of the solution.

11.16 C_2H_5OH, 46.07 amu; H_2O, 18.02 amu

(a) $25.0\ g\ C_2H_5OH \times \frac{1\ mol\ C_2H_5OH}{46.07\ g\ C_2H_5OH} = 0.5426\ mol\ C_2H_5OH$

$$100.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 5.549 \text{ mol } H_2O$$

$$X_{C_2H_5OH} = \frac{0.5426 \text{ mol}}{0.5426 \text{ mol} + 5.549 \text{ mol}} = 0.08907$$

$$X_{H_2O} = \frac{5.549 \text{ mol}}{0.5426 \text{ mol} + 5.549 \text{ mol}} = 0.9109$$

$$P_{soln} = X_{C_2H_5OH} P^o_{C_2H_5OH} + X_{H_2O} P^o_{H_2O}$$

$$P_{soln} = (0.08907)(61.2 \text{ mm Hg}) + (0.9109)(23.8 \text{ mm Hg}) = 27.1 \text{ mm Hg}$$

(b) $$100 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH} = 2.171 \text{ mol } C_2H_6O$$

$$25.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 1.387 \text{ mol } H_2O$$

$$X_{C_2H_5OH} = \frac{2.171 \text{ mol}}{2.171 \text{ mol} + 1.387 \text{ mol}} = 0.6102$$

$$X_{H_2O} = \frac{1.387 \text{ mol}}{2.171 \text{ mol} + 1.387 \text{ mol}} = 0.3898$$

$$P_{soln} = X_{C_2H_5OH} P^o_{C_2H_5OH} + X_{H_2O} P^o_{H_2O}$$

$$P_{soln} = (0.6102)(61.2 \text{ mm Hg}) + (0.3898)(23.8 \text{ mm Hg}) = 46.6 \text{ mm Hg}$$

11.17 (a) Because the vapor pressure of the solution (red curve) is higher than that of the first liquid (green curve), the vapor pressure of the second liquid must be higher than that of the solution (red curve). Because the second liquid has a higher vapor pressure than the first liquid, the second liquid has a lower boiling point.

(b)

11.18 $C_9H_8O_4$, 180.2 amu; $CHCl_3$ is the solvent. For $CHCl_3$, $K_b = 3.63 \frac{^oC \bullet kg}{mol}$

$$75.00 \text{ g } \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.075\,00 \text{ kg}$$

$$\Delta T_b = K_b \cdot m = \left(3.63\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{\left(1.50\ g\ x\ \frac{1\ mol}{180.2\ g}\right)}{0.075\ 00\ kg}\right) = 0.40^oC$$

Solution boiling point = $61.7^oC + \Delta T_b = 61.7^oC + 0.40^oC = 62.1^oC$

11.19 $MgCl_2$, 95.21 amu

$$110\ g\ x\ \frac{1\ kg}{1000\ g} = 0.110\ kg$$

$$\Delta T_f = K_f \cdot m \cdot i = \left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{\left(7.40\ g\ x\ \frac{1\ mol}{95.21\ g}\right)}{0.110\ kg}\right)(2.7) = 3.55^oC$$

Solution freezing point = $0.00^oC - \Delta T_f = 0.00^oC - 3.55^oC = -3.55^oC$

11.20 $\Delta T_f = K_f \cdot m \cdot i$; For KBr, i = 2.

Solution freezing point = $-2.95^oC = 0.00^oC - \Delta T_f$; $\Delta T_f = 2.95^oC$

$$m = \frac{\Delta T_f}{K_f \bullet i} = \frac{2.95^oC}{\left(1.86\ \frac{^oC \bullet kg}{mol}\right)(2)} = 0.793\ mol/kg = 0.793\ m$$

11.21 HCl, 36.46 amu; $\Delta T_f = K_f \cdot m \cdot i$

$$190\ g\ x\ \frac{1\ kg}{1000\ g} = 0.190\ kg$$

Solution freezing point = $-4.65^oC = 0.00^oC - \Delta T_f$; $\Delta T_f = 4.65^oC$

$$i = \frac{\Delta T_f}{K_f \bullet m} = \frac{4.65^oC}{\left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{9.12\ g\ x\ \frac{1\ mol}{36.46\ g}}{0.190\ kg}\right)} = 1.9$$

11.22 The red curve represents the vapor pressure of pure chloroform.

(a) The normal boiling point for a liquid is the temperature where the vapor pressure of the liquid equals 1 atm (760 mm Hg). The approximate boiling point of pure chloroform is 62^oC.

(b) The approximate boiling point of the solution is 69^oC.

$\Delta T_b = 69^oC - 62^oC = 7^oC$

$\Delta T_b = K_b \cdot m$; $\quad m = \dfrac{\Delta T_b}{K_b} = \dfrac{7^oC}{3.63 \dfrac{^oC \bullet kg}{mol}} = 2 \text{ mol/kg} = 2\ m$

11.23 For $CaCl_2$ there are 3 ions (solute particles)/$CaCl_2$

$\Pi = MRT$; For $CaCl_2$, $\Pi = 3MRT$

$\Pi = (3)(0.125 \text{ mol/L})\left(0.082\,06 \dfrac{L \bullet atm}{K \bullet mol}\right)(310 \text{ K}) = 9.54 \text{ atm}$

11.24 $\Pi = MRT$; $\quad M = \dfrac{\Pi}{RT} = \dfrac{(3.85 \text{ atm})}{\left(0.082\,06 \dfrac{L \bullet atm}{K \bullet mol}\right)(300 \text{ K})} = 0.156 \text{ M}$

11.25 $\Delta T_f = K_f \cdot m$; $m = \dfrac{\Delta T_f}{K_f} = \dfrac{2.10^oC}{37.7 \dfrac{^oC \bullet kg}{mol}} = 0.0557 \text{ mol/kg} = 0.0557\ m$

$35.00 \text{ g} \times \dfrac{1 \text{ kg}}{1000 \text{ g}} = 0.03500 \text{ kg}$

$\text{mol} = 0.0557 \dfrac{\text{mol}}{\text{kg}} \times 0.03500 \text{ kg} = 0.001\,95 \text{ mol naphthalene}$

$\text{molar mass of naphthalene} = \dfrac{0.250 \text{ g naphthalene}}{0.00195 \text{ mol naphthalene}} = 128 \text{ g/mol}$

11.26 $\Pi = MRT$; $\quad M = \dfrac{\Pi}{RT} = \dfrac{\left(149 \text{ mm Hg} \times \dfrac{1 \text{ atm}}{760 \text{ mm Hg}}\right)}{\left(0.08206 \dfrac{L \bullet atm}{K \bullet mol}\right)(298 \text{ K})} = 8.02 \times 10^{-3} \text{ M}$

300.0 mL = 0.3000 L

$(8.02 \times 10^{-3} \text{ mol/L})(0.3000 \text{ L}) = 0.002\,406 \text{ mol sucrose}$

$\text{molar mass of sucrose} = \dfrac{0.822 \text{ g sucrose}}{0.002\ 406 \text{ mol sucrose}} = 342 \text{ g/mol}$

11.27 (a) and (c)

(b) The mixture will begin to boil at ~50°C.
(d) After two cycles of boiling and condensing, the approximate composition of the liquid would 90% dichloromethane and 10% chloroform.

11.28 Both solvent molecules and small solute particles can pass through a semipermeable dialysis membrane. Only large colloidal particles such as proteins can't pass through. Only solvent molecules can pass through a semipermeable membrane used for osmosis.

Understanding Key Concepts

11.29 The upper curve is pure ether.
(a) The normal boiling point for ether is the temperature where the upper curve intersects the 760 mm Hg line, ~ 37°C.
(b) ΔT_b _3°C

$\Delta T_b = K_b \cdot m$; $\quad m = \dfrac{\Delta T_b}{K_b} = \dfrac{3^\circ C}{2.02 \dfrac{^\circ C \bullet kg}{mol}}$ _1.5 mol/kg _1.5 *m*

11.30 (a) < (b) < (c)

11.31 At any given temperature, the vapor pressure of a mixture of two pure liquids falls between the individual vapor pressures of the two pure liquids themselves. Because the vapor pressure of the mixture is greater than the vapor pressure of the solvent, the second liquid is more volatile (has a higher vapor pressure) than the solvent.

11.32 Assume that only the blue (open) spheres (solvent) can pass through the semipermeable membrane. There will be a net transfer of solvent from the right compartment (pure solvent) to the left compartment (solution) to achieve equilibrium.

11.33 At point 1, the temperature should be near the boiling point of the lower boiling solvent, $CHCl_3$, approximately 62°C.

At point 3, the temperature should be about halfway between the two boiling points at approximately 70°C.
At point 2, the temperature should be about halfway between the temperatures at points 1 and 3, approximately 66°C.

11.34 The vapor pressure of the NaCl solution is lower than that of pure H_2O. More H_2O molecules will go into the vapor from the pure H_2O than from the NaCl solution. More H_2O vapor molecules will go into the NaCl solution than into pure H_2O. The result is represented by (b).

11.35 (b) ~95°C

Additional Problems
Solutions and Energy Changes

11.36 The surface area of a solid plays an important role in determining how rapidly a solid dissolves. The larger the surface area, the more solid-solvent interactions, and the more rapidly the solid will dissolve. Powdered NaCl has a much larger surface area than a large block of NaCl, and it will dissolve more rapidly.

11.37 (a) a gas in a liquid – carbonated soft drink
(b) a solid in a solid – metal alloys (14-karat gold)
(c) a liquid in a solid – dental amalgam (Hg in Ag)

11.38 Substances tend to dissolve when the solute and solvent have the same type and magnitude of intermolecular forces; thus the rule of thumb "like dissolves like."

11.39 Both Br_2 and CCl_4 are nonpolar, and intermolecular forces for both are dispersion forces. H_2O is a polar molecule with dipole-dipole forces and hydrogen bonding. Therefore, Br_2 is more soluble in CCl_4.

11.40 Energy is required to overcome intermolecular forces holding solute particles together in the crystal. For an ionic solid, this is the lattice energy. Substances with higher lattice energies tend to be less soluble than substances with lower lattice energies.

11.41 SO_4^{2-} has the larger hydration energy because of its higher charge. Both SO_4^{2-} and ClO_4^- are comparable in size, so size is not a factor.

11.42 Ethyl alcohol and water are both polar with small dispersion forces. They both can hydrogen bond, and are miscible.
Pentyl alcohol is slightly polar and can hydrogen bond. It has, however, a relatively large dispersion force because of its size, which limits its water solubility.

11.43 The intermolecular forces associated with octane are dispersion forces. Both pentyl alcohol and methyl alcohol can hydrogen bond. Pentyl alcohol has relatively large dispersion forces because of its size. Methyl alcohol does not. Pentyl alcohol is soluble in octane; methyl alcohol is not.

11.44 $CaCl_2$, 110.98 amu
For a 1.00 *m* solution:
heat released = 81,300 J
mass of solution = 1000 g H_2O + 110.98 g $CaCl_2$ = 1110.98 g

$$\Delta T = \frac{q}{(\text{specific heat})(\text{mass of solution})} = \frac{81{,}300\ \text{J}}{[4.18\ \text{J/(K} \bullet \text{g)}](1110.98\ \text{g})} = 17.5\ \text{K} = 17.5^{\circ}\text{C}$$

Final temperature = $25.0^{\circ}C + 17.5^{\circ}C = 42.5^{\circ}C$

11.45 NH_4ClO_4, 117.48 amu
For a 1.00 *m* solution:
heat absorbed = 33,500 J
mass of solution = 1000 g H_2O + 117.48 g NH_4ClO_4 = 1117.48 g

$$\Delta T = \frac{q}{(\text{specific heat})(\text{mass of solution})} = \frac{-33{,}500\ \text{J}}{[4.18\ \text{J/(K} \bullet \text{g)}](1117.48\ \text{g})} = -7.2\ \text{K} = -7.2^{\circ}\text{C}$$

Final temperature = $25.0^{\circ}C - 7.2^{\circ}C = 17.8^{\circ}C$

Units of Concentration

11.46 $$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}; \qquad \text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

11.47 A saturated solution contains enough solute so that there is an equilibrium between dissolved solute and undissolved solid.
A supersaturated solution contains a greater-than-equilibrium amount of solute.

11.48 (a) Dissolve 0.150 mol of glucose in water; dilute to 1.00 L.
(b) Dissolve 1.135 mol of KBr in 1.00 kg of H_2O.
(c) Mix together 0.15 mol of CH_3OH with 0.85 mol of H_2O.

11.49 (a) Dissolve 15.5 mg urea in 100 mL water
(b) Choose a K^+ salt, say KCl, and dissolve 0.0075 mol (0.559 g) in water; dilute to100 mL.

11.50 $C_7H_6O_2$, 122.12 amu, 165 mL = 0.165 L

mol $C_7H_6O_2$ = (0.0268 mol/L)(0.165 L) = 0.004 42 mol

$$\text{mass } C_7H_6O_2 = 0.004\ 42 \text{ mol} \times \frac{122.12 \text{ g}}{1 \text{ mol}} = 0.540 \text{ g}$$

Dissolve 4.42 x 10^{-3} mol (0.540 g) of $C_7H_6O_2$ in enough $CHCl_3$ to make 165 mL of solution.

11.51 $C_7H_6O_2$, 122.12 amu

$$0.0268 \text{ mol } C_7H_6O_2 \times \frac{122.12 \text{ g } C_7H_6O_2}{1 \text{ mol } C_7H_6O_2} = 3.27 \text{ g } C_7H_6O_2$$

Dissolve 3.27 g of $C_7H_6O_2$ in 1.000 kg of $CHCl_3$, and take 165 mL of the solution.

11.52 (a) KCl, 74.6 amu

A 0.500 M KCl solution contains 37.3 g of KCl per 1.00 L of solution.

A 0.500 mass % KCl solution contains 5.00 g of KCl per 995 g of water.

The 0.500 M KCl solution is more concentrated (that is, it contains more solute per amount of solvent).

(b) Both solutions contain the same amount of solute. The 1.75 M solution contains less solvent than the 1.75 m solution. The 1.75 M solution is more concentrated.

11.53 (a) KI, 166.00 amu; KBr, 119.00 amu; assume 1.000 L = 1000 mL = 1000 g solution

$$10 \text{ ppm} = \frac{\text{mass KI}}{1000 \text{ g}} \times 10^6; \qquad \text{mass KI} = 0.010 \text{ g}$$

$$10{,}000 \text{ ppb} = \frac{\text{mass KBr}}{1000 \text{ g}} \times 10^9; \qquad \text{mass KBr} = 0.010 \text{ g}$$

Both solutions contain the same mass of solute in the same amount of solvent. Because the molar mass of KBr is less than that of KI, the number of moles of KBr is larger than the number of moles of KI. The KBr solution has a higher molarity than the KI solution.

(b) Because the mass % of the two solutions is the same, they both contain the same mass of solute and solution. Because the molar mass of KCl is less than that of citric acid, the number of moles of KCl is larger than the number of moles of citric acid. The KCl solution has a higher molarity than the citric acid solution.

11.54 (a) $C_6H_8O_7$, 192.12 amu

$$0.655 \text{ mol } C_6H_8O_7 \times \frac{192.12 \text{ g } C_6H_8O_7}{1 \text{ mol } C_6H_8O_7} = 126 \text{ g } C_6H_8O_7$$

$$\text{mass \% } C_6H_8O_7 = \frac{126 \text{ g}}{126 \text{ g} + 1000 \text{ g}} \times 100\% = 11.2 \text{ mass \%}$$

(b) 0.135 mg = 0.135 x 10^{-3} g

(5.00 mL H_2O)(1.00 g/mL) = 5.00 g H_2O

$$\text{mass \% KBr} = \frac{0.135 \times 10^{-3} \text{ g}}{(0.135 \times 10^{-3} \text{ g}) + 5.00 \text{ g}} \times 100\% = 0.002\ 70 \text{ mass \% KBr}$$

(c) mass % aspirin = $\frac{5.50\ \text{g}}{5.50\ \text{g} + 145\ \text{g}} \times 100\% = 3.65$ mass % aspirin

11.55 (a) molality = $\frac{0.655\ \text{mol}}{1.00\ \text{kg}} = 0.655\ m$

(b) KBr, 119.00 amu; 5.00 g = 0.005 00 kg

$$\text{molality} = \frac{\left(0.135 \times 10^{-3}\ \text{g} \times \frac{1\ \text{mol}}{119.00\ \text{g}}\right)}{0.005\,00\ \text{kg}} = 2.27 \times 10^{-4}\ \text{mol/kg} = 2.27 \times 10^{-4}\ m$$

(c) $C_9H_8O_4$, 180.16 amu; 145 g = 0.145 kg

$$\text{molality} = \frac{\left(5.50\ \text{g} \times \frac{1\ \text{mol}}{180.16\ \text{g}}\right)}{0.145\ \text{kg}} = 0.211\ \text{mol/kg} = 0.211\ m$$

11.56 $P_{O_3} = P_{total} \bullet X_{O_3}$

$$X_{O_3} = \frac{P_{O_3}}{P_{total}} = \frac{1.6 \times 10^{-9}\ \text{atm}}{1.3 \times 10^{-2}\ \text{atm}} = 1.2 \times 10^{-7}$$

Assume one mole of air (29 g/mol)

mol $O_3 = n_{air} \cdot X_{O_3} = (1\ \text{mol})(1.2 \times 10^{-7}) = 1.2 \times 10^{-7}$ mol O_3

O_3, 48.00 amu; mass $O_3 = 1.2 \times 10^{-7}$ mol $\times \frac{48.0\ \text{g}}{1\ \text{mol}} = 5.8 \times 10^{-6}$ g O_3

$$\text{ppm } O_3 = \frac{5.8 \times 10^{-6}\ \text{g}}{29\ \text{g}} \times 10^6 = 0.20\ \text{ppm}$$

11.57 Assume 1 mL of blood weighs 1 g. 1 dL = 0.1 L = 100 mL = 100 g

$$\text{ppb} = \frac{10 \times 10^{-6}\ \text{g}}{100\ \text{g}} \times 10^9 = 100\ \text{ppb}$$

11.58 (a) H_2SO_4, 98.08 amu; $\text{molality} = \frac{\left(25.0\ \text{g} \times \frac{1\ \text{mol}}{98.08\ \text{g}}\right)}{1.30\ \text{kg}} = 0.196\ \text{mol/kg} = 0.196\ m$

(b) $C_{10}H_{14}N_2$, 162.23 amu; CH_2Cl_2, 84.93 amu

$$2.25\ \text{g } C_{10}H_{14}N_2 \times \frac{1\ \text{mol } C_{10}H_{14}N_2}{162.23\ \text{g } C_{10}H_{14}N_2} = 0.0139\ \text{mol } C_{10}H_{14}N_2$$

$$80.0\ \text{g } CH_2Cl_2 \times \frac{1\ \text{mol } CH_2Cl_2}{84.93\ \text{g } CH_2Cl_2} = 0.942\ \text{mol } CH_2Cl_2$$

$$X_{C_{10}H_{14}N_2} = \frac{0.0139\ \text{mol}}{0.942\ \text{mol} + 0.0139\ \text{mol}} = 0.0145$$

$$X_{CH_2Cl_2} = \frac{0.942\ \text{mol}}{0.942\ \text{mol} + 0.0139\ \text{mol}} = 0.985$$

11.59 NaOCl, 74.44 amu

A 5.0 mass % aqueous solution of NaOCl contains 5.0 g NaOCl and 95 g H_2O.

$$\text{molality} = \frac{\left(5.0\ \text{g} \times \frac{1\ \text{mol}}{74.44\ \text{g}}\right)}{0.095\ \text{kg}} = 0.71\ \text{mol/kg} = 0.71\ m$$

$$5.0\ \text{g NaOCl} \times \frac{1\ \text{mol NaOCl}}{74.44\ \text{g NaOCl}} = 0.0672\ \text{mol NaOCl}$$

$$95\ \text{g } H_2O \times \frac{1\ \text{mol } H_2O}{18.02\ \text{g } H_2O} = 5.27\ \text{mol } H_2O$$

$$X_{NaOCl} = \frac{0.0672\ \text{mol}}{5.27\ \text{mol} + 0.0672\ \text{mol}} = 0.013$$

11.60 $$16.0\ \text{mass \%} = \frac{16.0\ \text{g } H_2SO_4}{16.0\ \text{g } H_2SO_4 + 84.0\ \text{g } H_2O}$$

H_2SO_4, 98.08 amu; density = 1.1094 g/mL

$$\text{volume of solution} = 100.0\ \text{g} \times \frac{1\,\text{mL}}{1.1094\ \text{g}} = 90.14\ \text{mL} = 0.090\ 14\ \text{L}$$

$$\text{molarity} = \frac{\left(16.0\ \text{g} \times \frac{1\ \text{mol}}{98.08\ \text{g}}\right)}{0.090\,14\ \text{L}} = 1.81\ \text{M}$$

11.61 $C_2H_6O_2$, 62.07 amu

A 40.0 mass % aqueous solution of $C_2H_6O_2$ contains 40.0 g $C_2H_6O_2$ and 60.0 g H_2O.

density = 1.0514 g/mL

$$\text{volume of solution} = 100.0\ \text{g} \times \frac{1\,\text{mL}}{1.0514\ \text{g}} = 95.1\ \text{mL} = 0.0951\ \text{L}$$

$$\text{molarity} = \frac{\left(40.0\ \text{g} \times \frac{1\ \text{mol}}{62.07\ \text{g}}\right)}{0.0951\ \text{L}} = 6.78\ \text{M}$$

11.62 $$\text{molality} = \frac{\left(40.0\ \text{g} \times \frac{1\ \text{mol}}{62.07\ \text{g}}\right)}{0.0600\ \text{kg}} = 10.7\ \text{mol/kg} = 10.7\ m$$

11.63 $\text{molality} = \dfrac{\left(16.0\ \text{g} \times \dfrac{1\ \text{mol}}{98.08\ \text{g}}\right)}{0.0840\ \text{kg}} = 1.94\ \text{mol/kg} = 1.94\ m$

11.64 $C_{19}H_{21}NO_3$, 311.34 amu; 1.5 mg = 1.5 x 10^{-3} g

$1.3 \times 10^{-3}\ \text{mol/kg} = \dfrac{\left(1.5 \times 10^{-3}\ \text{g} \times \dfrac{1\ \text{mol}}{311.34\ \text{g}}\right)}{\text{kg of solvent}}$; solve for kg of solvent.

$\text{kg of solvent} = \dfrac{\left(1.5 \times 10^{-3}\ \text{g} \times \dfrac{1\ \text{mol}}{311.34\ \text{g}}\right)}{1.3 \times 10^{-3}\ \text{mol/kg}} = 0.0037\ \text{kg}$

Because the solution is very dilute, kg of solvent ≈ kg of solution.

$\text{g of solution} = (0.0037\ \text{kg})\left(\dfrac{1000\ \text{g}}{1\ \text{kg}}\right) = 3.7\ \text{g}$

11.65 $C_{12}H_{22}O_{11}$, 342.30 amu

$32.5\ \text{g}\ C_{12}H_{22}O_{11} \times \dfrac{1\ \text{mol}\ C_{12}H_{22}O_{11}}{342.30\ \text{g}\ C_{12}H_{22}O_{11}} = 0.0949\ \text{mol}\ C_{12}H_{22}O_{11}$

$0.850\ m = 0.850\ \text{mol/kg} = \dfrac{0.0949\ \text{mol}}{\text{kg of}\ H_2O}$; $\text{kg of}\ H_2O = \dfrac{0.0949\ \text{mol}}{0.850\ \text{mol/kg}} = 0.112\ \text{kg}$

$\text{mass of}\ H_2O = 0.112\ \text{kg} \times \dfrac{1000\ \text{g}}{1\ \text{kg}} = 112\ \text{g}\ H_2O$

11.66 $C_6H_{12}O_6$, 180.16 amu; H_2O, 18.02 amu; Assume 1.00 L of solution.

mass of solution = (1000 mL)(1.0624 g/mL) = 1062.4 g

$\text{mass of solute} = 0.944\ \text{mol} \times \dfrac{180.16\ \text{g}}{1\ \text{mol}} = 170.1\ \text{g}\ C_6H_{12}O_6$

mass of H_2O = 1062.4 g - 170.1 g = 892.3 g H_2O

$\text{mol}\ C_6H_{12}O_6 = 0.944\ \text{mol}$; $\text{mol}\ H_2O = 892.3\ \text{g} \times \dfrac{1\ \text{mol}}{18.02\ \text{g}} = 49.5\ \text{mol}$

(a) $X_{C_6H_{12}O_6} = \dfrac{\text{mol}\ C_6H_{12}O_6}{\text{mol}\ C_6H_{12}O_6 + \text{mol}\ H_2O} = \dfrac{0.944\ \text{mol}}{0.944\ \text{mol} + 49.5\ \text{mol}} = 0.0187$

(b) $\text{mass \%} = \dfrac{\text{mass}\ C_6H_{12}O_6}{\text{total mass of solution}} \times 100\% = \dfrac{170.1\ \text{g}}{1062.4\ \text{g}} \times 100\% = 16.0\%$

(c) $\text{molality} = \dfrac{\text{mol}\ C_6H_{12}O_6}{\text{kg}\ H_2O} = \dfrac{0.944\ \text{mol}}{0.8923\ \text{kg}} = 1.06\ \text{mol/kg} = 1.06\ m$

11.67 $C_{12}H_{22}O_{11}$, 342.30 amu; Assume 1.00 L of solution.

mass of solution = (1000 mL)(1.0432 g/mL) = 1043.2 g

mass of solute = 0.335 mol $C_{12}H_{22}O_{11}$ x $\frac{342.30\ g\ C_{12}H_{22}O_{11}}{1\ mol\ C_{12}H_{22}O_{11}}$ = 114.7 g $C_{12}H_{22}O_{11}$

mass of H_2O = 1043.2 g - 114.7 g = 928.5 g H_2O

mol $C_{12}H_{22}O_{11}$ = 0.335 mol; 928.5 g H_2O x $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$ = 51.53 mol H_2O

$$X_{C_{12}H_{22}O_{11}} = \frac{0.335\ mol}{51.53\ mol + 0.335\ mol} = 0.006\ 46$$

mass % $C_{12}H_{22}O_{11}$ = $\frac{114.7\ g}{1043.2\ g}$ x 100% = 11.0 mass % $C_{12}H_{22}O_{11}$

molality = $\frac{0.335\ mol}{0.9285\ kg}$ = 0.361 mol/kg = 0.361 *m*

Solubility and Henry's Law

11.68 $M = k \cdot P = (0.091\ \frac{mol}{L \bullet atm})(0.75\ atm) = 0.068\ M$

11.69 $M = k \cdot P$; $k = \frac{M}{P} = \frac{0.195\ M}{1.00\ atm} = 0.195\ mol/(L \cdot atm)$

$P = 25.5\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg} = 0.0336\ atm$

$M = k \cdot P = (0.195\ \frac{mol}{L \bullet atm})(0.0336\ atm) = 6.55 \times 10^{-3}\ M$

11.70 $M = k \cdot P$

Calculate k: $k = \frac{M}{P} = \frac{2.21 \times 10^{-3}\ mol/L}{1.00\ atm} = 2.21 \times 10^{-3}\ \frac{mol}{L \bullet atm}$

Convert 4 mg/L to mol/L:

4 mg = 4×10^{-3} g

$$O_2\ molarity = \frac{\left(4 \times 10^{-3}\ g \times \frac{1\ mol}{32.00\ g}\right)}{1.00\ L} = 1.25 \times 10^{-4}\ M$$

$$P_{O_2} = \frac{M}{k} = \frac{1.25 \times 10^{-4}\ \frac{mol}{L}}{2.21 \times 10^{-3}\ \frac{mol}{L \bullet atm}} = 0.06\ atm$$

11.71 $k = 1.93 \times 10^{-3}\ mol/(L \cdot atm)$

$$M = k \cdot P = [1.93 \times 10^{-3}\ mol/(L \cdot atm)]\left(68\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right) = 1.73 \times 10^{-4}\ mol/L$$

$$1.73 \times 10^{-4} \text{ mol/L} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} \times \frac{1 \text{ mg}}{1 \times 10^{-3} \text{ g}} = 5.5 \text{ mg/L}$$

11.72 [Xe] = 10 mmol/L = 0.010 M at STP

$$M = k \cdot P; \; k = \frac{M}{P} = \frac{0.010 \text{ M}}{1.0 \text{ atm}} = 0.010 \text{ mol/(L} \cdot \text{ atm)}$$

11.73 Assuming H_2O as the solvent, NH_3 does not obey Henry's law because NH_3 can both hydrogen bond and react with H_2O.

Colligative Properties

11.74 The difference in entropy between the solvent in a solution and a pure solvent is responsible for colligative properties.

11.75 Osmotic pressure is the amount of pressure that needs to be applied to cause osmosis to stop.

11.76 NaCl is a nonvolatile solute. Methyl alcohol is a volatile solute. When NaCl is added to water, the vapor pressure of the solution is decreased, which means that the boiling point of the solution will increase. When methyl alcohol is added to water, the vapor pressure of the solution is increased which means that the boiling point of the solution will decrease.

11.77 When 100 mL of 9 M H_2SO_4 at 0^oC is added to 100 mL of liquid water at 0^oC, the temperature rises because ΔH_{soln} for H_2SO_4 is exothermic.
When 100 mL of 9 M H_2SO_4 at 0^oC is added to 100 g of solid ice at 0^oC, some of the ice will melt (an endothermic process) and the temperature will fall because the H_2SO_4 (solute) lowers the freezing point of the ice/water mixture.

11.78

11.79 Molality is a temperature independent concentration unit. For freezing point depression and boiling point elevation, molality is used so that the solute concentration is independent of temperature changes. Molarity is temperature dependent. Molarity can be used for osmotic pressure because osmotic pressure is measured at a fixed

temperature.

11.80 (a) CH_4N_2O, 60.06 amu; H_2O, 18.02 amu

$$10.0 \text{ g } CH_4N_2O \times \frac{1 \text{ mol } CH_4N_2O}{60.06 \text{ g } CH_4N_2O} = 0.167 \text{ mol } CH_4N_2O$$

$$150.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 8.32 \text{ mol } H_2O$$

$$X_{H_2O} = \frac{8.32 \text{ mol}}{8.32 \text{ mol} + 0.167 \text{ mol}} = 0.980$$

$$P_{soln} = P^o_{H_2O} \bullet X_{H_2O} = (71.93 \text{ mm Hg})(0.980) = 70.5 \text{ mm Hg}$$

(b) LiCl, 42.39 amu; $10.0 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} = 0.236 \text{ mol LiCl}$

LiCl dissociates into $Li^+(aq)$ and $Cl^-(aq)$ in H_2O.

mol Li^+ = mol Cl^- = mol LiCl = 0.236 mol

$$150.0 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 8.32 \text{ mol } H_2O$$

$$X_{H_2O} = \frac{8.32 \text{ mol}}{8.32 \text{ mol} + 0.236 \text{ mol} + 0.236 \text{ mol}} = 0.946$$

$$P_{soln} = P^o_{H_2O} \bullet X_{H_2O} = (71.93 \text{ mm Hg})(0.946) = 68.0 \text{ mm Hg}$$

11.81 $C_6H_{12}O_6$, 180.16 amu; CH_3OH, 32.04 amu

$$16.0 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180.16 \text{ g } C_6H_{12}O_6} = 0.0888 \text{ mol } C_6H_{12}O_6$$

$$80.0 \text{ g } CH_3OH \times \frac{1 \text{ mol } CH_3OH}{32.04 \text{ g } CH_3OH} = 2.50 \text{ mol } CH_3OH$$

$$X_{CH_3OH} = \frac{2.50 \text{ mol}}{2.50 \text{ mol} + 0.0888 \text{ mol}} = 0.966$$

$$P_{soln} = P^o_{CH_3OH} \bullet X_{CH_3OH} = (140 \text{ mm Hg})(0.966) = 135 \text{ mm Hg}$$

11.82 For H_2O, $K_b = 0.51 \frac{^oC \bullet kg}{mol}$; 150.0 g = 0.1500 kg

(a) $\Delta T_b = K_b \cdot m = \left(0.51 \frac{^oC \bullet kg}{mol}\right)\left(\frac{0.167 \text{ mol}}{0.1500 \text{ kg}}\right) = 0.57^oC$

Solution boiling point = $100.00^oC + \Delta T_b = 100.00^oC + 0.57^oC = 100.57^oC$

(b) $\Delta T_b = K_b \cdot m = \left(0.51 \frac{^oC \bullet kg}{mol}\right)\left(\frac{2(0.236 \text{ mol})}{0.1500 \text{ kg}}\right) = 1.6^oC$

Solution boiling point = $100.00^oC + \Delta T_b = 100.00^oC + 1.6^oC = 101.6^oC$

11.83 For H_2O, $K_f = 1.86 \frac{^oC \bullet kg}{mol}$; 150.0 g = 0.1500 kg

(a) $\Delta T_f = K_f \cdot m = \left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{0.167\ mol}{0.1500\ kg}\right) = 2.07^oC$

Solution freezing point = $0.00^oC - \Delta T_f = 0.00^oC - 2.07^oC = -2.07^oC$

(b) $\Delta T_f = K_f \cdot m = \left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{2(0.236\ mol)}{0.1500\ kg}\right) = 5.85^oC$

Solution freezing point = $0.00^oC - \Delta T_f = 0.00^oC - 5.85^oC = -5.85^oC$

11.84 $\Delta T_f = K_f \cdot m \cdot i$

Solution freezing point = $-4.3^oC = 0.00^oC - \Delta T_f$; $\Delta T_f = 4.3^oC$

$$i = \frac{\Delta T_f}{K_f \bullet m} = \frac{4.3^oC}{\left(1.86\ \frac{^oC \bullet kg}{mol}\right)(1.0\ mol/kg)} = 2.3$$

11.85 $\Delta T_b = K_b \cdot m \cdot i = \left(0.51\frac{^oC \bullet kg}{mol}\right)(0.75\ mol/kg)(1.85) = 0.71^oC$

Solution boiling point = $100.00^oC + \Delta T_b = 100.00^oC + 0.71^oC = 100.71^oC$

11.86 Acetone, C_3H_6O, 58.08 amu, $P^o_{C_3H_6O} = 285$ mm Hg

Ethyl acetate, $C_4H_8O_2$, 88.11 amu, $P^o_{C_4H_8O_2} = 118$ mm Hg

$$25.0\ g\ C_3H_6O\ \times \frac{1\ mol\ C_3H_6O}{58.08\ g\ C_3H_6O} = 0.430\ mol\ C_3H_6O$$

$$25.0\ g\ C_4H_8O_2\ \times \frac{1\ mol\ C_4H_8O_2}{88.11\ g\ C_4H_8O_2} = 0.284\ mol\ C_4H_8O_2$$

$$X_{C_3H_6O} = \frac{0.430\ mol}{0.430\ mol + 0.284\ mol} = 0.602; \quad X_{C_4H_8O_2} = \frac{0.284\ mol}{0.430\ mol + 0.284\ mol} = 0.398$$

$P_{soln} = P^o_{C_3H_6O} \bullet X_{C_3H_6O} + P^o_{C_4H_8O_2} \bullet X_{C_4H_8O_2}$

$P_{soln} = (285\ mm\ Hg)(0.602) + (118\ mm\ Hg)(0.398) = 219\ mm\ Hg$

11.87 $CHCl_3$, 119.38 amu, $P^o_{CHCl_3} = 205$ mm Hg; CH_2Cl_2, 84.93 amu, $P^o_{CH_2Cl_2} = 415$ mm Hg

$$15.0\ g\ CHCl_3\ \times \frac{1\ mol\ CHCl_3}{119.38\ g\ CHCl_3} = 0.126\ mol\ CHCl_3$$

$$37.5\ g\ CH_2Cl_2\ \times \frac{1\ mol\ CH_2Cl_2}{84.93\ g\ CH_2Cl_2} = 0.442\ mol\ CH_2Cl_2$$

$$X_{CHCl_3} = \frac{0.126\ mol}{0.126\ mol + 0.442\ mol} = 0.222; \quad X_{CH_2Cl_2} = \frac{0.442\ mol}{0.126\ mol + 0.442\ mol} = 0.778$$

$P_{soln} = P^o_{CHCl_3} \bullet X_{CHCl_3} + P^o_{CH_2Cl_2} \bullet X_{CH_2Cl_2}$

$P_{soln} = (205\ mm\ Hg)(0.222) + (415\ mm\ Hg)(0.778) = 368\ mm\ Hg$

11.88 In the liquid, $X_{acetone} = 0.602$ and $X_{ethyl\ acetate} = 0.398$
In the vapor, $P_{Total} = 219$ mm Hg
$P_{acetone} = P^{o}_{acetone} \cdot X_{acetone} = (285\ mm\ Hg)(0.602) = 172\ mm\ Hg$
$P_{ethyl\ acetate} = P^{o}_{ethyl\ acetate} \cdot X_{ethyl\ acetate} = (118\ mm\ Hg)(0.398) = 47\ mm\ Hg$

$$X_{acetone} = \frac{P_{acetone}}{P_{total}} = \frac{172\ mm\ Hg}{219\ mm\ Hg} = 0.785; \quad X_{ethyl\ acetate} = \frac{P_{ethyl\ acetate}}{P_{total}} = \frac{47\ mm\ Hg}{219\ mm\ Hg} = 0.215$$

11.89 In the liquid, $X_{CHCl_3} = 0.222$ and $X_{CH_2Cl_2} = 0.778$
In the vapor, $P_{total} = 368$ mm Hg
$P_{CHCl_3} = P^{o}_{CHCl_3} \bullet X_{CHCl_3} = (205\ mm\ Hg)(0.222) = 45.5\ mm\ Hg$
$P_{CH_2Cl_2} = P^{o}_{CH_2Cl_2} \bullet X_{CH_2Cl_2} = (415\ mm\ Hg)(0.778) = 323\ mm\ Hg$

$$X_{CHCl_3} = \frac{P_{CHCl_3}}{P_{total}} = \frac{45.5\ mm\ Hg}{368\ mm\ Hg} = 0.124; \qquad X_{CH_2Cl_2} = \frac{P_{CH_2Cl_2}}{P_{total}} = \frac{323\ mm\ Hg}{368\ mm\ Hg} = 0.876$$

11.90 $C_9H_8O_4$, 180.16 amu; 215 g = 0.215 kg

$$\Delta T_b = K_b \cdot m = 0.47^{o}C; \qquad K_b = \frac{\Delta T_b}{m} = \frac{0.47^{o}C}{\left(\frac{5.00\ g \times \frac{1\ mol}{180.16\ g}}{0.215\ kg}\right)} = 3.6\ \frac{^{o}C \bullet kg}{mol}$$

11.91 $C_6H_8O_6$, 176.13 amu; 50.0 g = 0.0500 kg

$$\Delta T_f = K_f \cdot m = 1.33^{o}C; \qquad K_f = \frac{\Delta T_f}{m} = \frac{1.33\ ^{o}C}{\left(\frac{3.00\ g \times \frac{1\ mol}{176.13\ g}}{0.0500\ kg}\right)} = 3.90\ \frac{^{o}C \bullet kg}{mol}$$

11.92 $$\Delta T_b = K_b \cdot m = 1.76^{o}C; \qquad m = \frac{\Delta T_b}{K_b} = \frac{1.76^{o}C}{3.07\ \frac{^{o}C \bullet kg}{mol}} = 0.573\ m$$

11.93 $C_6H_{12}O_6$, 180.16 amu

For ethyl alcohol, $K_b = 1.22\ \frac{^{o}C \bullet kg}{mol}$; 285 g = 0.285 kg

$$\Delta T_b = K_b \cdot m = \left(1.22\ \frac{^{o}C \bullet kg}{mol}\right)\left(\frac{26.0\ g \times \frac{1\ mol}{180.16\ g}}{0.285\ kg}\right) = 0.618^{o}C$$

Solution boiling point = normal boiling point + $\Delta T_b = 79.1^{o}C$
Normal boiling point = $79.1^{o}C - \Delta T_b = 79.1^{o}C - 0.618^{o}C = 78.5^{o}C$

11.94 $\Pi = MRT$

(a) NaCl 58.44 amu; 350.0 mL = 0.3500 L

There are 2 moles of ions/mole of NaCl

$$\Pi = (2)\left(\frac{5.00\ \text{g x}\ \frac{1\,\text{mol}}{58.44\ \text{g}}}{0.3500\ \text{L}}\right)\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(323\ \text{K}) = 13.0\ \text{atm}$$

(b) CH_3CO_2Na, 82.03 amu; 55.0 mL = 0.0550 L

There are 2 moles of ions/mole of CH_3CO_2Na

$$\Pi = (2)\left(\frac{6.33\ \text{g x}\ \frac{1\ \text{mol}}{82.03\ \text{g}}}{0.0550\ \text{L}}\right)\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(283\,\text{K}) = 65.2\ \text{atm}$$

11.95 $$\Pi = MRT = \left(\frac{11.5\,\text{x}\,10^{-3}\ \text{g x}\ \frac{1\ \text{mol}}{5990\ \text{g}}}{0.006\,60\ \text{L}}\right)\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(298\,\text{K}) = 0.007\ 11\ \text{atm}$$

$$\Pi = 0.007\ 11\ \text{atm x}\ \frac{760\ \text{mm Hg}}{1\ \text{atm}} = 5.41\ \text{mm Hg}$$

$$\text{height of } H_2O \text{ column} = 5.41\ \text{mm Hg x}\ \frac{13.534\ \text{mm}\ H_2O}{1.00\ \text{mm Hg}} = 73.2\ \text{mm}$$

$$\text{height of } H_2O \text{ column} = 73.2\ \text{mm x}\ \frac{1\ \text{m}}{1000\ \text{mm}} = 0.0732\ \text{m}$$

11.96 $\Pi = MRT$; $$M = \frac{\Pi}{RT} = \frac{4.85\ \text{atm}}{\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(300\ \text{K})} = 0.197\ \text{M}$$

11.97 $\Pi = MRT$; $$M = \frac{\Pi}{RT} = \frac{7.7\ \text{atm}}{\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(310\ \text{K})} = 0.30\ \text{M}$$

Uses of Colligative Properties

11.98 Osmotic pressure is most often used for the determination of molecular mass because, of the four colligative properties, osmotic pressure gives the largest colligative property change per mole of solute.

11.99 $C_6H_{12}O_6$ does not dissociate in aqueous solution. LiCl and NaCl both dissociate into two solute particles per formula unit in aqueous solution. $CaCl_2$ dissociates into three solute particles per formula unit in aqueous solution. Assume that you have 1.00 g of each

substance. Calculate the number of moles of solute particles in 1.00 g of each substance.

$C_6H_{12}O_6$, 180.2 amu; moles solute particles = $1.00\ g \times \frac{1\ mol}{180.2\ g} = 0.005\ 55$ moles

LiCl, 42.4 amu; moles solute particles = $2\left(1.00\ g \times \frac{1\ mol}{42.4\ g}\right) = 0.0472$ moles

NaCl, 58.4 amu; moles solute particles = $2\left(1.00\ g \times \frac{1\ mol}{58.4\ g}\right) = 0.0342$ moles

$CaCl_2$, 111.0 amu; moles solute particles = $3\left(1.00\ g \times \frac{1\ mol}{111.0\ g}\right) = 0.0270$ moles

LiCl produces more solute particles/gram than any of the other three substances. LiCl would be the most efficient per unit mass.

11.100 $\Pi = 407.2\ mm\ Hg \times \frac{1\ atm}{760\ mm\ Hg} = 0.5358\ atm$

$\Pi = MRT;\ M = \frac{\Pi}{RT} = \frac{0.5358\ atm}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298.15\ K)} = 0.021\ 90\ M$

$200.0\ mL \times \frac{1\ L}{1000\ mL} = 0.2000\ L$

mol cellobiose = (0.2000 L)(0.021 90 mol/L) = 4.380×10^{-3} mol

molar mass of cellobiose = $\frac{1.500\ g\ cellobiose}{4.380 \times 10^{-3}\ mol\ cellobiose} = 342.5\ g/mol$

molecular mass = 342.5 amu

11.101 height of Hg column = $32.9\ cm\ H_2O \times \frac{1.00\ cm\ Hg}{13.534\ cm\ H_2O} = 2.43\ cm\ Hg$

$\Pi = 2.43\ cm\ Hg \times \frac{1.00\ atm}{76.0\ cm\ Hg} = 0.0320\ atm$

$\Pi = MRT;\quad M = \frac{\Pi}{RT} = \frac{0.0320\ atm}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.00131\ M$

$20.0\ mL \times \frac{1\ L}{1000\ mL} = 0.0200\ L$

$15.0\ mg \times \frac{1.00\ g}{1000\ mg} = 0.0150\ g$

mol met-enkephalin = (0.0200 L)(0.001 31 mol/L) = 2.62×10^{-5} mol

molar mass of met-enkephalin = $\frac{0.0150\ \text{g met-enkephalin}}{2.62\ \text{x}\ 10^{-5}\ \text{mol met-enkephalin}} = 573\ \text{g/mol}$

molecular mass = 573 amu

11.102 HCl is a strong electrolyte in H_2O and completely dissociates into two solute particles per each HCl.
HF is a weak electrolyte in H_2O. Only a few percent of the HF molecules dissociates into ions.

11.103 Na_2SO_4, 142.0 amu; $m = \frac{\left(71\ \text{g x}\ \frac{1\ \text{mol}}{142.0\ \text{g}}\right)}{1.00\ \text{kg}} = 0.50\ \text{mol/kg} = 0.50\ m$

$\Delta T_b = K_b \cdot m = \left(0.51\ \frac{^{o}\text{C} \bullet \text{kg}}{\text{mol}}\right)(0.50\ m) = 0.26^{o}\text{C}$

The experimental ΔT is approximately 3 times that predicted by the equation above because Na_2SO_4 dissociates into three solute particles (2 Na^+ and SO_4^{2-}) in aqueous solution.

11.104 First, determine the empirical formula:
Assume 100.0 g of β-carotene.

10.51% H $\qquad$ 10.51 g H x $\frac{1\ \text{mol H}}{1.008\ \text{g H}} = 10.43\ \text{mol H}$

89.49% C $\qquad$ 89.49 g C x $\frac{1\ \text{mol C}}{12.01\ \text{g C}} = 7.45\ \text{mol C}$

$C_{7.45}H_{10.43}$; Divide each subscript by the smaller, 7.45.

$C_{7.45\ /\ 7.45}H_{10.43\ /\ 7.45}$

$CH_{1.4}$

Multiply each subscript by 5 to obtain integers. Empirical formula is C_5H_7, 67.1 amu.
Second, calculate the molecular mass:

$\Delta T_f = K_f \cdot m$; $\qquad m = \frac{\Delta T_f}{K_f} = \frac{1.17^{o}\text{C}}{37.7\ \frac{^{o}\text{C} \bullet \text{kg}}{\text{mol}}} = 0.0310\ \text{mol/kg} = 0.0310\ m$

$1.50\ \text{g x}\ \frac{1\text{kg}}{1000\ \text{g}} = 1.50\ \text{x}\ 10^{-3}\ \text{kg}$

mol β-carotene = $(1.50\ \text{x}\ 10^{-3}\ \text{kg})(0.0310\ \text{mol/kg}) = 4.65\ \text{x}\ 10^{-5}\ \text{mol}$

molar mass of β-carotene = $\frac{0.0250\ \text{g}\ \beta\text{-carotene}}{4.65\ \text{x}\ 10^{-5}\ \text{mol}\ \beta\text{-carotene}} = 538\ \text{g/mol}$

molecular mass = 538 amu

Finally, determine the molecular formula:
Divide the molecular mass by the empirical formula mass.

$\frac{538\ \text{amu}}{67.1\ \text{amu}} = 8$; molecular formula is $C_{(8 \times 5)}H_{(8 \times 7)}$, or $C_{40}H_{56}$

11.105 First, determine the empirical formula:
Assume a 100.0 g sample of lysine.

49.29% C $\quad 49.29\ \text{g C} \times \frac{1\ \text{mol C}}{12.011\ \text{g C}} = 4.10\ \text{mol C}$

9.65% H $\quad 9.65\ \text{g H} \times \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 9.57\ \text{mol H}$

19.16% N $\quad 19.16\ \text{g N} \times \frac{1\ \text{mol N}}{14.007\ \text{g N}} = 1.37\ \text{mol N}$

21.89% O $\quad 21.89\ \text{g O} \times \frac{1\ \text{mol O}}{15.999\ \text{g O}} = 1.37\ \text{mol O}$

$C_{4.10}H_{9.57}N_{1.37}O_{1.37}$; Divide each subscript by the smallest, 1.37.
$C_{4.10\ /\ 1.37}H_{9.57\ /\ 1.37}N_{1.37\ /\ 1.37}O_{1.37\ /\ 1.37}$
Empirical formula is C_3H_7NO, 73.09 amu
Second, calculate the molecular mass:

$\Delta T_f = K_f \cdot m = 1.37\ ^oC$; $\quad m = \frac{\Delta T_f}{K_f} = \frac{1.37\ ^oC}{8.00\ \frac{^oC \bullet kg}{mol}} = 0.171\ \text{mol/kg} = 0.171\ m$

$1.200\ \text{g} \times \frac{1\text{kg}}{1000\ \text{g}} = 1.200 \times 10^{-3}\ \text{kg}$

$30.0\ \text{mg} \times \frac{1.00\ \text{g}}{1000\ \text{mg}} = 0.0300\ \text{g}$

mol lysine = $(1.200 \times 10^{-3}\ \text{kg})(0.171\ \text{mol/kg}) = 2.05 \times 10^{-4}\ \text{mol}$

molar mass of lysine = $\frac{0.0300\ \text{g lysine}}{2.05 \times 10^{-4}\ \text{mol lysine}} = 146\ \text{g/mol}$

molecular mass = 146 amu
Finally, determine the molecular formula:
Divide the molecular mass by the empirical formula mass.

$\frac{146\ \text{amu}}{73.09\ \text{amu}} = 2$; molecular formula is $C_{(2 \times 3)}H_{(2 \times 7)}N_{(2 \times 1)}O_{(2 \times 1)}$, or $C_6H_{14}N_2O_2$

General Problems

11.106 K_f for snow (H_2O) is $1.86\ \frac{^oC \bullet kg}{mol}$. Reasonable amounts of salt are capable of lowering the freezing point (ΔT_f) of the snow below an air temperature of -2°C. Reasonable amounts of salt, however, are not capable of causing a ΔT_f of more than 30°C which would be required if it is to melt snow when the air temperature is -30°C.

11.107 KBr, 119.00 amu; for KBr, i = 2

$$125\text{ g} \times \frac{1\text{kg}}{1000\text{ g}} = 0.125\text{ kg}$$

$\Delta T_b = 103.2\ ^oC - 100.0\ ^oC = 3.2\ ^oC$

$$\Delta T_b = K_b \cdot m \cdot i; \qquad m = \frac{\Delta T_b}{K_b \bullet 2} = \frac{3.2\ ^oC}{\left(0.51\ \frac{^oC \bullet kg}{mol}\right)(2)} = 3.137\text{ mol/kg} = 3.137\ m$$

mol KBr = (0.125 kg)(3.137 mol/kg) = 0.392 mol KBr

$$\text{mass of KBr} = 0.392\text{ mol KBr} \times \frac{119.00\text{ g KBr}}{1\text{ mol KBr}} = 47\text{ g KBr}$$

11.108 $C_2H_6O_2$, 62.07 amu; $\Delta T_f = 22.0^oC$

$$\Delta T_f = K_f \cdot m; \qquad m = \frac{\Delta T_f}{K_f} = \frac{22.0^oC}{1.86\ \frac{^oC \bullet kg}{mol}} = 11.8\text{ mol/kg} = 11.8\ m$$

mol $C_2H_6O_2$ = (3.55 kg)(11.8 mol/kg) = 41.9 mol $C_2H_6O_2$

$$\text{mass } C_2H_6O_2 = 41.9\text{ mol } C_2H_6O_2 \times \frac{62.07\text{ g } C_2H_6O_2}{1\text{ mol } C_2H_6O_2} = 2.60 \times 10^3\text{ g } C_2H_6O_2$$

11.109 The vapor pressure of toluene is lower than the vapor pressure of benzene at the same temperature. When 1 mL of toluene is added to 100 mL of benzene, the vapor pressure of the solution decreases, which means that the boiling point of the solution will increase. When 1 mL of benzene is added to 100 mL of toluene, the vapor pressure of the solution increases, which means that the boiling point of the solution will decrease.

11.110 When solid $CaCl_2$ is added to liquid water, the temperature rises because ΔH_{soln} for $CaCl_2$ is exothermic.
When solid $CaCl_2$ is added to ice at 0^oC, some of the ice will melt (an endothermic process) and the temperature will fall because the $CaCl_2$ lowers the freezing point of an ice/water mixture.

11.111 AgCl, 143.32 amu; there are 2 ions/AgCl

$\Pi = 2MRT$

$$\Pi = 2\left(\frac{0.007 \times 10^{-3}\text{ g} \times \frac{1\text{ mol}}{143.32\text{ g}}}{0.001\text{ L}}\right)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(278\text{ K}) = 0.002\text{ atm}$$

11.112 $C_{10}H_8$, 128.17 amu; $\Delta T_f = 0.35^oC$

$$\Delta T_f = K_f \cdot m; m = \frac{\Delta T_f}{K_f} = \frac{0.35^{o}C}{5.12\ \frac{^{o}C \bullet kg}{mol}} = 0.0684\ \text{mol/kg} = 0.0684\ m$$

$$150.0\ \text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 0.1500\ \text{kg}$$

mol $C_{10}H_8$ = (0.1500 kg)(0.0684 mol/kg) = 0.0103 mol $C_{10}H_8$

$$\text{mass } C_{10}H_8 = 0.0103\ \text{mol } C_{10}H_8 \times \frac{128.17\ \text{g } C_{10}H_8}{1\ \text{mol } C_{10}H_8} = 1.3\ \text{g } C_{10}H_8$$

11.113 Br_2, 159.81 amu; CCl_4, 153.82 amu

$$P^{o}_{Br_2} = 30.5\ \text{kPa} \times \frac{760\ \text{mm Hg}}{101.325\ \text{kPa}} = 228.8\ \text{mm Hg}$$

$$P^{o}_{CCl_4} = 16.5\ \text{kPa} \times \frac{760\ \text{mm Hg}}{101.325\ \text{kPa}} = 123.8\ \text{mm Hg}$$

$$1.50\ \text{g } Br_2 \times \frac{1\ \text{mol } Br_2}{159.81\ \text{g } Br_2} = 9.39 \times 10^{-3}\ \text{mol } Br_2$$

$$145.0\ \text{g } CCl_4 \times \frac{1\ \text{mol } CCl_4}{153.82\ \text{g } CCl_4} = 0.943\ \text{mol } CCl_4$$

$$X_{Br_2} = \frac{9.39 \times 10^{-3}\ \text{mol}}{(0.943\ \text{mol}) + (9.39 \times 10^{-3}\ \text{mol})} = 0.009\ 86$$

$$X_{CCl_4} = \frac{0.943\ \text{mol}}{(0.943\ \text{mol}) + (9.39 \times 10^{-3}\ \text{mol})} = 0.990$$

$$P_{soln} = P^{o}_{Br_2} \bullet X_{Br_2} + P^{o}_{CCl_4} \bullet X_{CCl_4}$$

P_{soln} = (228.8 mm Hg)(0.009 86) + (123.8 mm Hg)(0.990) = 125 mm Hg

11.114 NaCl, 58.44 amu; there are 2 ions/NaCl

A 3.5 mass % aqueous solution of NaCl contains 3.5 g NaCl and 96.5 g H_2O.

$$\text{molality} = \frac{\left(3.5\ \text{g} \times \frac{1\ \text{mol}}{58.44\ \text{g}}\right)}{0.0965\ \text{kg}} = 0.62\ \text{mol/kg} = 0.62\ m$$

$$\Delta T_f = K_f \cdot 2 \cdot m = \left(1.86\ \frac{^{o}C \bullet kg}{mol}\right)(2)(0.62\ \text{mol/kg}) = 2.3^{o}C$$

Solution freezing point = $0.0^{o}C - \Delta T_f = 0.0^{o}C - 2.3^{o}C = -2.3^{o}C$

$$\Delta T_b = K_b \cdot 2 \cdot m = \left(0.51\ \frac{^{o}C \bullet kg}{mol}\right)(2)(0.62\ \text{mol/kg}) = 0.63^{o}C$$

Solution boiling point = $100.00^{o}C + \Delta T_b = 100.00^{o}C + 0.63^{o}C = 100.63^{o}C$

11.115 (a) Assume a total mass of solution of 1000.0 g.

$$\text{ppm} = \frac{\text{mass of solute ion}}{\text{total mass of solution}} \times 10^6$$

For each ion: $\text{mass of solute ion} = \frac{(\text{ppm})(1000.0\ \text{g})}{10^6}$

Ion	Mass	Moles
Cl^-	19.0 g	0.536 mol
Na^+	10.5 g	0.457 mol
SO_4^{2-}	2.65 g	0.0276 mol
Mg^{2+}	1.35 g	0.0555 mol
Ca^{2+}	0.400 g	0.009 98 mol
K^+	0.380 g	0.009 72 mol
HCO_3^-	0.140 g	0.002 29 mol
Br^-	0.065 g	0.000 81 mol
Total	34.5 g	1.099 mol

Mass of H_2O = 1000.0 g - 34.5 g = 965.5 g H_2O = 0.9655 kg H_2O

$$\text{molality} = \frac{1.099\ \text{mol}}{0.9655\ \text{kg}} = 1.138\ \text{mol/kg} = 1.138\ m$$

(b) Assume M = *m* for a dilute solution.

$$\Pi = MRT = (1.138\ \text{mol/L})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(300\ \text{K}) = 28.0\ \text{atm}$$

11.116 (a) 90 mass % isopropyl alcohol $= \frac{10.5\ \text{g}}{10.5\ \text{g} + \text{mass of } H_2O} \times 100\%$

Solve for the mass of H_2O.

$$\text{mass of } H_2O = \left(10.5\ \text{g} \times \frac{100}{90}\right) - 10.5\ \text{g} = 1.2\ \text{g}$$

mass of solution = 10.5 g + 1.2 g = 11.7 g

11.7 g of rubbing alcohol contains 10.5 g of isopropyl alcohol.

(b) C_3H_8O, 60.10 amu

mass C_3H_8O = (0.90)(50.0 g) = 45 g

$$45\ \text{g } C_3H_8O \times \frac{1\ \text{mol } C_3H_8O}{60.10\ \text{g } C_3H_8O} = 0.75\ \text{mol } C_3H_8O$$

11.117 $C_6H_{12}O_6$, 180.16 amu; 50.0 mL = 0.0500 L; 17.5 mg = 17.5×10^{-3} g

$\Pi = MRT$

$$T = \frac{\Pi}{MR} = \frac{\left(37.8\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}}\right)}{\left(\frac{\left(17.5 \times 10^{-3}\ \text{g} \times \frac{1\ \text{mol}}{180.16\ \text{g}}\right)}{0.0500\ \text{L}}\right)\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)} = 312\ \text{K}$$

11.118 First, determine the empirical formula.

3.47 mg = 3.47 x 10^{-3} g sample

10.10 mg = 10.10 x 10^{-3} g CO_2

2.76 mg = 2.76 x 10^{-3} g H_2O

$$\text{mass C} = 10.10 \times 10^{-3}\ \text{g } CO_2 \times \frac{12.01\ \text{g C}}{44.01\ \text{g } CO_2} = 2.76 \times 10^{-3}\ \text{g C}$$

$$\text{mass H} = 2.76 \times 10^{-3}\ \text{g } H_2O \times \frac{2 \times 1.008\ \text{g H}}{18.02\ \text{g } H_2O} = 3.09 \times 10^{-4}\ \text{g H}$$

mass O = 3.47 x 10^{-3} g - 2.76 x 10^{-3} g C - 3.09 x 10^{-4} g H = 4.01 x 10^{-4} g O

$$2.76 \times 10^{-3}\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 2.30 \times 10^{-4}\ \text{mol C}$$

$$3.09 \times 10^{-4}\ \text{g H} \times \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 3.07 \times 10^{-4}\ \text{mol H}$$

$$4.01 \times 10^{-4}\ \text{g O} \times \frac{1\ \text{mol O}}{16.00\ \text{g O}} = 2.51 \times 10^{-5}\ \text{mol O} = 0.251 \times 10^{-4}\ \text{mol O}$$

To simplify the empirical formula, divide each mol quantity by 10^{-4}.

$C_{2.30}H_{3.07}O_{0.251}$; Divide all subscripts by the smallest, 0.251.

$C_{2.30\ /\ 0.251}H_{3.07\ /\ 0.251}O_{0.251\ /\ 0.251}$

$C_{9.16}H_{12.23}O$, empirical formula is $C_9H_{12}O$ (136 amu)

Second, determine the molecular mass.

$$7.55\ \text{mg} = 7.55 \times 10^{-3}\ \text{g estradiol};\ 0.500\ \text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 5.00 \times 10^{-4}\ \text{kg camphor}$$

$$\Delta T_f = K_f \cdot m;\ m = \frac{\Delta T_f}{K_f} = \frac{2.10^{o}\text{C}}{37.7\ \frac{^{o}\text{C} \bullet \text{kg}}{\text{mol}}} = 0.0557\ \text{mol/kg} = 0.0557\ m$$

$$m = \frac{\text{mol estradiol}}{\text{kg solvent}}$$

mol estradiol = m x (kg solvent) = (0.0557 mol/kg)(5.00 x 10^{-4} kg) = 2.79 x 10^{-5} mol

$$\text{molar mass} = \frac{7.55 \times 10^{-3}\ \text{g estradiol}}{2.79 \times 10^{-5}\ \text{mol estradiol}} = 271\ \text{g/mol};\ \text{molecular mass} = 271\ \text{amu}$$

Finally, determine the molecular formula:

Divide the molecular mass by the empirical formula mass.

$$\frac{271\ \text{amu}}{136\ \text{amu}} = 2;$$ molecular formula is $C_{(2 \times 9)}H_{(2 \times 12)}O_{(2 \times 1)}$, or $C_{18}H_{24}O_2$

11.119 $CCl_3CO_2H(aq) \rightleftharpoons H^+(aq) + CCl_3CO_2^-(aq)$

1.00 - x x x

$\Delta T_f = K_f \cdot m$; $m = \dfrac{\Delta T_f}{K_f} = \dfrac{2.53^{o}C}{1.86\ \frac{^{o}C \bullet kg}{mol}} = 1.36\ m$

1.36 = 1.00 - x + x + x = 1 + x; x = 0.36

36% of the acid molecules are dissociated.

11.120 (a) H_2SO_4, 98.08 amu; $2.238\ mol\ H_2SO_4 \times \dfrac{98.08\ g\ H_2SO_4}{1\ mol\ H_2SO_4} = 219.50\ g\ H_2SO_4$

mass of 2.238 *m* solution = 219.50 g H_2SO_4 + 1000 g H_2O = 1219.50 g

volume of 2.238 *m* solution = $1219.50\ g \times \dfrac{1.0000\ mL}{1.1243\ g} = 1084.68\ mL = 1.0847\ L$

molarity of 2.238 *m* solution = $\dfrac{2.238\ mol}{1.0847\ L} = 2.063\ M$

The molarity of the H_2SO_4 solution is less than the molarity of the $BaCl_2$ solution. Because equal volumes of the two solutions are mixed, H_2SO_4 is the limiting reactant and the number of moles of H_2SO_4 determines the number of moles of $BaSO_4$ produced as the white precipitate.

$(0.05000\ L) \times (2.063\ mol\ H_2SO_4/L) \times \dfrac{1\ mol\ BaSO_4}{1\ mol\ H_2SO_4} \times \dfrac{233.39\ g\ BaSO_4}{1\ mol\ BaSO_4} = 24.07\ g\ BaSO_4$

(b) More precipitate will form because of the excess $BaCl_2$ in the solution.

11.121 KCl, 74.55amu; KNO_3, 101.10 amu; $Ba(NO_3)_2$, 261.34 amu

$\Pi = MRT$; $M = \dfrac{\Pi}{RT} = \dfrac{\left(744.7\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.040\ 07\ M$

$0.040\ 07\ M = \dfrac{mol\ ions}{0.500\ L}$; mol ions = (0.040 07 mol/L)(0.500 L) = 0.020 035 mol ions

mass Cl = 1.000 g x 0.2092 = 0.2092 g Cl

$\text{mass KCl} = 0.2092\ g\ Cl \times \dfrac{1\ mol\ Cl}{35.453\ g\ Cl} \times \dfrac{1\ mol\ KCl}{1\ mol\ Cl} \times \dfrac{74.55\ g\ KCl}{1\ mol\ KCl} = 0.440\ g$ KCl

$\text{mol ions from KCl} = 0.440\ g\ KCl \times \dfrac{1\ mol\ KCl}{74.55\ g\ KCl} \times \dfrac{2\ mol\ ions}{1\ mol\ KCl} = 0.0118\ mol\ ions$

mol ions from KNO_3 and $Ba(NO_3)_2$ = 0.020 035 - 0.0118 = 0.008 235 mol ions

Let x = mass KNO_3 and y = mass $Ba(NO_3)_2$

x + y = 1.000 g - 0.440 g = 0.560 g

$\left(\dfrac{x}{101.10}\right)2 + \left(\dfrac{y}{261.34}\right)3 = 0.008\ 235\ mol\ ions$

x = 0.560 - y

0.0198x + 0.0115y = 0.008 235

$0.0198(0.560 - y) + 0.0115y = 0.008\,235$
$0.011\,09 - 0.0198y + 0.0115y = 0.008\,235$
$0.002\,855 = 0.0083y;\ y = \dfrac{0.002\,855}{0.0083} = 0.3440;\ x = 0.560 - 0.3440 = 0.216$

$\text{mass \% KCl} = \dfrac{0.440\ \text{g}}{1.000\ \text{g}} \times 100\% = 44.0\%$

$\text{mass \% } KNO_3 = \dfrac{0.216\ \text{g}}{1.000\ \text{g}} \times 100\% = 21.6\%$

$\text{mass \% } Ba(NO_3)_2 = \dfrac{0.344\ \text{g}}{1.000\ \text{g}} \times 100\% = 34.4\%$

11.122 Let $x = X_{H_2O}$ and $y = X_{CH_3OH}$ and assume $n_{total} = 1.00$ mol

$(14.5\ \text{mm Hg})x + (82.5\ \text{mm Hg})y = 39.4\ \text{mm Hg}$
$(26.8\ \text{mm Hg})x + (140.3\ \text{mm Hg})y = 68.2\ \text{mm Hg}$

$x = \dfrac{68.2 - 140.3y}{26.8}$

$\dfrac{14.5(68.2 - 140.3y)}{26.8} + 82.5y = 39.4$

$\dfrac{(988.9 - 2034.35y)}{26.8} + 82.5y = 39.4$

$36.90 - 75.91y + 82.5y = 39.4;\ 6.59 = 2.5;\ y = \dfrac{2.5}{6.59} = 0.3794$

$x = \dfrac{[68.2 - 140.3(0.3794)]}{26.8} = 0.5586$

$X_{LiCl} = 1 - X_{H_2O} - X_{CH_3OH} = 1 - 0.5586 - 0.3794 = 0.0620$

The mole fraction equals the number of moles of each component because $n_{total} = 1.00$ mol.

$\text{mass LiCl} = 0.0620\ \text{mol LiCl} \times \dfrac{42.39\ \text{g LiCl}}{1\ \text{mol LiCl}} = 2.6\ \text{g LiCl}$

$\text{mass } H_2O = 0.5588\ \text{mol } H_2O \times \dfrac{18.02\ \text{g } H_2O}{1\ \text{mol } H_2O} = 10.1\ \text{g } H_2O$

$\text{mass } CH_3OH = 0.3794\ \text{mol } CH_3OH \times \dfrac{32.04\ \text{g } CH_3OH}{1\ \text{mol } CH_3OH} = 12.2\ \text{g } CH_3OH$

$\text{total mass} = 2.6\ \text{g} + 10.1\ \text{g} + 12.2\ \text{g} = 24.9\ \text{g}$

$\text{mass \% LiCl} = \dfrac{2.6\ \text{g}}{24.9\ \text{g}} \times 100\% = 10\%$

$\text{mass \% } H_2O = \dfrac{10.1\ \text{g}}{24.9\ \text{g}} \times 100\% = 41\%$

mass % $CH_3OH = \frac{12.2\ g}{24.9\ g} \times 100\% = 49\%$

11.123 KI, 166.00 amu

$\Delta T_f = K_f \cdot m \cdot i$; $m = \frac{\Delta T_f}{K_f \bullet i} = \frac{1.95^oC}{\left(1.86\ \frac{^oC \bullet kg}{mol}\right)(2)} = 0.524$ mol/kg = 0.524 *m*

$\Pi = i \cdot MRT$; $M = \frac{\Pi}{i \bullet R\,T} = \frac{25.0\ atm}{(2)\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.511$ M = 0.511 mol/L

1.000 L of solution contains 0.511 mol KI and is 0.524 *m*.

mass KI = 0.511 mol KI x $\frac{166.00\ g\ KI}{1\ mol\ KI} = 84.83$ g KI

Calculate the mass of solvent in this solution.

0.524 *m* = 0.524 mol/kg = $\frac{0.511\ mol}{mass\ of\ solvent}$

mass of solvent = $\frac{0.511\ mol}{0.524\ mol/kg} = 0.9752$ kg = 975.2 g

mass of solution = mass KI + mass of solvent = 84.83 g + 975.2 g = 1060 g

density = $\frac{1060\ g}{1000\ mL} = 1.06$ g/mL

11.124 Solution freezing point = $-1.03^oC = 0.00^oC - \Delta T_f$; $\Delta T_f = 1.03^oC$

$\Delta T_f = K_f \cdot m$; $m = \frac{\Delta T_f}{K_f} = \frac{1.03^oC}{1.86\ \frac{^oC \bullet kg}{mol}} = 0.554$ mol/kg = 0.554 *m*

$\Pi = MRT$; $M = \frac{\Pi}{RT} = \frac{(12.16\ atm)}{\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.497\ \frac{mol}{L}$

Assume 1.000 L = 1000 mL of solution.

mass of solution = (1000 mL)(1.063 g/mL) = 1063 g

mass of H_2O in 1000 mL of solution = $\frac{1000\ g\ H_2O}{0.554\ mol\ of\ solute} \times 0.497$ mol = 897 g H_2O

mass of solute = total mass - mass of H_2O = 1063 g - 897 g = 166 g solute

molar mass = $\frac{166\ g}{0.497\ mol} = 334$ g/mol

11.125 C_6H_6, 78.11 amu

299 mm Hg = $P^o_{C_6H_6} \cdot X_{C_6H_6} + P^o_X \cdot X_X$

299 mm Hg = (395 mm Hg) $\cdot X_{C_6H_6}$ + (96 mm Hg) $\cdot X_X$

$X_{C_6H_6} + X_X = 1$; $X_X = 1 - X_{C_6H_6}$

299 mm Hg = (395 mm Hg) $\cdot X_{C_6H_6}$ + (96 mm Hg)(1 - $X_{C_6H_6}$)

299 mm Hg = (395 mm Hg) $\cdot X_{C_6H_6}$ + 96 mm Hg - (96 mm Hg) $\cdot X_{C_6H_6}$

299 mm Hg - 96 mm Hg = (395 mm Hg) $\cdot X_{C_6H_6}$ - (96 mm Hg) $\cdot X_{C_6H_6}$

203 mm Hg = (299 mm Hg) $\cdot X_{C_6H_6}$

$X_{C_6H_6}$ = 203 mm Hg/299 mm Hg = 0.679

Assume the mixture contains 1.00 mol (78.11 g) of C_6H_6. Then a 50/50 mixture will also contain 78.11 g of X.

$$X_{C_6H_6} = \frac{1 \text{ mol } C_6H_6}{1 \text{ mol } C_6H_6 + \text{mol X}} = 0.679$$

1 mol C_6H_6 = (0.679)(1 mol C_6H_6 + mol X)

$$\frac{1 \text{ mol } C_6H_6}{0.679} = 1 \text{ mol } C_6H_6 + \text{mol X}$$

$$\frac{1 \text{ mol } C_6H_6}{0.679} - 1 \text{ mol } C_6H_6 = \text{mol X}$$

mol X = 0.473 mol

molar mass X = 78.11 g/0.473 mol = 165 g/mol

11.126 (a) NaCl, 58.44 amu; $CaCl_2$, 110.98 amu; H_2O, 18.02 amu

$$\text{mol NaCl} = 100.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} = 1.711 \text{ mol NaCl}$$

$$\text{mol } CaCl_2 = 100.0 \text{ g } CaCl_2 \times \frac{1 \text{ mol } CaCl_2}{110.98 \text{ g } CaCl_2} = 0.9011 \text{ mol } CaCl_2$$

mass of solution = (1000 mL)(1.15 g/mL) = 1150 g

mass of H_2O in solution = mass of solution - mass NaCl - mass $CaCl_2$

= 1150 g - 100.0 g - 100.0 g = 950 g

$$= 950 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.950 \text{ kg}$$

$\Delta T_b = K_b \cdot (m_{NaCl} \bullet i + m_{CaCl_2} \bullet i)$

$$\Delta T_b = \left(0.51 \frac{^oC \bullet kg}{mol}\right)\left(\frac{(1.711 \text{ mol NaCl} \bullet 2) + (0.9011 \text{ mol } CaCl_2 \bullet 3)}{0.950 \text{ kg}}\right) = 3.3^oC$$

solution boiling point = 100.0°C + ΔT_b = 100.0°C + 3.3°C = 103.3°C

(b) $$\text{mol } H_2O = 950 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 52.7 \text{ mol } H_2O$$

$P_{Solution} = P^o \bullet X_{H_2O}$

$P_{Solution} = P^o$

$$\bullet \left(\frac{52.7 \text{ mol } H_2O}{(52.7 \text{ mol } H_2O) + (1.711 \text{ mol NaCl} \bullet 2) + (0.9011 \text{ mol } CaCl_2 \bullet 3)} \right)$$

$P_{Solution}$ = (23.8 mm Hg)(0.896) = 21.3 mm Hg

11.127 HIO_3, 175.91 amu

mass of 1.00 L solution = (1.00 x 10^3 mL)(1.07 g/mL) = 1.07 x 10^3 g

1.00 L of solution contains 1 mol (175.91 g) HIO_3.

mass of H_2O = 1070 g - 175.91 g = 894 g = 0.894 kg

m = 1.00 mol/0.894 kg = 1.12 m

$\Delta T_f = K_f \cdot m \cdot i$

$$i = \frac{\Delta T_f}{K_f \bullet m} = \frac{2.78^\circ C}{\left(1.86 \frac{^\circ C \bullet kg}{mol}\right)(1.12 \text{ mol/kg})} = 1.33;$$ The acid is 33% dissociated.

11.128 (a) KI, 166.00 amu

Assume you have 1.000 L of 1.24 M solution.

mass of solution = (1000 mL)(1.15 g/mL) = 1150 g

$$\text{mass of KI in solution} = 1.24 \text{ mol KI} \times \frac{166.00 \text{ g KI}}{1 \text{ mol KI}} = 206 \text{ g KI}$$

mass of H_2O in solution = mass of solution - mass KI = 1150 g - 206 g = 944 g

$$= 944 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.944 \text{ kg}$$

$$\text{molality} = \frac{1.24 \text{ mol KI}}{0.944 \text{ kg } H_2O} = 1.31 \ m$$

(b) For KI, i = 2 assuming complete dissociation.

$$\Delta T_f = K_f \cdot m \cdot i = \left(1.86 \frac{^\circ C \bullet kg}{mol}\right)(1.31 \text{ m})(2) = 4.87^\circ C$$

Solution freezing point = 0.00°C - ΔT_f = 0.00°C - 4.87°C = - 4.87°C

(c) $$i = \frac{\Delta T_f}{K_f \bullet m} = \frac{4.46^\circ C}{\left(1.86 \frac{^\circ C \bullet kg}{mol}\right)(1.31 \text{ mol/kg})} = 1.83$$

Because the calculated i is only 1.83 and not 2, the percent dissociation for KI is 83%.

11.129 (a) For NaCl, i = 2 and for $MgCl_2$, i = 3; T = 25°C = 25 + 273 = 298 K

$$\Pi = i \cdot MRT = [(2)(0.470 \text{ mol/L}) + (3)(0.068 \text{ mol/L})]\left(0.082\,06 \frac{L \bullet atm}{K \bullet mol}\right)(298 \text{ K}) = 28.0 \text{ atm}$$

(b) Calculate the molarity for an osmotic pressure = 100.0 atm.

$$\Pi = MRT;\ M = \frac{\Pi}{RT} = \frac{(100.0\ atm)}{\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 4.09\ mol/L$$

$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$

$$V_{conc} = \frac{M_{dil} \times V_{dil}}{M_{conc}} = \frac{[(2)(0.470\ mol/L) + (3)(0.068\ mol/L)](1.00\ L)}{4.09\ mol/L} = 0.28\ L$$

A volume of 1.00 L of seawater can reduced to 0.28 L by an osmotic pressure of 100.0 atm. The volume of fresh water that can be obtained is (1.00 L - 0.28 L) = 0.72 L.

11.130 NaCl, 58.44 amu; $C_{12}H_{22}O_{11}$, 342.3 amu

Let X = mass NaCl and Y = mass $C_{12}H_{22}O_{11}$, then X + Y = 100.0 g.

$$500.0\ g \times \frac{1\ kg}{1000\ g} = 0.5000\ kg$$

Solution freezing point = $-2.25^oC = 0.00^oC - \Delta T_{f;} = \Delta T_f = 0.00^oC + 2.25^oC = 2.25^oC$

$\Delta T_f = K_f \cdot (m_{NaCl} \bullet i + m_{C_{12}H_{22}O_{11}})$

$$\Delta T_b = \left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{(mol\ NaCl \bullet 2) + (mol\ C_{12}H_{22}O_{11})}{0.5000\ kg}\right) = 2.25^oC$$

$$mol\ NaCl = X\ g\ NaCl \times \frac{1\ mol\ NaCl}{58.44\ g\ NaCl} = X/58.44\ mol$$

$$mol\ C_{12}H_{22}O_{11} = Y\ g\ C_{12}H_{22}O_{11} \times \frac{1\ mol\ C_{12}H_{22}O_{11}}{342.3\ g\ C_{12}H_{22}O_{11}} = Y/342.3\ mol$$

$$\Delta T_b = \left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{((X/58.44) \bullet 2\ mol) + ((Y/342.3)\ mol)}{0.5000\ kg}\right) = 2.25^oC$$

$X = 100 - Y$

$$\left(1.86\ \frac{^oC \bullet kg}{mol}\right)\left(\frac{\{[(100 - Y)/58.44] \bullet 2\ mol\}\} + [(Y/342.3)\ mol]}{0.5000\ kg}\right) = 2.25^oC$$

$$\left(\frac{[(200/58.44) - (2Y/58.44) + (Y/342.3)]\ mol}{0.5000\ kg}\right) = \frac{2.25^oC}{\left(1.86\ \frac{^oC \bullet kg}{mol}\right)} = 1.21\ mol/kg$$

$$\left(\frac{[(3.42) - (0.0313Y)]\ mol}{0.5000\ kg}\right) = 1.21\ mol/kg$$

$[(3.42) - (0.0313Y)] = (0.5000\ kg)(1.21) = 0.605$

$-0.0313\ Y = 0.605 - 3.42 = -2.81$

$Y = (-2.81)/(-0.0313) = 89.9$ g of $C_{12}H_{22}O_{11}$

$X = 100.0\ g - Y = 100.0\ g - 89.9\ g = 10.1$ g of NaCl

Multi-Concept Problems

11.131 (a) 382.6 mL = 0.3826 L; $20.0^{o}C = 293.2$ K

PV = nRT

$$n_{H_2} = \frac{P\,V}{R\,T} = \frac{\left(755\ mm\ Hg\ x\ \frac{1.0\ atm}{760\ mm\ Hg}\right)(0.3826\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(293.2\ K)} = 0.0158\ mol\ H_2$$

(b) $M + x\,HCl \rightarrow x/2\,H_2 + MCl_x$

moles HCl reacted = $0.0158\ mol\ H_2 \times \frac{x\ mol\ HCl}{x/2\ mol\ H_2} = 0.0316\ mol\ HCl$

moles Cl reacted = moles HCl reacted = 0.0316 mol Cl

mass Cl = $0.0316\ mol\ Cl \times \frac{35.453\ g\ Cl}{1\ mol\ Cl} = 1.120\ g\ Cl$

mass MCl_x = mass M + mass Cl = 1.385 g + 1.120 g = 2.505 g MCl_x

(c) $\Delta T_f = K_f \cdot m$; $m = \frac{\Delta T_f}{K_f} = \frac{3.53^{o}C}{1.86\ \frac{^{o}C \bullet kg}{mol}} = 1.90\ mol/kg = 1.90\ m$

(d) 25.0 g = 0.0250 kg

$$1.90\ m = 1.90\ \frac{mol}{kg} = \frac{x\ mol\ ions}{0.0250\ kg}$$

mol ions = (1.90 mol/kg)(0.0250 kg) = 0.0475 mol ions

(e) mol M = mol ions - mol Cl = 0.0475 mol - 0.0316 mol = 0.0159 mol M

$\frac{Cl}{M} = \frac{0.0316\ mol}{0.0159\ mol} = 2$, the formula is MCl_2.

molar mass = $\frac{2.505\ g}{0.0159\ mol} = 157.5$ g/mol; molecular mass = 157.5 amu

(f) atomic mass of M = 157.5 amu - 2(35.453 amu) = 86.6 amu; M = Sr

11.132 (a) 20.00 mL = 0.02000 L

mol NaOH = (0.02000 L)(2.00 mol/L) = 0.0400 mol NaOH

mol $CO_2 = 0.0400\ mol\ NaOH \times \frac{1\ mol\ CO_2}{2\ mol\ NaOH} = 0.0200\ mol\ CO_2$

mol $C = 0.0200\ mol\ CO_2 \times \frac{1\ mol\ C}{1\ mol\ CO_2} = 0.0200\ mol\ C$

mass $C = 0.0200\ mol\ C \times \frac{12.011\ g\ C}{1\ mol\ C} = 0.240\ g\ C$

mass H = mass of compound - mass of C = 0.270 g - 0.240 g = 0.030 g H

mol H = 0.030 g H x $\frac{1 \text{ mol H}}{1.008 \text{ g H}}$ = 0.030 mol H

The mole ratio of C and H in the molecule is $C_{0.0200}\ H_{0.030}$.

$C_{0.0200}\ H_{0.030}$, divide both subscripts by the smaller of the two, 0.0200.

$C_{0.0200\ /\ 0.0200}\ H_{0.030\ /\ 0.0200}$

$C_1H_{1.5}$, multiply both subscripts by 2.

$C_{(2\ x\ 1)}\ H_{(2\ x\ 1.5)}$

C_2H_3 (27.05 amu) is the empirical formula.

(b) $\Delta T_f = K_f \cdot m$; $m = \frac{\Delta T_f}{K_f} = \frac{(179.8^oC \ - \ 177.9^oC)}{37.7 \frac{^oC \bullet kg}{mol}}$ = 0.050 mol/kg = 0.050 *m*

50.0 g x $\frac{1 \text{ kg}}{1000 \text{ g}}$ = 0.0500 kg

mol solute = (0.050 mol/kg)(0.0500 kg) = 0.0025 mol

molar mass = $\frac{0.270 \text{ g}}{0.0025 \text{ mol}}$ = 108 g/mol; molecular mass = 108 amu

(c) To find the molecular formula, first divide the molecular mass by the mass of the empirical formula unit.

$\frac{108}{27} = 4$

Multiply the subscripts in the empirical formula by the result of this division, 4.

$C_{(4\ x\ 2)}\ H_{(4\ x\ 3)}$

C_8H_{12} is the molecular formula of the compound.

11.133 CO_2, 44.01 amu; H_2O, 18.02 amu

mol C = 106.43 mg CO_2 x $\frac{1 \text{ g}}{1000 \text{ mg}}$ x $\frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2}$ x $\frac{1 \text{ mol C}}{1 \text{ mol } CO_2}$ = 0.002 418 mol C

mass C = 0.002 418 mol C x $\frac{12.011 \text{ g C}}{1 \text{ mol C}}$ = 0.029 04 g C

mol H = 32.100 mg H_2O x $\frac{1 \text{ g}}{1000 \text{ mg}}$ x $\frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O}$ x $\frac{2 \text{ mol H}}{1 \text{ mol } H_2O}$ = 0.003 563 mol H

mass H = 0.003 563 mol H x $\frac{1.008 \text{ g H}}{1 \text{ mol H}}$ = 0.003 592 g H

mass O = $\left(36.72 \text{ mg x } \frac{1 \text{ g}}{1000 \text{ mg}}\right)$ - 0.029 04 g C - 0.003 592 g H = 0.004 088 g O

mol O = 0.004 088 g O x $\frac{1 \text{ mol O}}{16.00 \text{ g O}}$ = 0.000 255 5 mol O

$C_{0.002\ 418}H_{0.003\ 563}O_{0.000\ 255\ 5}$ Divide all subscripts by the smallest, 0.000 255 5.

$C_{0.002\ 418\ /\ 0.000\ 255\ 5}H_{0.003\ 563\ /\ 0.000\ 255\ 5}O_{0.000\ 255\ 5\ /\ 0.000\ 255\ 5}$

$C_{9.5}H_{14}O$ Multiply all subscripts by 2.
$C_{(9.5 \times 2)}H_{(14 \times 2)}O_{(1 \times 2)}$
Empirical formula is $C_{19}H_{28}O_2$, 288 amu

$T = 25^oC = 25 + 273 = 298\ K$

$$\Pi = MRT;\ M = \frac{\Pi}{RT} = \frac{\left(21.5\ mm\ Hg \times \frac{1\ atm}{760\ mm\ Hg}\right)}{\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 0.001\ 16\ mol/L$$

15.0 mL = 0.0150 L
mol solute = (0.001 16 mol/L)(0.0150 L) = 1.74×10^{-5} mol

$$\text{molar mass} = \frac{\left(5.00\ mg \times \frac{1\ g}{1000\ mg}\right)}{1.74 \times 10^{-5}\ mol} = 287\ g/mol$$

The molar mass and the empirical formula mass are essentially identical, so the molecular formula and the empirical formula are the same. The molecular formula is $C_{19}H_{28}O_2$.

11.134 AgCl, 143.32 amu
Solution freezing point = $-4.42^oC = 0.00^oC - \Delta T_f$; $\Delta T_f = 0.00^oC + 4.42^oC = 4.42^oC$
$\Delta T_f = K_f \cdot m$

$$\text{total ion } m = \frac{\Delta T_f}{K_f} = \frac{4.42^oC}{1.86\ \frac{^oC \bullet kg}{mol}} = 2.376\ mol/kg = 2.376\ m$$

$$150.0\ g \times \frac{1\ kg}{1000\ g} = 0.1500\ kg$$

total mol of ions = (2.376 mol/kg)(0.1500 kg) = 0.3564 mol of ions
An excess of $AgNO_3$ reacts with all Cl^- to produce 27.575 g AgCl.

$$\text{total mol } Cl^- = 27.575\ g\ AgCl \times \frac{1\ mol\ AgCl}{143.32\ g\ AgCl} \times \frac{1\ mol\ Cl^-}{1\ mol\ AgCl} = 0.1924\ mol\ Cl^-$$

Let P = mol XCl and Q = mol YCl_2.
0.3564 mol ions = 2 x mol XCl + 3 x mol YCl_2 = (2 x P) + (3 x Q)
0.1924 mol Cl^- = mol XCl + 2 x mol YCl_2 = P + (2 x Q)
P = 0.1924 - (2 x Q)
0.3564 = 2 x [0.1924 - (2 x Q)] + (3 x Q) = 0.3848 - (4 x Q) + (3 x Q)
Q = 0.3848 - 0.3564 = 0.0284 mol YCl_2
P = 0.1924 - (2 x Q) = 0.1924 - (2 x 0.0284) = 0.1356 mol XCl

$$\text{mass Cl in XCl} = 0.1356\ mol\ XCl \times \frac{1\ mol\ Cl}{1\ mol\ XCl} \times \frac{35.453\ g\ Cl}{1\ mol\ Cl} = 4.81\ g\ Cl$$

mass Cl in YCl_2 = 0.0284 mol YCl_2 x $\frac{2 \text{ mol Cl}}{1 \text{ mol } YCl_2}$ x $\frac{35.453 \text{ g Cl}}{1 \text{ mol Cl}}$ = 2.01 g Cl

total mass of XCl and YCl_2 = 8.900 g
mass of X + Y = total mass - mass Cl = 8.900 g - 4.81 g - 2.01 g = 2.08 g
X is an alkali metal and there are 0.1356 mol of X in XCl.
If X = Li, then mass of X = (0.1356 mol)(6.941 g/mol) = 0.941 g
If X = Na, then mass of X = (0.1356 mol)(22.99 g/mol) = 3.12 g but this is not possible because 3.12 g is greater than the total mass of X + Y. Therefore, X is Li.
mass of Y = 2.08 - mass of X = 2.08 g - 0.941 g = 1.14 g
Y is an alkaline earth metal and there are 0.0284 mol of Y in YCl_2.
molar mass of Y = 1.14 g/0.0284 mol = 40.1 g/mol. Therefore, Y is Ca.

mass LiCl = 0.1356 mol LiCl x $\frac{42.39 \text{ g LiCl}}{1 \text{ mol LiCl}}$ = 5.75 g LiCl

mass $CaCl_2$ = 0.0284 mol $CaCl_2$ x $\frac{110.98 \text{ g } CaCl_2}{1 \text{ mol } CaCl_2}$ = 3.15 g $CaCl_2$

12 Chemical Kinetics

12.1 $3\ I^-(aq) + H_3AsO_4(aq) + 2\ H^+(aq) \rightarrow I_3^-(aq) + H_3AsO_3(aq) + H_2O(l)$

(a) $-\frac{\Delta[I^-]}{\Delta t} = 4.8 \times 10^{-4}$ M/s

$$\frac{\Delta[I_3^-]}{\Delta t} = \frac{1}{3}\left(-\frac{\Delta[I^-]}{\Delta t}\right) = \left(\frac{1}{3}\right)(4.8 \times 10^{-4}\ \text{M/s}) = 1.6 \times 10^{-4}\ \text{M/s}$$

(b) $-\frac{\Delta[H^+]}{\Delta t} = 2\left(\frac{\Delta[I_3^-]}{\Delta t}\right) = (2)(1.6 \times 10^{-4}\ \text{M/s}) = 3.2 \times 10^{-4}$ M/s

12.2 $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$

time	$[N_2O_5]$	$[O_2]$
200 s	0.0142 M	0.0029 M
300 s	0.0120 M	0.0040 M

Rate of decomposition of $N_2O_5 = -\frac{\Delta[N_2O_5]}{\Delta t} = -\frac{0.0120\ \text{M} - 0.0142\ \text{M}}{300\ \text{s} - 200\ \text{s}} = 2.2 \times 10^{-5}$ M/s

Rate of formation of $O_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0040\ \text{M} - 0.0029\ \text{M}}{300\ \text{s} - 200\ \text{s}} = 1.1 \times 10^{-5}$ M/s

12.3 $\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$

1st order in BrO_3^-, 1st order in Br^-, 2nd order in H^+, 4th order overall

$\text{Rate} = k[H_2][I_2]$, 1st order in H_2, 1st order in I_2, 2nd order overall

$\text{Rate} = k[CH_3CHO]^{3/2}$, 3/2 order in CH_3CHO, 3/2 order overall

12.4 $H_2O_2(aq) + 3\ I^-(aq) + 2\ H^+(aq) \rightarrow I_3^-(aq) + 2\ H_2O(l)$

$$\text{Rate} = \frac{\Delta[I_3^-]}{\Delta t} = k[H_2O_2]^m[I^-]^n$$

(a) $\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{2.30 \times 10^{-4}\ \text{M/s}}{1.15 \times 10^{-4}\ \text{M/s}} = 2$ $\qquad \frac{[H_2O_2]_3}{[H_2O_2]_1} = \frac{0.200\ \text{M}}{0.100\ \text{M}} = 2$

Because both ratios are the same, m = 1.

$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{2.30 \times 10^{-4}\ \text{M/s}}{1.15 \times 10^{-4}\ \text{M/s}} = 2$ $\qquad \frac{[I^-]_2}{[I^-]_1} = \frac{0.200\ \text{M}}{0.100\ \text{M}} = 2$

Because both ratios are the same, n = 1.

The rate law is: $\text{Rate} = k[H_2O_2][I^-]$

(b) $k = \frac{\text{Rate}}{[H_2O_2][I^-]}$

Using data from Experiment 1: $k = \dfrac{1.15 \times 10^{-4}\ M/s}{(0.100\ M)(0.100\ M)} = 1.15 \times 10^{-2}\ /(M \cdot s)$

(c) Rate = $k[H_2O_2][I^-] = [1.15 \times 10^{-2}/(M \cdot s)](0.300\ M)(0.400\ M) = 1.38 \times 10^{-3}$ M/s

12.5

Rate Law	Units of k
Rate = $k[(CH_3)_3CBr]$	1/s
Rate = $k[Br_2]$	1/s
Rate = $k[BrO_3^-][Br^-][H^+]^2$	$1/(M^3 \cdot s)$
Rate = $k[H_2][I_2]$	$1/(M \cdot s)$
Rate = $[CH_3CHO]^{3/2}$	$1/(M^{1/2} \cdot s)$

12.6 (a) The reactions in vessels (a) and (b) have the same rate, the same number of B molecules, but different numbers of A molecules. Therefore, the rate does not depend on A and its reaction order is zero. The same conclusion can be drawn from the reactions in vessels (c) and (d).
The rate for the reaction in vessel (c) is four times the rate for the reaction in vessel (a). Vessel (c) has twice as many B molecules than does vessel (a). Because the rate quadruples when the concentration of B doubles, the reaction order for B is two.
(b) rate = $k[B]^2$

12.7 (a) $\ln \dfrac{[Co(NH_3)_5Br^{2+}]_t}{[Co(NH_3)_5Br^{2+}]_o} = -kt$

$k = 6.3 \times 10^{-6}/s$; $\quad t = 10.0\ h \times \dfrac{3600\ s}{1\ h} = 36{,}000\ s$

$\ln[Co(NH_3)_5Br^{2+}]_t = -kt + \ln[Co(NH_3)_5Br^{2+}]_o$

$\ln[Co(NH_3)_5Br^{2+}]_t = -(6.3 \times 10^{-6}/s)(36{,}000\ s) + \ln(0.100)$

$\ln[Co(NH_3)_5Br^{2+}]_t = -2.5294$; $\quad$ After 10.0 h, $[Co(NH_3)_5Br^{2+}] = e^{-2.5294} = 0.080$ M

(b) $[Co(NH_3)_5Br^{2+}]_o = 0.100$ M
If 75% of the $Co(NH_3)_5Br^{2+}$ reacts then 25% remains.
$[Co(NH_3)_5Br^{2+}]_t = (0.25)(0.100\ M) = 0.025$ M

$$\ln \frac{[Co(NH_3)_5Br^{2+}]_t}{[Co(NH_3)_5Br^{2+}]_o} = -kt; \quad t = \frac{\ln \dfrac{[Co(NH_3)_5Br^{2+}]_t}{[Co(NH_3)_5Br^{2+}]_o}}{-k}$$

$$t = \frac{\ln\left(\dfrac{0.025}{0.100}\right)}{-(6.3 \times 10^{-6}/s)} = 2.2 \times 10^5\ s; \quad t = 2.2 \times 10^5\ s \times \frac{1\ h}{3600\ s} = 61\ h$$

12.8

Slope = -0.03989/min = -6.6 x 10^{-4}/s and k = -slope
A plot of ln[cyclopropane] versus time is linear, indicating that the data fit the equation for a first-order reaction. k = 6.6 x 10^{-4}/s (0.040/min)

12.9 (a) k = 1.8 x 10^{-5}/s

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.8 \times 10^{-5}/s} = 38{,}500 \text{ s}; \qquad t_{1/2} = 38{,}500 \text{ s} \times \frac{1 \text{ h}}{3600 \text{ s}} = 11 \text{ h}$$

(b) 0.30 M $\xrightarrow{t_{1/2}}$ 0.15 M $\xrightarrow{t_{1/2}}$ 0.075 M $\xrightarrow{t_{1/2}}$ 0.0375 M $\xrightarrow{t_{1/2}}$ 0.019 M

(c) Because 25% of the initial concentration corresponds to 1/4 or $(1/2)^2$ of the initial concentration, the time required is two half-lives: $t = 2t_{1/2} = 2(11 \text{ h}) = 22 \text{ h}$

12.10 After one half-life, there would be four A molecules remaining. After two half-lives, there would be two A molecules remaining. This is represented by the drawing at t = 10 min. 10 min is equal to two half-lives, therefore, $t_{1/2}$ = 5 min for this reaction. After 15 min (three half-lives) only one A molecule would remain.

12.11

(a) A plot of 1/[HI] versus time is linear. The reaction is second-order.

(b) $k = \text{slope} = 0.0308/(M \cdot \text{min})$

(c) $t = \frac{1}{k}\left[\frac{1}{[HI]_t} - \frac{1}{[HI]_o}\right] = \frac{1}{0.0308\ /\ (M \bullet \text{min})}\left[\frac{1}{0.100\ M} - \frac{1}{0.500\ M}\right] = 260\ \text{min}$

(d) It requires one half-life ($t_{1/2}$) for the [HI] to drop from 0.400 M to 0.200 M.

$t_{1/2} = \frac{1}{k[HI]_o} = \frac{1}{[0.0308/(\text{Mcdot min})](0.400\ M)} = 81.2\ \text{min}$

12.12 (a) $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$

$\underline{F(g) + NO_2(g) \rightarrow NO_2F(g)}$

Overall reaction $2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$

Because F(g) is produced in the first reaction and consumed in the second, it is a reaction intermediate.

(b) In each reaction there are two reactants, so each elementary reaction is bimolecular.

12.13 (a) $\text{Rate} = k[O_3][O]$ (b) $\text{Rate} = k[Br]^2[Ar]$ (c) $\text{Rate} = k[Co(CN)_5(H_2O)^{2-}]$

12.14 $Co(CN)_5(H_2O)^{2-}(aq) \rightarrow Co(CN)_5^{2-}(aq) + H_2O(l)$ (slow)

$\underline{Co(CN)_5^{2-}(aq) + I^-(aq) \rightarrow Co(CN)_5I^{3-}(aq)}$ (fast)

Overall reaction $Co(CN)_5(H_2O)^{2-}(aq) + I^-(aq) \rightarrow Co(CN)_5I^{3-}(aq) + H_2O(l)$

The predicted rate law for the overall reaction is the rate law for the first (slow) elementary reaction: $\text{Rate} = k[Co(CN)_5(H_2O)^{2-}]$

The predicted rate law is in accord with the observed rate law.

12.15 (a) $E_a = 100\ \text{kJ/mol} - 20\ \text{kJ/mol} = 80\ \text{kJ/mol}$

(b) The reaction is endothermic because the energy of the products is higher than the energy of the reactants.

(c)

12.16 (a) $\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$k_1 = 3.7 \times 10^{-5}/\text{s}$, $T_1 = 25^oC = 298\ K$

$k_2 = 1.7 \times 10^{-3}/\text{s}$, $T_2 = 55^oC = 328\ K$

$$E_a = -\frac{[\ln k_2 - \ln k_1]R}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(1.7 \times 10^{-3}) - \ln(3.7 \times 10^{-5})][8.314 \times 10^{-3}\ \text{kJ/(Kcdot mol)}]}{\left(\frac{1}{328\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 104\ \text{kJ/mol}$$

(b) $k_1 = 3.7 \times 10^{-5}$/s, $T_1 = 25^oC = 298$ K
solve for k_2, $T_2 = 35^oC = 308$ K

$$\ln k_2 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln k_1$$

$$\ln k_2 = \left(\frac{-104\ \text{kJ/mol}}{8.314 \times 10^{-3}\ \text{kJ/(K}\bullet\text{mol)}}\right)\left(\frac{1}{308\ \text{K}} - \frac{1}{298\ \text{K}}\right) + \ln (3.7 \times 10^{-5})$$

$\ln k_2 = -8.84$; $k_2 = e^{-8.84} = 1.4 \times 10^{-4}$/s

12.17 Assume that concentration is proportional to the number of each molecule in a box.
(a) From boxes (1) and (2), the concentration of A doubles, B and C_2 remain the same and the rate does not change. This means the reaction is zeroth-order in A.
From boxes (1) and (3), the concentration of C_2 doubles, A and B remain the same and the rate doubles. This means the reaction is first-order in C_2.
From boxes (1) and (4), the concentration of B triples, A and C_2 remain the same and the rate triples. This means the reaction is first-order in B.
(b) Rate = k [B][C_2]
(c)

$$\begin{aligned} &B + C_2 \rightarrow BC_2 && \text{(slow)} \\ &A + BC_2 \rightarrow AC + BC \\ &\underline{A + BC \rightarrow AC + B} \\ &2\,A + C_2 \rightarrow 2\,AC && \text{(overall)} \end{aligned}$$

(d) B doesn't appear in the overall reaction because it is consumed in the first step and regenerated in the third step. B is therefore a catalyst. BC_2 and BC are intermediates because they are formed in one step and then consumed in a subsequent step in the reaction.

12.18 Nitroglycerin contains three nitro groups per molecule. Because the bonds in nitro groups are relatively weak (about 200 kJ/mol) and because the explosion products (CO_2, N_2, H_2O, and O_2) are extremely stable, a great deal of energy is released (very exothermic) during an explosion.

12.19 Secondary explosives are generally less sensitive to heat and shock than primary explosives. This would indicate that secondary explosives should have a higher activation energy than primary explosives.

12.20 $C_5H_8N_4O_{12}(s) \rightarrow 4\,CO_2(g) + 4\,H_2O(g) + 2\,N_2(g) + C(s)$

$\Delta H^o_{rxn} = [4\ \Delta H^o_f\ (CO_2) + 4\ \Delta H^o_f\ (H_2O)]\ -\ \Delta H^o_f\ (C_5H_8N_4O_{12})$
$\Delta H^o_{rxn} = [(4\ mol)(-393.5\ kJ/mol) + (4\ mol)(-241.8\ kJ/mol)]\ -\ [(1\ mol)(537\ kJ/mol)]$
$\Delta H^o_{rxn} = -3078\ kJ$

12.21 $C_5H_8N_4O_{12}(s) \rightarrow 4\ CO_2(g) + 4\ H_2O(g) + 2\ N_2(g) + C(s)$
$C_5H_8N_4O_{12}$, 316.14 amu; $1.54\ kg = 1.54 \times 10^3\ g$; $800^oC = 1073\ K$
From the reaction, 1 mole of PETN produces 10 moles of gas.

$$\text{mol gas} = 1.54 \times 10^3\ \text{g PETN} \times \frac{1\ \text{mol PETN}}{316.14\ \text{g PETN}} \times \frac{10\ \text{mol gas}}{1\ \text{mol PETN}} = 48.7\ \text{mol}$$

$PV = nRT$

$$V = \frac{nRT}{P} = \frac{(48.7\ \text{mol})\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(1073\ \text{K})}{0.975\ \text{atm}} = 4.40 \times 10^3\ \text{L}$$

Understanding Key Concepts

12.22 (a) Because Rate = k[A][B], the rate is proportional to the product of the number of A molecules and the number of B molecules. The relative rates of the reaction in vessels (a) – (d) are 2 : 1 : 4 : 2.
(b) Because the same reaction takes place in each vessel, the k's are all the same.

12.23 (a) Because Rate = k[A], the rate is proportional to the number of A molecules in each reaction vessel. The relative rates of the reaction are 2 : 4 : 3.
(b) For a first-order reaction, half-lives are independent of concentration. The half-lives are the same.
(c) Concentrations will double, rates will double, and half-lives will be unaffected.

12.24 (a) For the first-order reaction, half of the A molecules are converted to B molecules each minute.

(b) Because half of the A molecules are converted to B molecules in 1 min, the half-life is 1 minute.

12.25 (a) Two molecules of A are converted to two molecules of B every minute. This means the rate is constant throughout the course of the reaction. The reaction is zeroth-order.

(b)

(c) Rate = k

$$k = \frac{(2)\left(\frac{6.0 \text{ x } 10^{21} \text{ molecules}}{1.0 \text{ L}}\right)\left(\frac{1 \text{ mol}}{6.022 \text{ x } 10^{23} \text{ molecules}}\right)}{\text{min}} \text{ x } \frac{1 \text{ min}}{60 \text{ s}} = 3.3 \text{ x } 10^{-4} \text{ M/s}$$

12.26 (a) Because the half-life is inversely proportional to the concentration of A molecules, the reaction is second-order in A.

(b) Rate = $k[A]^2$

(c) The second box represents the passing of one half-life, and the third box represents the passing of a second half-life for a second-order reaction. A relative value of k can be calculated.

$$k = \frac{1}{t_{1/2}[A]} = \frac{1}{(1)(16)} = 0.0625$$

$t_{1/2}$ in going from box 3 to box 4 is: $t_{1/2} = \frac{1}{k[A]} = \frac{1}{(0.0625)(4)} = 4$ min

(For fourth box, t = 7 min)

12.27 (a) bimolecular (b) unimolecular (c) termolecular

12.28 (a) BC + D $\rightarrow$ B + CD

(b) 1. B–C + D (reactants), A (catalyst); 2. B---C---A (transition state), D (reactant); 3. A–C (intermediate), B (product), D (reactant); 4. A---C---D (transition state), B (product); 5. A (catalyst), C–D + B (products)

(c) The first step is rate determining because the first maximum in the potential energy curve is greater than the second (relative) maximum; Rate = k[A][BC]

(d) Endothermic

12.29

Additional Problems
Reaction Rates

12.30 M/s or $\frac{\text{mol}}{\text{L} \bullet \text{s}}$

12.31 molecules/($cm^3 \cdot s$)

12.32 (a) Rate = $-\frac{\Delta[\text{cyclopropane}]}{\Delta t} = -\frac{0.080\ \text{M} - 0.098\ \text{M}}{5.0\ \text{min} - 0.0\ \text{min}} = 3.6 \times 10^{-3}$ M/min

Rate = $3.6 \times 10^{-3}\ \frac{\text{M}}{\text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 6.0 \times 10^{-5}$ M/s

(b) Rate = $-\frac{\Delta[\text{cyclopropane}]}{\Delta t} = -\frac{0.044\ \text{M} - 0.054\ \text{M}}{20.0\ \text{min} - 15.0\ \text{min}} = 2.0 \times 10^{-3}$ M/min

Rate = $2.0 \times 10^{-3}\ \frac{\text{M}}{\text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 3.3 \times 10^{-5}$ M/s

12.33 (a) Rate = $-\frac{\Delta[NO_2]}{\text{Deltat}} = -\frac{(5.59 \times 10^{-3}\ \text{M}) - (6.58 \times 10^{-3}\ \text{M})}{100\ \text{s} - 50\ \text{s}} = 2.0 \times 10^{-5}$ M/s

(b) Rate = $-\frac{\Delta[NO_2]}{\text{Deltat}} = -\frac{(4.85 \times 10^{-3}\ \text{M}) - (5.59 \times 10^{-3}\ \text{M})}{150\ \text{s} - 100\ \text{s}} = 1.5 \times 10^{-5}$ M/s

12.34

(a) The instantaneous rate of decomposition of N_2O_5 at t = 200 s is determined from the slope of the curve at t = 200 s.

Rate = $-\frac{\Delta[N_2O_5]}{\text{Deltat}} = -\ \text{slope} = -\frac{(1.20 \times 10^{-2}\ \text{M}) - (1.69 \times 10^{-2}\ \text{M})}{300\ \text{s} - 100\ \text{s}} = 2.4 \times 10^{-5}$ M/s

(b) The initial rate of decomposition of N_2O_5 is determined from the slope of the curve at t = 0 s. This is equivalent to the slope of the curve from 0 s to 100 s because in this time interval the curve is almost linear.

Initial rate = $-\frac{\Delta[N_2O_5]}{\Delta t} = -\ \text{slope} = -\frac{(1.69 \times 10^{-2}\ \text{M}) - (2.00 \times 10^{-2}\ \text{M})}{100\ \text{s} - 0\ \text{s}} = 3.1 \times 10^{-5}$ M/s

12.35

(a) The instantaneous rate of decomposition of NO_2 at t = 100 s is determined from the slope of the curve at t = 100 s.

$$\text{Rate} = -\frac{\Delta[NO_2]}{\text{Deltat}} = -\text{slope} = -\frac{(4.00 \times 10^{-3}\ \text{M}) - (7.00 \times 10^{-3}\ \text{M})}{190\ \text{s} - 20\ \text{s}} = 1.8 \times 10^{-5}\ \text{M/s}$$

(b) The initial rate of decomposition of NO_2 is determined from the slope of the curve at t = 0 s. This is equivalent to the slope of the curve from 0 s to 50 s because in this time interval the curve is almost linear.

$$\text{Initial rate} = -\frac{\Delta[NO_2]}{\Delta t} = -\text{slope} = -\frac{(6.58 \times 10^{-3}\ \text{M}) - (8.00 \times 10^{-3}\ \text{M})}{50\ \text{s} - 0\ \text{s}} = 2.8 \times 10^{-5}\ \text{M/s}$$

12.36 (a) $-\frac{\Delta[H_2]}{\Delta t} = -3\frac{\Delta[N_2]}{\Delta t}$; The rate of consumption of H_2 is 3 times faster.

(b) $\frac{\Delta[NH_3]}{\Delta t} = -2\frac{\Delta[N_2]}{\Delta t}$; The rate of formation of NH_3 is 2 times faster.

12.37 (a) $-\frac{\Delta[O_2]}{\Delta t} = -\frac{5}{4}\frac{\Delta[NH_3]}{\Delta t}$; The rate of consumption of O_2 is 1.25 times faster.

(b) $\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[NH_3]}{\Delta t}$; The rate of formation of NO is the same.

$\frac{\Delta[H_2O]}{\Delta t} = -\frac{6}{4}\frac{\Delta[NH_3]}{\Delta t}$; The rate of formation of H_2O is 1.5 times faster.

12.38 $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$; $\quad -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

12.39 (a) $-\frac{\Delta[I^-]}{\Delta t} = -3\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = 3(1.5 \times 10^{-3}\ \text{M/s}) = 4.5 \times 10^{-3}\ \text{M/s}$

(b) $\frac{\Delta[SO_4^{2-}]}{\Delta t} = -2\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = 2(1.5 \times 10^{-3}\ \text{M/s}) = 3.0 \times 10^{-3}\ \text{M/s}$

Rate Laws

12.40 $\text{Rate} = k[NO]^2[Br_2]$; 2nd order in NO; 1st order in Br_2; 3rd order overall

12.41 $\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$; 1st order in $CHCl_3$; 1/2 order in Cl_2; 3/2 order overall

12.42 $\text{Rate} = k[H_2][ICl]$; units for k are $\frac{L}{\text{mol} \bullet \text{s}}$ or $1/(M \cdot s)$

12.43 Rate = $k[NO]^2[H_2]$, units for k are $1/(M^2 \cdot s)$

12.44 (a) Rate = $k[CH_3Br][OH^-]$
(b) Because the reaction is first-order in OH^-, if the $[OH^-]$ is decreased by a factor of 5, the rate will also decrease by a factor of 5.
(c) Because the reaction is first-order in each reactant, if both reactant concentrations are doubled, the rate will increase by a factor of 2 x 2 = 4.

12.45 (a) Rate = $k[Br^-][BrO_3^-][H^+]^2$
(b) The overall reaction order is 1 + 1 + 2 = 4.
(c) Because the reaction is second-order in H^+, if the $[H^+]$ is tripled, the rate will increase by a factor of $3^2 = 9$.
(d) Because the reaction is first-order in both Br^- and BrO_3^-, if both reactant concentrations are halved, the rate will decrease by a factor of 4 (1/2 x 1/2 = 1/4).

12.46 (a) Rate = $k[CH_3COCH_3]^m$

$$m = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln\left(\frac{[CH_3COCH_3]_2}{[CH_3COCH_3]_1}\right)} = \frac{\ln\left(\frac{7.8 \times 10^{-5}}{5.2 \times 10^{-5}}\right)}{\ln\left(\frac{9.0 \times 10^{-3}}{6.0 \times 10^{-3}}\right)} = 1; \quad Rate = k[CH_3COCH_3]$$

(b) From Experiment 1: $k = \frac{Rate}{[CH_3COCH_3]} = \frac{5.2 \times 10^{-5}\ M/s}{6.0 \times 10^{-3}\ M} = 8.7 \times 10^{-3}/s$
(c) Rate = $k[CH_3COCH_3] = (8.7 \times 10^{-3}/s)(1.8 \times 10^{-3} M) = 1.6 \times 10^{-5}$ M/s

12.47 (a) Rate = $k[CH_3NNCH_3]^m$

$$m = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln\left(\frac{[CH_3NNCH_3]_2}{[CH_3NNCH_3]_1}\right)} = \frac{\ln\left(\frac{2.0 \times 10^{-6}}{6.0 \times 10^{-6}}\right)}{\ln\left(\frac{8.0 \times 10^{-3}}{2.4 \times 10^{-2}}\right)} = 1; \quad Rate = k[CH_3NNCH_3]$$

(b) From Experiment 1: $k = \frac{Rate}{[CH_3NNCH_3]} = \frac{6.0 \times 10^{-6}\ M/s}{2.4 \times 10^{-2}\ M} = 2.5 \times 10^{-4}/s$
(c) Rate = $k[CH_3NNCH_3] = (2.5 \times 10^{-4}/s)(0.020\ M) = 5.0 \times 10^{-6}$ M/s

12.48 (a) Rate = $k[NH_4^+]^m[NO_2^-]^n$

$$m = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln\left(\frac{[NH_4^+]_2}{[NH_4^+]_1}\right)} = \frac{\ln\left(\frac{3.6\ x\ 10^{-6}}{7.2\ x\ 10^{-6}}\right)}{\ln\left(\frac{0.12}{0.24}\right)} = 1; \quad n = \frac{\ln\left(\frac{Rate_3}{Rate_2}\right)}{\ln\left(\frac{[NO_2^-]_3}{[NO_2^-]_2}\right)} = \frac{\ln\left(\frac{5.4\ x\ 10^{-6}}{3.6\ x\ 10^{-6}}\right)}{\ln\left(\frac{0.15}{0.10}\right)} = 1$$

Rate = $k[NH_4^+][NO_2^-]$

(b) From Experiment 1: $k = \frac{Rate}{[NH_4^+][NO_2^-]} = \frac{7.2\ x\ 10^{-6}\ M/s}{(0.24\ M)(0.10\ M)} = 3.0\ x\ 10^{-4}/(M \cdot s)$

(c) Rate = $k[NH_4^+][NO_2^-] = [3.0\ x\ 10^{-4}/(M \cdot s)](0.39\ M)(0.052\ M) = 6.1\ x\ 10^{-6}$ M/s

12.49 (a) Rate = $k[NO]^m[Cl_2]^n$

$$m = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln\left(\frac{[NO]_2}{[NO]_1}\right)} = \frac{\ln\left(\frac{4.0\ x\ 10^{-2}}{1.0\ x\ 10^{-2}}\right)}{\ln\left(\frac{0.26}{0.13}\right)} = 2; \quad n = \frac{\ln\left(\frac{Rate_3}{Rate_1}\right)}{\ln\left(\frac{[Cl_2]_3}{[Cl_2]_1}\right)} = \frac{\ln\left(\frac{5.0\ x\ 10^{-3}}{1.0\ x\ 10^{-2}}\right)}{\ln\left(\frac{0.10}{0.20}\right)} = 1$$

Rate = $k[NO]^2[Cl_2]$

(b) From Experiment 1: $k = \frac{Rate}{[NO]^2[Cl_2]} = \frac{1.0\ x\ 10^{-2}\ M/s}{(0.13\ M)^2(0.20\ M)} = 3.0/(M^2 \cdot s)$

(c) Rate = $k[NO]^2[Cl_2] = [3.0/(M^2 \cdot s)](0.12\ M)^2(0.12\ M) = 5.2\ x\ 10^{—3}$ M/s

Integrated Rate Law; Half-Life

12.50 $\ln\frac{[C_3H_6]_t}{[C_3H_6]_0} = \_\ kt$, $k = 6.7\ x\ 10^{-4}$/s

(a) $t = 30\ min\ x\ \frac{60\ s}{1\ min} = 1800\ s$

$\ln[C_3H_6]_t = \_\ kt + \ln[C_3H_6]_0 = \_\ (6.7\ x\ 10^{-4}/s)(1800\ s) + \ln(0.0500) = -4.202$

$[C_3H_6]_t = e^{-4.202} = 0.015$ M

(b) $t = \frac{\ln\frac{[C_3H_6]_t}{[C_3H_6]_0}}{\_\ k} = \frac{\ln\left(\frac{0.0100}{0.0500}\right)}{\_\ (6.7\ x\ 10^{-4}/s)} = 2402\ s; \quad t = 2402\ s\ x\ \frac{1\ min}{60\ s} = 40\ min$

(c) $[C_3H_6]_0 = 0.0500$ M; If 25% of the C_3H_6 reacts then 75% remains.

$[C_3H_6]_t = (0.75)(0.0500\ M) = 0.0375$ M.

$$t = \frac{\ln\frac{[C_3H_6]_t}{[C_3H_6]_0}}{\_\ k} = \frac{\ln\left(\frac{0.0375}{0.0500}\right)}{\_\ (6.7\ x\ 10^{-4}/s)} = 429\ s; \quad t = 429\ s\ x\ \frac{1\ min}{60\ s} = 7.2\ min$$

12.51 $\ln\frac{[CH_3NC]_t}{[CH_3NC]_0} = -kt$, $k = 5.11 \times 10^{-5}$/s

(a) $t = 2.00 \text{ hr} \times \frac{60 \text{ min}}{1 \text{ hr}} \times \frac{60 \text{ s}}{1 \text{ min}} = 7200 \text{ s}$

$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0 = -(5.11 \times 10^{-5}/\text{s})(7200 \text{ s}) + \ln(0.0340) = -3.749$

$[CH_3NC]_t = e^{-3.749} = 0.0235$ M

(b) $t = \frac{\ln\frac{[CH_3NC]_t}{[CH_3NC]_0}}{-k} = \frac{\ln\left(\frac{0.0300}{0.0340}\right)}{-5.11 \times 10^{-5}/\text{s})} = 2449$ s; $\quad t = 2449 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 40.8$ min

(c) $[CH_3NC]_0 = 0.0340$ M; If 20% of the CH_3NC reacts then 80% remains.

$[CH_3NC]_t = (0.80)(0.0340 \text{ M}) = 0.0272$ M.

$t = \frac{\ln\frac{[CH_3NC]_t}{[CH_3NC]_0}}{-k} = \frac{\ln\left(\frac{0.0272}{0.0340}\right)}{-(5.11 \times 10^{-5}/\text{s})} = 4367$ s; $\quad t = 4367 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 72.8$ min

12.52 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.7 \times 10^{-4}/\text{s}} = 1034 \text{ s} = 17$ min

$t = \frac{\ln\frac{[C_3H_6]_t}{[C_3H_6]_o}}{-k} = \frac{\ln\frac{(0.0625)(0.0500)}{(0.0500)}}{-6.7 \times 10^{-4}/\text{s}} = 4140$ s

$t = 4140 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 69$ min

This is also 4 half-lives. $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5 \xrightarrow{t_{1/2}} 6.25$

12.53 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.11 \times 10^{-5}/\text{s}} = 13{,}562$ s

$t_{1/2} = 13{,}562 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ hr}}{60 \text{ min}} = 3.77$ hr

$t = \frac{\ln\frac{[CH_3NC]_t}{[CH_3NC]_o}}{-k} = \frac{\ln\frac{(0.125)(0.0340)}{(0.0340)}}{-5.11 \times 10^{-5}/\text{s}} = 40{,}694$ s

$t = 40{,}694 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ hr}}{60 \text{ min}} = 11.3$ hr

This is also 3 half-lives. $100 \xrightarrow{t_{1/2}} 50 \xrightarrow{t_{1/2}} 25 \xrightarrow{t_{1/2}} 12.5$

12.54 $t_{1/2} = 8.0$ h

$$0.60\ M \xrightarrow{t_{1/2}} 0.30\ M \xrightarrow{t_{1/2}} 0.15\ M$$ requires 2 half-lives so it will take 16.0 h.

12.55 $t_{1/2} = 3.33$ h

$$0.800\ M \xrightarrow{t_{1/2}} 0.400\ M \xrightarrow{t_{1/2}} 0.200\ M \xrightarrow{t_{1/2}} 0.100\ M \xrightarrow{t_{1/2}} 0.0500\ M$$
requires 4 half-lives so it will take 13.3 h.

12.56 $kt = \dfrac{1}{[C_4H_6]_t} - \dfrac{1}{[C_4H_6]_0}$, $\quad k = 4.0 \times 10^{-2}/(M \cdot s)$

(a) $t = 1.00\ h \times \dfrac{60\ min}{1\ hr} \times \dfrac{60\ s}{1\ min} = 3600\ s$

$$\frac{1}{[C_4H_6]_t} = kt + \frac{1}{[C_4H_6]_0} = (4.0 \times 10^{-2}/(M \bullet s))(3600\ s) + \frac{1}{0.0200\ M}$$

$$\frac{1}{[C_4H_6]_t} = 194/M \text{ and } [C_4H_6] = 5.2 \times 10^{-3}\ M$$

(b) $t = \dfrac{1}{k}\left[\dfrac{1}{[C_4H_6]_t} - \dfrac{1}{[C_4H_6]_0}\right]$

$$t = \frac{1}{4.0 \times 10^{-2}/(M \bullet s)}\left[\frac{1}{(0.0020\ M)} - \frac{1}{(0.0200\ M)}\right] = 11{,}250\ s$$

$$t = 11{,}250\ s \times \frac{1\ min}{60\ s} \times \frac{1\ hr}{60\ min} = 3.1\ h$$

12.57 $kt = \dfrac{1}{[HI]_t} - \dfrac{1}{[HI]_0}$, $\quad k = 9.7 \times 10^{-6}/(M \cdot s)$

(a) $t = 6.00\ day \times \dfrac{24\ hr}{1\ day} \times \dfrac{60\ min}{1\ hr} \times \dfrac{60\ s}{1\ min} = 518{,}400\ s$

$$\frac{1}{[HI]_t} = kt + \frac{1}{[HI]_0} = (9.7 \times 10^{-6}/(M \bullet s))(518{,}400\ s) + \frac{1}{0.100\ M}$$

$$\frac{1}{[HI]_t} = 15.03/M \text{ and } [HI] = 0.067\ M$$

(b) $t = \frac{1}{k}\left[\frac{1}{[HI]_t} - \frac{1}{[HI]_0}\right]$

$t = \frac{1}{9.7 \text{ x } 10^{-6}/(M \bullet s)}\left[\frac{1}{(0.020 \text{ M})} - \frac{1}{(0.100 \text{ M})}\right] = 4{,}123{,}711 \text{ s}$

$t = 4{,}123{,}711 \text{ s x } \frac{1 \text{ min}}{60 \text{ s}} \text{ x } \frac{1 \text{ hr}}{60 \text{ min}} \text{ x } \frac{1 \text{ day}}{24 \text{ hr}} = 48 \text{ days}$

12.58 $t_{1/2} = \frac{1}{k[C_4H_6]_o} = \frac{1}{[4.0 \text{ x } 10^{-2}/(\text{Mcdot s})](0.0200 \text{ M})} = 1250 \text{ s} = 21 \text{ min}$

$t = t_{1/2} = \frac{1}{k[C_4H_6]_o} = \frac{1}{[4.0 \text{ x } 10^{-2}/(\text{Mcdot s})](0.0100 \text{ M})} = 2500 \text{ s} = 42 \text{ min}$

12.59 $t_{1/2} = \frac{1}{k[HI]_o} = \frac{1}{[9.7 \text{ x } 10^{-6}/(M \bullet s)](0.100 \text{ M})} = 1{,}030{,}928 \text{ s}$

$1{,}030{,}928 \text{ s x } \frac{1 \text{ min}}{60 \text{ s}} \text{ x } \frac{1 \text{ hr}}{60 \text{ min}} \text{ x } \frac{1 \text{ day}}{24 \text{ hr}} = 12 \text{ days}$

$t = t_{1/2} = \frac{1}{k[HI]_o} = \frac{1}{[9.7 \text{ x } 10^{-6}/(M \bullet s)](0.0250 \text{ M})} = 4{,}123{,}711 \text{ s}$

$4{,}123{,}711 \text{ s x } \frac{1 \text{ min}}{60 \text{ s}} \text{ x } \frac{1 \text{ hr}}{60 \text{ min}} \text{ x } \frac{1 \text{ day}}{24 \text{ hr}} = 48 \text{ days}$

12.60

time (min)	$[N_2O]$	$\ln[N_2O]$	$1/[N_2O]$
0	0.250	-1.386	4.00
60	0.218	-1.523	4.59
90	0.204	-1.590	4.90
120	0.190	-1.661	5.26
180	0.166	-1.796	6.02

A plot of ln $[N_2O]$ versus time is linear. The reaction is first-order in N_2O.
k = -slope = -(-2.28 x 10^{-3}/min) = 2.28 x 10^{-3}/min

$k = 2.28 \text{ x } 10^{-3}/\text{min} \text{ x } \frac{1 \text{ min}}{60 \text{ s}} = 3.79 \text{ x } 10^{-5}/\text{s}$

12.61

time (s)	[NOBr]	ln[NOBr]	1/[NOBr]
0	0.0400	-3.219	25.0
10	0.0303	-3.497	33.0

20	0.0244	-3.713	41.0
30	0.0204	-3.892	49.0
40	0.0175	-4.046	57.1

A plot of 1/[NOBr] versus time is linear. The reaction is second-order in NOBr.
k = slope = 0.80/(M · s)

12.62 $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{248\ s} = 2.79 \times 10^{-3}/s$

12.63 $t_{1/2} = \frac{1}{k[A]_o}$; $t_{1/2} = 25\ min \times \frac{60\ s}{1\ min} = 1500\ s$

$k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{(1500\ s)(0.036\ M)} = 1.8 \times 10^{-2}\ M^{-1}\ s^{-1}$

12.64 (a) The units for the rate constant, k, indicate the reaction is zeroth-order.
(b) For a zeroth-order reaction, $[A]_t - [A]_o = -kt$

$t = 30\ min \times \frac{60\ s}{1\ min} = 1800\ s$

$[A]_t = -kt + [A]_o = -(3.6 \times 10^{-5}\ M/s)(1800\ s) + 0.096\ M = 0.031\ M$

(c) Let $[A]_t = [A]_o/2$

$t_{1/2} = \frac{[A]_o/2 - [A]_o}{-k} = \frac{0.096/2\ M - 0.096\ M}{-3.6 \times 10^{-5}\ M/s} = 1333\ s$

$t_{1/2} = 1333\ s \times \frac{1\ min}{60\ s} = 22\ min$

12.65 (a)

A plot of [AB] versus time is linear. The reaction is zeroth-order and k = - slope.

$$k = -\frac{0.140\ M - 0.200\ M}{80.0\ min - 0\ min} = 7.50 \times 10^{-4}\ M/min$$

$$k = 7.50 \times 10^{-4}\ M/min \times \frac{1\ min}{60\ s} = 1.25 \times 10^{-5}\ M/s$$

(b) $[A]_t - [A]_o = -kt$

$[A]_t = -kt + [A]_o = -(7.50 \times 10^{-4}\ M/min)(126\ min) + 0.200\ M = 0.105\ M$

(c) $[A]_t - [A]_o = -kt$

$$t = \frac{[A]_t - [A]_o}{-k} = \frac{0.100\ M - 0.200\ M}{-7.50 \times 10^{-4}\ M/min} = 133\ min$$

Reaction Mechanisms

12.66 An elementary reaction is a description of an individual molecular event that involves the breaking and/or making of chemical bonds. By contrast, the overall reaction describes only the stoichiometry of the overall process but provides no information about how the reaction occurs.

12.67 Molecularity is the number of reactant molecules or atoms for an elementary reaction. Reaction order is the sum of the exponents of the concentration terms in the rate law.

12.68 There is no relationship between the coefficients in a balanced chemical equation for an overall reaction and the exponents in the rate law unless the overall reaction occurs in a single elementary step, in which case the coefficients in the balanced equation are the exponents in the rate law.

12.69 The rate-determining step is the slowest step in a multistep reaction. The coefficients in the balanced equation for the rate-determining step are the exponents in the rate law.

12.70 (a) $H_2(g) + ICl(g) \rightarrow HI(g) + HCl(g)$
$\underline{HI(g) + ICl(g) \rightarrow I_2(g) + HCl(g)}$
Overall reaction $H_2(g) + 2\ ICl(g) \rightarrow I_2(g) + 2\ HCl(g)$
(b) Because HI(g) is produced in the first step and consumed in the second step, it is a reaction intermediate.
(c) In each reaction there are two reactant molecules, so each elementary reaction is bimolecular.

12.71 (a) $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$
$\underline{NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g)}$
Overall reaction $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$
(b) Because $NOCl_2$ is produced in the first step and consumed in the second step, $NOCl_2$ is a reaction intermediate.
(c) Each elementary step is bimolecular.

12.72 (a) bimolecular, Rate = $k[O_3][Cl]$ (b) unimolecular, Rate = $k[NO_2]$
(c) bimolecular, Rate = $k[ClO][O]$ (d) termolecular, Rate = $k[Cl]^2[N_2]$

12.73 (a) unimolecular, Rate = $k[I_2]$ (b) termolecular, Rate = $k[NO]^2[Br_2]$
(c) bimolecular, Rate = $k[CH_3Br][OH^-]$ (d) unimolecular, Rate = $k[N_2O_5]$

12.74 (a) $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$
$\underline{Cl(g) + NO_2Cl(g) \rightarrow NO_2(g) + Cl_2(g)}$
Overall reaction $2\ NO_2Cl(g) \rightarrow 2\ NO_2(g) + Cl_2(g)$
(b) 1. unimolecular; 2. bimolecular
(c) Rate = $k[NO_2Cl]$

12.75 (a) $Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$
$\underline{Mo(CO)_5 + L \rightarrow Mo(CO)_5L}$
Overall reaction $Mo(CO)_6 + L \rightarrow Mo(CO)_5L + CO$
(b) 1. unimolecular; 2. bimolecular
(c) Rate = $k[Mo(CO)_6]$

12.76 $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$ (slow)
$F(g) + NO_2(g) \rightarrow NO_2F(g)$ (fast)

12.77 $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$ (slow)
$NO_2(g) + O(g) \rightarrow O_2(g) + NO(g)$ (fast)

The Arrhenius Equation

12.78 Very few collisions involve a collision energy greater than or equal to the activation energy, and only a fraction of those have the proper orientation for reaction.

12.79 The two reactions have frequency factors that differ by a factor of 10.

12.80 Plot ln k versus 1/T to determine the activation energy, E_a

Slope = -1.25×10^4 K

$E_a = -R(\text{slope}) = -[8.314 \times 10^{-3}\ \text{kJ/(K} \cdot \text{mol)}](-1.25 \times 10^4\ \text{K}) = 104\ \text{kJ/mol}$

12.81 Plot ln k versus 1/T to determine the activation energy, E_a.

Slope = -1.359×10^4 K

$E_a = -R(\text{slope}) = -[8.314 \times 10^{-3}\ \text{kJ/(K} \cdot \text{mol)}](-1.359 \times 10^4\ \text{K}) = 113\ \text{kJ/mol}$

12.82 (a) $\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$k_1 = 1.3/(\text{M} \cdot \text{s})$, $T_1 = 700$ K

$k_2 = 23.0/(\text{M} \cdot \text{s})$, $T_2 = 800$ K

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(23.0) - \ln(1.3)][8.314 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}]}{\left(\frac{1}{800\ \text{K}} - \frac{1}{700\ \text{K}}\right)} = 134\ \text{kJ/mol}$$

(b) $k_1 = 1.3/(\text{M} \cdot \text{s})$, $T_1 = 700$ K

solve for k_2, $T_2 = 750$ K

$$\ln k_2 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln k_1$$

$$\ln k_2 = \left(\frac{-133.8\ \text{kJ/mol}}{8.314\ \text{x}\ 10^{-3}\ \text{kJ/(K}\bullet\text{mol)}}\right)\left(\frac{1}{750\ \text{K}} - \frac{1}{700\ \text{K}}\right) + \ln\ (1.3)\ =\ 1.795$$

$k_2 = e^{1.795} = 6.0/(M \cdot s)$

12.83 $$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

(a) Because the rate doubles, $k_2 = 2k_1$

$k_1 = 1.0 \text{ x } 10^{-3}/s$, $T_1 = 25^oC = 298$ K

$k_2 = 2.0 \text{ x } 10^{-3}/s$, $T_2 = 35^oC = 308$ K

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(2.0\ \text{x}\ 10^{-3}) - \ln(1.0\ \text{x}\ 10^{-3})][8.314\ \text{x}\ 10^{-3}\ \text{kJ/(Kcdot mol)}]}{\left(\frac{1}{308\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 53\ \text{kJ/mol}$$

(b) Because the rate triples, $k_2 = 3k_1$

$k_1 = 1.0 \text{ x } 10^{-3}/s$, $T_1 = 25^oC = 298$ K

$k_2 = 3.0 \text{ x } 10^{-3}/s$, $T_2 = 35^oC = 308$ K

$$E_a = -\frac{[\ln(3.0\ \text{x}\ 10^{-3}) - \ln(1.0\ \text{x}\ 10^{-3})][8.314\ \text{x}\ 10^{-3}\ \text{kJ/(Kcdot mol)}]}{\left(\frac{1}{308\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 84\ \text{kJ/mol}$$

12.84 $$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

assume $k_1 = 1.0/(M \cdot s)$ at $T_1 = 25^oC = 298$ K

assume $k_2 = 15/(M \cdot s)$ at $T_2 = 50^oC = 323$ K

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(15) - \ln(1.0)][8.314\ \text{x}\ 10^{-3}\ \text{kJ/(K}\bullet\text{mol)}]}{\left(\frac{1}{323\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 87\ \text{kJ/mo1}$$

12.85 $$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

assume $k_1 = 1.0/(M \cdot s)$ at $T_1 = 15^oC = 288$ K

assume $k_2 = 6.37/(M \cdot s)$ at $T_2 = 45^oC = 318$ K

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln (6.37) - \ln (1.0)][8.314 \text{ x } 10^{-3} \text{ kJ/(K• mol)}]}{\left(\frac{1}{318 \text{ K}} - \frac{1}{288 \text{ K}}\right)} = 47.0 \text{ kJ/mo1}$$

12.86

12.87 (a) (b)

Catalysis

12.88 A catalyst does participate in the reaction, but it is not consumed because it reacts in one step of the reaction and is regenerated in a subsequent step.

12.89 A catalyst doesn't appear in the chemical equation for a reaction because a catalyst reacts in one step of the reaction but is regenerated in a subsequent step.

12.90 A catalyst increases the rate of a reaction by changing the reaction mechanism and lowering the activation energy.

12.91 A homogeneous catalyst is one that exists in the same phase as the reactants.
Example: NO(g) acts as a homogeneous catalyst for the conversion of $O_2(g)$ to $O_3(g)$.
A heterogeneous catalyst is one that exists in a different phase from the reactants.
Example: solid Ni, Pd, or Pt for catalytic hydrogenation, $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$.

12.92 (a) $O_3(g) + O(g) \rightarrow 2\ O_2(g)$ (b) Cl acts as a catalyst.
(c) ClO is a reaction intermediate.
(d) A catalyst reacts in one step and is regenerated in a subsequent step. A reaction intermediate is produced in one step and consumed in another.

12.93 (a)
$$2\ SO_2(g) + 2\ NO_2(g) \rightarrow 2\ SO_3(g) + 2\ NO(g)$$
$$\underline{2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)}$$
Overall reaction $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$
(b) $NO_2(g)$ acts as a catalyst because it is used in the first step and regenerated in the second. NO(g) is a reaction intermediate because it is produced in the first step and consumed in the second.

12.94 (a)
$$NH_2NO_2(aq) + OH^-(aq) \rightarrow NHNO_2^-(aq) + H_2O(l)$$
$$\underline{NHNO_2^-(aq) \rightarrow N_2O(g) + OH^-(aq)}$$
Overall reaction $NH_2NO_2(aq) \rightarrow N_2O(g) + H_2O(l)$
(b) OH^- acts as a catalyst because it is used in the first step and regenerated in the second. $NHNO_2^-$ is a reaction intermediate because it is produced in the first step and consumed in the second.
(c) The rate will decrease because added acid decreases the concentration of OH^-, which appears in the rate law since it is a catalyst.

12.95 The reaction in Problem 12.77 involves a catalyst (NO) because NO is used in the first step and is regenerated in the second step. The reaction also involves an intermediate (NO_2) because NO_2 is produced in the first step and is used up in the second step.

General Problems

12.96 $2\ AB_2 \rightarrow A_2 + 2\ B_2$
(a) Measure the change in the concentration of AB_2 as a function of time.
(b) and (c) If a plot of $[AB_2]$ versus time is linear, the reaction is zeroth-order and k = -slope. If a plot of ln $[AB_2]$ versus time is linear, the reaction is first-order and k = -slope. If a plot of $1/[AB_2]$ versus time is linear, the reaction is second-order and k = slope.

12.97 $A \rightarrow B + C$
(a) Measure the change in the concentration of A as a function of time at several different temperatures.
(b) Plot ln [A] versus time, for each temperature. Straight line graphs will result and k at each temperature equals -slope. Graph ln k versus 1/K, where K is the kelvin temperature. Determine the slope of the line. E_a = -R(slope) where R = 8.314×10^{-3}

kJ/(K · mol).

12.98 (a) Rate = $k[B_2][C]$

(b) $B_2 + C \rightarrow CB + B$ (slow)

$CB + A \rightarrow AB + C$ (fast)

(c) C is a catalyst. C does not appear in the chemical equation because it is consumed in the first step and regenerated in the second step.

12.99 (a)

(b) Reaction 2 is the fastest (smallest E_a), and reaction 3 is the slowest (largest E_a).

(c) Reaction 3 is the most endothermic (positive ΔE), and reaction 1 is the most exothermic (largest negative ΔE).

12.100 The first maximum represents the potential energy of the transition state for the first step. The second maximum represents the potential energy of the transition state for the second step. The saddle point between the two maxima represents the potential energy of the intermediate products.

12.101 Because 0.060 M is half of 0.120 M, 5.2 h is the half-life.

For a first-order reaction, the half-life is independent of initial concentration. Because 0.015 M is half of 0.030 M, it will take one half-life, 5.2 h.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5.2\ \text{h}} = 0.133/\text{h}$$

$$\ln\frac{[N_2O_5]_t}{[N_2O_5]_0} = -kt$$

$$t = \frac{\ln\dfrac{[N_2O_5]_t}{[N_2O_5]_0}}{-k} = \frac{\ln\left(\dfrac{0.015}{0.480}\right)}{-(0.133/\text{h})} = 26\ \text{h}$$ (Note that t is five half-lives.)

12.102 (a) The reaction rate will increase with an increase in temperature at constant volume.

(b) The reaction rate will decrease with an increase in volume at constant temperature because reactant concentrations will decrease.

(c) The reaction rate will increase with the addition of a catalyst.
(d) Addition of an inert gas at constant volume will not affect the reaction rate.

12.103 As the temperature of a gas is raised by 10°C, even though the collision frequency increases by on

12.104 (a) Rate = $k[C_2H_4Br_2]^m[I^-]^n$

$$m = \frac{\ln\left(\frac{Rate_2}{Rate_1}\right)}{\ln\left(\frac{[C_2H_4Br_2]_2}{[C_2H_4Br_2]_1}\right)} = \frac{\ln\left(\frac{1.74 \text{ x } 10^{-4}}{6.45 \text{ x } 10^{-5}}\right)}{\ln\left(\frac{0.343}{0.127}\right)} = 1$$

$$n = \frac{\ln\left(\frac{Rate_3 \bullet [C_2H_4Br_2]_2}{Rate_2 \bullet [C_2H_4Br_2]_3}\right)}{\ln\left(\frac{[I^-]_3}{[I^-]_2}\right)} = \frac{\ln\left(\frac{(1.26 \text{ x } 10^{-4})(0.343)}{(1.74 \text{ x } 10^{-4})(0.203)}\right)}{\ln\left(\frac{0.125}{0.102}\right)} = 1$$

Rate = $k[C_2H_4Br_2][I^-]$

(b) From Experiment 1:

$$k = \frac{\text{Rate}}{[C_2H_4Br_2][I^-]} = \frac{6.45 \text{ x } 10^{-5} \text{ M/s}}{(0.127 \text{ M})(0.102 \text{ M})} = 4.98 \text{ x } 10^{-3}/(\text{M} \cdot \text{s})$$

(c) Rate = $k[C_2H_4Br_2][I^-]$ = $[4.98 \text{ x } 10^{-3}(\text{M} \cdot \text{s})](0.150 \text{ M})(0.150 \text{ M}) = 1.12 \text{ x } 10^{-4}$ M/s

12.105 (a) From the data in the table for Experiment 1, we see that 0.20 mol of A reacts with 0.10 mol of B to produce 0.10 mol of D. The balanced equation for the reaction is:
$2 A + B \rightarrow D$

(b) From the data in the table, initial Rates = $-\frac{\Delta A}{\Delta t}$ have been calculated.

For example, from Experiment 1:

$$\text{Initial rate} = -\frac{\Delta A}{\Delta t} = -\frac{(4.80 \text{ M} - 5.00 \text{ M})}{60 \text{ s}} = 3.33 \text{ x } 10^{-3} \text{ M/s}$$

Initial concentrations and initial rate data have been collected in the table below.

EXPT	$[A]_o$ (M)	$[B]_o$ (M)	$[C]_o$ (M)	Initial Rate (M/s)
1	5.00	2.00	1.00	$3.33 \text{ x } 10^{-3}$
2	10.00	2.00	1.00	$6.66 \text{ x } 10^{-3}$
3	5.00	4.00	1.00	$3.33 \text{ x } 10^{-3}$
4	5.00	2.00	2.00	$6.66 \text{ x } 10^{-3}$

Rate = $k[A]^m[B]^n[C]^p$
From Expts 1 and 2, [A] doubles and the initial rate doubles; therefore m = 1.
From Expts 1 and 3, [B] doubles but the initial rate does not change; therefore n = 0.
From Expts 1 and 4, [C] doubles and the initial rate doubles; therefore p = 1.
The reaction is: first-order in A; zeroth-order in B; first-order in C; second-order overall.
(c) Rate = k[A][C]
(d) C is a catalyst. C appears in the rate law, but it is not consumed in the reaction.
(e) $A + C \rightarrow AC$ (slow)
$AC + B \rightarrow AB + C$ (fast)
$A + AB \rightarrow D$ (fast)
(f) From data in Expt 1:

$$k = \frac{\text{Rate}}{[A][C]} = \frac{\Delta D/\Delta t}{[A][C]} = \frac{0.10\ M/60\ s}{(5.00\ M)(1.00\ M)} = 3.4 \times 10^{-4}/(M \cdot s)$$

12.106 For E_a = 50 kJ/mol

$$f = e^{-E_a/RT} = \exp\left\{\frac{-50\ \text{kJ/mol}}{[8.314 \times 10^{-3}\ \text{kJ/(K•mol)}](300\ K)}\right\} = 2.0 \times 10^{-9}$$

For E_a = 100 kJ/mol

$$f = e^{-E_a/RT} = \exp\left\{\frac{-100\ \text{kJ/mol}}{[8.314 \times 10^{-3}\ \text{kJ/(K•mol)}](300\ K)}\right\} = 3.9 \times 10^{-18}$$

12.107 $$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$k_2 = 2.5k_1$
$k_1 = 1.0$, $T_1 = 20^oC = 293$ K
$k_2 = 2.5$, $T_2 = 30^oC = 303$ K

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(2.5) - \ln(1.0)][8.314 \times 10^{-3}\ \text{kJ/(K•mol)}]}{\left(\frac{1}{303\ K} - \frac{1}{293\ K}\right)} = 68\ \text{kJ/mol}$$

$k_1 = 1.0$, $T_1 = 120^oC = 393$ K
$k_2 = ?$, $T_2 = 130^oC = 403$ K
Solve for k_2.

$$\ln k_2 = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln k_1$$

$$\ln k_2 = \frac{-68\ \text{kJ/mol}}{[8.314\ \text{x}\ 10^{-3}\ \text{kJ/(K•mol)}]}\left(\frac{1}{403\ \text{K}} - \frac{1}{393\ \text{K}}\right) + \ln(1.0) = 0.516$$

$k_2 = e^{0.516} = 1.7$; The rate increases by a factor of 1.7.

12.108 (a) $2\ NO(g) + Br_2(g) \rightarrow 2\ NOBr(g)$

(b) Since $NOBr_2$ is generated in the first step and consumed in the second step, $NOBr_2$ is a reaction intermediate.

(c) Rate = $k[NO][Br_2]$

(d) It can't be the first step. It must be the second step.

12.109 $[A] = -kt + [A]_o$

$[A]_o/2 = -kt_{1/2} + [A]_o$

$[A]_o/2 - [A]_o = -kt_{1/2}$

$-[A]_o/2 = -kt_{1/2}$

$[A]_o/2 = kt_{1/2}$

For a zeroth-order reaction, $t_{1/2} = \frac{[A]_o}{2\ k}$.

For a zeroth-order reaction, each half-life is half of the previous one.

For a first-order reaction, each half-life is the same as the previous one.

For a second-order reaction, each half-life is twice the previous one.

12.110 (a)

$2\ NO(g) \rightleftharpoons N_2O_2(g)$ (fast)

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ (slow)

$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

Overall reaction $2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$

(b) N_2O_2 and N_2O are reaction intermediates because they are produced in one step of the reaction and used up in a subsequent step.

(c) Rate = $k_2[N_2O_2][H_2]$

(d) Because the forward and reverse rates in step 1 are equal, $k_1[NO]^2 = k_{-1}[N_2O_2]$. Solving for $[N_2O_2]$ and substituting into the rate law for the second step gives

$$\text{Rate} = k_2[N_2O_2][H_2] = \frac{k_1 k_2}{k_{-1}}[NO]^2[H_2]$$

Because the rate law for the overall reaction is equal to the rate law for the rate-determining step, the rate law for the overall reaction is

$$\text{Rate} = k[NO]^2[H_2] \text{ where } k = \frac{k_1 k_2}{k_{-1}}$$

12.111 (a) $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

(b) From the data in the table, initial rates = $-\frac{\Delta[I^-]}{\Delta t}$ have been calculated.

For example, from Experiment 1:

$$\text{Initial rate} = -\frac{\Delta[I^-]}{\text{Deltat}} = -\frac{(2.17 \times 10^{-4}\ M - 2.40 \times 10^{-4}\ M)}{10\ s} = 2.30 \times 10^{-6}\ M/s$$

Initial concentrations and initial rate data have been collected in the table below.

EXPT	$[I^-]_o$ (M)	$[OCl^-]_o$ (M)	$[OH^-]_o$ (M)	Initial Rate (M/s)
1	2.40×10^{-4}	1.60×10^{-4}	1.00	2.30×10^{-6}
2	1.20×10^{-4}	1.60×10^{-4}	1.00	1.20×10^{-6}
3	2.40×10^{-4}	4.00×10^{-5}	1.00	6.00×10^{-7}
4	1.20×10^{-4}	1.60×10^{-4}	2.00	6.00×10^{-7}

Rate = $k[I^-]^m[OCl^-]^n[OH^-]^p$

From Expts 1 and 2, $[I^-]$ is cut in half and the initial rate is cut in half; therefore m = 1.
From Expts 1 and 3, $[OCl^-]$ is reduced by a factor of four and the initial rate is reduced by a factor of four; therefore n = 1.
From Expts 2 and 4, $[OH^-]$ is doubled and the initial rate is cut in half; therefore p = -1.

$$\text{Rate} = k\frac{[I^-][OCl^-]}{[OH^-]}$$

From data in Expt 1:

$$k = \frac{\text{Rate}\ [OH^-]}{[I^-][OCl^-]} = \frac{(2.30 \times 10^{-6}\ M/s)(1.00\ M)}{(2.40 \times 10^{-4}\ M)(1.60 \times 10^{-4}\ M)} = 60/s$$

(c) The reaction does not occur by a single-step mechanism because OH^- appears in the rate law but not in the overall reaction.

(d)

$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$ (fast)

$HOCl(aq) + I^-(aq) \rightarrow HOI(aq) + Cl^-(aq)$ (slow)

$HOI(aq) + OH^-(aq) \rightarrow H_2O(l) + OI^-(aq)$ (fast)

Overall reaction $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

Because the forward and reverse rates in step 1 are equal, $k_1[OCl^-][H_2O] = k_{-1}[HOCl][OH^-]$. Solving for [HOCl] and substituting into the rate law for the second step gives

$$\text{Rate} = k_2[HOCl][I^-] = \frac{k_1 k_2}{k_{-1}}\frac{[OCl^-][H_2O][I^-]}{[OH^-]}$$

$[H_2O]$ is constant and can be combined into k.

Because the rate law for the overall reaction is equal to the rate law for the rate-determining step, the rate law for the overall reaction is

$$\text{Rate} = k\frac{[OCl^-][I^-]}{[OH^-]} \quad \text{where } k = \frac{k_1 k_2 [H_2O]}{k_{-1}}$$

12.112 (a) $\text{Rate}_f = k_f[A]$ and $\text{Rate}_r = k_r[B]$

(b)

(c) When $\text{Rate}_f = \text{Rate}_r$, $k_f[A] = k_r[B]$, and $\frac{[B]}{[A]} = \frac{k_f}{k_r} = \frac{(3.0 \text{ x } 10^{-3})}{(1.0 \text{ x } 10^{-3})} = 3$

12.113 (a) $1 \rightarrow 1/2 \rightarrow 1/4 \rightarrow 1/8$
After three half-lives, 1/8 of the strontium-90 will remain.

(b) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{29 \text{ y}} = 0.0239/\text{y} = 0.024/\text{y}$

(c) $t = \frac{\ln \frac{(Sr\_90)_t}{(Sr\_90)_o}}{-k} = \frac{\ln \frac{(0.01)}{(1)}}{-0.0239/\text{y}} = 193 \text{ y}$

12.114 $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \text{ x } 10^{-4}/\text{y}$

$$t = \frac{\ln \frac{(^{14}C)_t}{(^{14}C)_o}}{-k} = \frac{\ln \frac{(2.3)}{(15.3)}}{-1.21 \text{ x } 10^{-4}/\text{y}} = 1.6 \text{ x } 10^4 \text{ y}$$

12.115 $\text{Rate} = k[N_2O_4]$; $k = \frac{\text{Rate}}{[N_2O_4]}$

At 25°C, $k_1 = \frac{5.0 \text{ x } 10^3 \text{ M/s}}{0.10 \text{ M}} = 5.0 \text{ x } 10^4 \text{ s}^{-1}$

At 40°C, $k_2 = \frac{2.3 \text{ x } 10^4 \text{ M/s}}{0.15 \text{ M}} = 1.5 \text{ x } 10^5 \text{ s}^{-1}$

$25^oC = 25 + 273 = 298$ K and $40^oC = 40 + 273 = 313$ K

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(1.5 \times 10^5) - \ln(5.0 \times 10^4)][8.314 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}]}{\left(\frac{1}{313\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 56.8\ \text{kJ/mol}$$

12.116 $X \rightarrow$ products is a first-order reaction

$$t = 60\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} = 3600\ \text{s}$$

$$\ln\frac{[X]_t}{[X]_o} = -kt; \qquad k = \frac{\ln\frac{[X]_t}{[X]_o}}{-t}$$

At 25^oC, calculate k_1: $\quad k_1 = \dfrac{\ln\left(\frac{0.600\ \text{M}}{1.000\ \text{M}}\right)}{-3600\ \text{s}} = 1.42 \times 10^{-4}\ \text{s}^{-1}$

At 35^oC, calculate k_2: $\quad k_2 = \dfrac{\ln\left(\frac{0.200\ \text{M}}{0.600\ \text{M}}\right)}{-3600\ \text{s}} = 3.05 \times 10^{-4}\ \text{s}^{-1}$

At an unknown temperature calculate k_3. $\quad k_3 = \dfrac{\ln\left(\frac{0.010\ \text{M}}{0.200\ \text{M}}\right)}{-3600\ \text{s}} = 8.32 \times 10^{-4}\ \text{s}^{-1}$

$T_1 = 25^oC = 25 + 273 = 298$ K
$T_2 = 35^oC = 35 + 273 = 308$ K

Calculate E_a using k_1 and k_2.

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(3.05 \times 10^{-4}) - \ln(1.42 \times 10^{-4})][8.314 \times 10^{-3}\ \text{kJ/(Kcdot mol)}]}{\left(\frac{1}{308\ \text{K}} - \frac{1}{298\ \text{K}}\right)} = 58.3$$

kJ/mol

Use E_a, k_1, and k_3 to calculate T_3.

$$\frac{1}{T_3} = \frac{\ln\left(\frac{k_3}{k_1}\right)}{\left(\frac{-E_a}{R}\right)} + \frac{1}{T_1} = \frac{\ln\left(\frac{8.32 \text{ x } 10^{-4}}{1.42 \text{ x } 10^{-4}}\right)}{\left(\frac{-58.3 \text{ kJ/mol}}{8.314 \text{ x } 10^{-3} \text{ kJ/(K • mol)}}\right)} + \frac{1}{298 \text{ K}} = 0.003104/\text{K}$$

$$T_3 = \frac{1}{0.003104/\text{K}} = 322 \text{ K} = 322 - 273 = 49^{\circ}\text{C}$$

At 3:00 p.m. raise the temperature to 49°C to finish the reaction by 4:00 p.m.

12.117

	$N_2O_4(g)$	$\rightarrow$	$2\ NO_2(g)$
before (mm Hg)	17.0		0
change (mm Hg)	-x		+2x
after (mm Hg)	17.0 - x		2x

2x = 1.3 mm Hg
x = 1.3 mm Hg/2 = 0.65 mm Hg
$P_t(N_2O_4)$ = 17.0 - x = 17.0 - 0.65 = 16.35 mm Hg

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.3 \text{ x } 10^{-5} \text{ s}} = 5.3 \text{ x } 10^4 \text{ s}^{-1}$$

$$\ln \frac{P_t}{P_o} = -kt; \quad t = \frac{\ln \frac{P_t}{P_o}}{-k} = \frac{\ln \frac{16.35}{17}}{-5.3 \text{ x } 10^4 \text{ s}^{-1}} = 7.4 \text{ x } 10^{-7} \text{ s}$$

12.118 (a) When equal volumes of two solutions are mixed, both concemtrations are cut in half.
$[H_3O^+]_o = [OH^-]_o = 1.0$ M
When 99.999% of the acid is neutralized, $[H_3O^+] = [OH^-] = 1.0 \text{ M} - (1.0 \text{ M} \times 0.99999) = 1.0 \text{ x } 10^{-5}$ M

Using the 2nd order integrated rate law:

$$kt = \frac{1}{[H_3O^+]_t} - \frac{1}{[H_3O^+]_o}; \qquad t = \frac{1}{k}\left[\frac{1}{[H_3O^+]_t} - \frac{1}{[H_3O^+]_o}\right]$$

$$t = \frac{1}{(1.3 \text{ x } 10^{11} \text{ M}^{-1}\text{s}^{-1})}\left[\frac{1}{(1.0 \text{ x } 10^{-5} \text{ M})} - \frac{1}{(1.0 \text{ M})}\right] = 7.7 \text{ x } 10^{-7} \text{ s}$$

(b) The rate of an acid-base neutralization reaction would be limited by the speed of mixing, which is much slower than the intrinsic rate of the reaction itself.

12.119 $$\frac{1}{([O_2])^2} = 8\ k\ t + \frac{1}{([O_2]_o)^2}$$

$$\frac{1}{([O_2])^2} = 8(25 \text{ M}^{-2}\text{s}^{-1})(100.0 \text{ s}) + \frac{1}{(0.0100 \text{ M})^2}$$

$$\frac{1}{([O_2])^2} = 30{,}000\ M^{-2}$$

$$[O_2] = \sqrt{\frac{1}{30{,}000\ M^{-2}}} = 0.005\ 77\ M$$

	$2\ NO(g)$	+ $O_2(g)$	$\rightarrow$	$2\ NO_2(g)$
before (M)	0.0200	0.0100	0	
change (M)	-2x	-x	+2x	
after (M)	0.0200 - 2x	0.0100 - x	2x	

$[O_2] = 0.005\ 77\ M = 0.0100\ M - x$
$x = 0.0100\ M - 0.005\ 77\ M = 0.004\ 23\ M$
$[NO] = 0.0200\ M - 2x = 0.0200\ M - 2(0.004\ 23\ M) = 0.0115\ M$
$[O_2] = 0.005\ 77\ M$
$[NO_2] = 2x = 2(0.004\ 23\ M) = 0.008\ 46\ M$

12.120 Looking at the two experiments at 600 K, when the NO_2 concentration is doubled, the rate increased by a factor of 4. Therefore, the reaction is 2nd order.
Rate = $k\ [NO_2]^2$
Calculate k_1 at 600 K: $k_1 = \text{Rate}/[NO_2]^2 = 5.4 \times 10^{-7}\ M\ s^{-1}/(0.0010\ M)^2 = 0.54\ M^{-1}\ s^{-1}$
Calculate k_2 at 700 K: $k_2 = \text{Rate}/[NO_2]^2 = 5.2 \times 10^{-6}\ M\ s^{-1}/(0.0020\ M)^2 = 13\ M^{-1}\ s^{-1}$
Calculate E_a using k_1 and k_2.

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(13) - \ln(0.54)][8.314 \times 10^{-3}\ kJ/(K \bullet mol)]}{\left(\frac{1}{700\ K} - \frac{1}{600\ K}\right)} = 111\ kJ/mol$$

Calculate k_3 at 650 K using E_a and k_1.

Solve for k_3.

$$\ln k_3 = \frac{-E_a}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) + \ln k_1$$

$$\ln k_3 = \frac{-111\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)]}\left(\frac{1}{650\ K} - \frac{1}{600\ K}\right) + \ln(0.54) = 1.0955$$

$k_3 = e^{1.0955} = 3.0\ M^{-1}\ s^{-1}$

$$k_3 t = \frac{1}{[NO_2]_t} - \frac{1}{[NO_2]_o}; \qquad t = \frac{1}{k_3}\left[\frac{1}{[NO_2]_t} - \frac{1}{[NO_2]_o}\right]$$

$$t = \frac{1}{(3.0\ M^{-1}s^{-1})}\left[\frac{1}{(0.0010\ M)} - \frac{1}{(0.0050\ M)}\right] = 2.7 \times 10^{2}\ s$$

12.121 Rate = $k\,[A]^x[B]^y$

Comparing Experiments 1 and 2, the concentration of B does not change, the concentration of A doubles, and the rate doubles. This means the reaction is first-order in A (x = 1).

Comparing Experiments 1 and 3, the rate would drop to 0.9×10^{-5} M/s as a result of the concentration of A being cut in half. Then with the the concentration of B doubling, the rate increases by a factor of 4, to 3.6×10^{-5} M/s. This means the reaction is second-order in B (y = 2).

$$\text{At 600 K, } k_1 = \frac{\text{Rate}}{[A][B]^2} = \frac{4.3 \times 10^{-5}\ M/s}{(0.50\ M)(0.50\ M)^2} = 3.4 \times 10^{-4}\ M^{-2}\ s^{-1}$$

$$\text{At 700 K, } k_2 = \frac{\text{Rate}}{[A][B]^2} = \frac{1.8 \times 10^{-5}\ M/s}{(0.20\ M)(0.10\ M)^2} = 9.0 \times 10^{-3}\ M^{-2}\ s^{-1}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = -\frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = -\frac{[\ln(9.0 \times 10^{-3}) - \ln(3.4 \times 10^{-4})][8.314 \times 10^{-3}\ kJ/(Kcdot\ mol)]}{\left(\frac{1}{700\ K} - \frac{1}{600\ K}\right)} = 114\ kJ/mol$$

12.122 $A \rightarrow C$ is a first-order reaction.

The reaction is complete at 200 s when the absorbance of C reaches 1.200.

Because there is a one to one stoichiometry between A and C, the concentration of A must be proportional to 1.200 - absorbance of C. Any two data points can be used to find k. Let $[A]_o \propto 1.200$ and at 100 s, $[A]_t \propto 1.200 - 1.188 = 0.012$

$$\ln\frac{[A]_t}{[A]_o} = -kt; \qquad k = \frac{\ln\frac{[A]_t}{[A]_o}}{-t}; \qquad k = \frac{\ln\left(\frac{0.012\ M}{1.200\ M}\right)}{-100\ s} = 0.0461\ s^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0461\ s^{-1}} = 15\ s$$

12.123 Rate = $k\,[HI]^x$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k\,[0.30]^x}{k\,[0.10]^x}$$

$$x = \frac{\log \frac{Rate_2}{Rate_1}}{\log \frac{(0.30)}{(0.10)}} = \frac{\log \frac{1.6 \text{ x } 10^{-4}}{1.8 \text{ x } 10^{-5}}}{\log \frac{(0.30)}{(0.10)}} = \frac{0.949}{0.477} = 2$$

$Rate = k\,[HI]^2$

At 700 K, $k_1 = \frac{Rate}{[HI]^2} = \frac{1.8 \text{ x } 10^{-5} \text{ M/s}}{(0.10 \text{ M})^2} = 1.8 \text{ x } 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$

At 800 K, $k_2 = \frac{Rate}{[HI]^2} = \frac{3.9 \text{ x } 10^{-3} \text{ M/s}}{(0.20 \text{ M})^2} = 9.7 \text{ x } 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

$$\ln\left(\frac{k_2}{k_1}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = - \frac{[\ln k_2 - \ln k_1](R)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$E_a = - \frac{[\ln (9.7 \text{ x } 10^{-2}) - \ln (1.8 \text{ x } 10^{-3})][8.314 \text{ x } 10^{-3} \text{ kJ/(K • mol)}]}{\left(\frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}}\right)} = 186 \text{ kJ/mol}$$

Calculate k_4 at 650 K using E_a and k_1.
Solve for k_4.

$$\ln k_4 = \frac{-E_a}{R}\left(\frac{1}{T_4} - \frac{1}{T_1}\right) + \ln k_1$$

$$\ln k_4 = \frac{-186 \text{ kJ/mol}}{[8.314 \text{ x } 10^{-3} \text{ kJ/(K • mol)}]}\left(\frac{1}{650 \text{ K}} - \frac{1}{700 \text{ K}}\right) + \ln(1.8 \text{ x } 10^{-3}) = -8.788$$

$k_4 = e^{-8.788} = 1.5 \text{ x } 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

$$[HI] = \sqrt{\frac{Rate}{k_4}} = \sqrt{\frac{1.0 \text{ x } 10^{-5} \text{ M/s}}{1.5 \text{ x } 10^{-4} \text{ M}^{-1}\text{s}^{-1}}} = 0.26 \text{ M}$$

12.124 For radioactive decay, $\ln \frac{N}{N_o} = -kt$

For ^{235}U, $k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{7.1 \text{ x } 10^8 \text{ y}} = 9.76 \text{ x } 10^{-10} \text{ y}^{-1}$

For ^{238}U, $k_2 = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.51 \text{ x } 10^9 \text{ y}} = 1.54 \text{ x } 10^{-10} \text{ y}^{-1}$

For ^{235}U, $\ln \frac{N_1}{N_o 1} = -k_1 t$ and $\ln \frac{N_1}{N_o 1} + k_1 t = 0$

For ^{238}U, $\ln \frac{N_2}{N_o 2} = -k_2 t$ and $\ln \frac{N_2}{N_o 2} + k_2 t = 0$

Set the two equations that are equal to zero equal to each other and solve for t.

$$\ln \frac{N_1}{N_o 1} + k_1 t = \ln \frac{N_2}{N_o 2} + k_2 t$$

$$\ln \frac{N_1}{N_o 1} - \ln \frac{N_2}{N_o 2} = k_2 t - k_1 t = (k_2 - k_1)t$$

$$\ln \frac{\left(\frac{N_1}{N_o 1}\right)}{\left(\frac{N_2}{N_o 2}\right)} = (k_2 - k_1)t, \text{ now } N_{o1} = N_{o2}, \text{ so } \ln \frac{N_1}{N_2} = (k_2 - k_1)t$$

$\frac{N_1}{N_2} = 7.25 \times 10^{-3}$, so $\ln(7.25 \times 10^{-3}) = (1.54 \times 10^{-10}\ y^{-1} - 9.76 \times 10^{-10}\ y^{-1})t$

$$t = \frac{-4.93}{-8.22 \times 10^{-10}\ y^{-1}} = 6.0 \times 10^9\ y$$

The age of the elements is 6.0×10^9 y (6 billion years).

Multi-Concept Problems

12.125 (a) $k = A e^{-\frac{E_a}{RT}} = (6.0 \times 10^8/(M \cdot s))\ e^{-\frac{6.3\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](298\ K)}} = 4.7 \times 10^7/(M \cdot s)$

(b) N has 3 electron clouds, is sp^2 hybridized, and the molecule is bent.

(c)

(d) The reaction has such a low activation energy because the F–F bond is very weak and the N–F bond is relatively strong.

12.126 $2\ HI(g) \rightarrow H_2(g) + I_2(g)$

(a) $\text{mass HI} = 1.50\ L \times \frac{1000\ mL}{1\ L} \times \frac{0.0101\ g}{1\ mL} = 15.15\ g\ HI$

$$15.15\ g\ HI \times \frac{1\ mol\ HI}{127.91\ g\ HI} = 0.118\ mol\ HI$$

$$[HI] = \frac{0.118\ mol}{1.50\ L} = 0.0787\ mol/L$$

$$-\frac{\Delta[HI]}{\Delta t} = k[HI]^2 = (0.031/(M \cdot min))(0.0787\ M)^2 = 1.92 \times 10^{-4}\ M/min$$

$2\ HI(g) \rightarrow H_2(g) + I_2(g)$

$$\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\left(-\frac{\Delta[HI]}{\Delta t}\right) = \frac{1.92 \times 10^{-4}\ M/min}{2} = 9.60 \times 10^{-5}\ M/min$$

$(9.60 \times 10^{-5}\ M/min)(1.50\ L)(6.022 \times 10^{23}\ molecules/mol) = 8.7 \times 10^{19}\ molecules/min$

(b) Rate = $k[HI]^2$

$$\frac{1}{[HI]_t} = kt + \frac{1}{[HI]_o} = (0.031/(M \cdot min))\left(8.00\ h\ x\ \frac{60.0\ min}{1\ h}\right) + \frac{1}{0.0787\ M} = 27.59/M$$

$$[HI]_t = \frac{1}{27.59/M} = 0.0362\ M$$

From stoichiometry, $[H_2]_t = 1/2\ ([HI]_o - [HI]_t) = 1/2\ (0.0787\ M - 0.0362\ M) = 0.0212\ M$

$410^oC = 683\ K$

$PV = nRT$

$$P_{H_2} = \left(\frac{n}{V}\right)RT = (0.0212\ mol/L)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(683\ K) = 1.2\ atm$$

12.127 $2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$

$k = 4.7/(M \cdot s)$

(a) The units for k indicate a second-order reaction.

(b) $383^oC = 656\ K$

$PV = nRT$

$$[NO_2]_o = \frac{n}{V} = \frac{P}{RT} = \frac{\left(746\ mm\ Hg\ x\ \frac{1.000\ atm}{760\ mm\ Hg}\right)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(656\ K)} = 0.01823\ mol/L$$

initial rate = $k[NO_2]_o^2 = [4.7/(M \cdot s)](0.01823\ mol/L)^2 = 1.56 \times 10^{-3}\ mol/(L \cdot s)$

$$\text{initial rate for } O_2 = \frac{\text{initial rate for } NO_2}{2} = \frac{1.56\ x\ 10^{-3}\ mol/(L \bullet s)}{2} = 7.80 \times 10^{-4}\ mol/(L \cdot s)$$

initial rate for $O_2 = [7.80 \times 10^{-4}\ mol/(L \cdot s)](32.00\ g/mol) = 0.025\ g/(L \cdot s)$

(c) $$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0} = [4.7/(M \bullet s)](60\ s) + \frac{1}{0.01823\ M}$$

$\frac{1}{[NO_2]_t} = 336.9/M$ and $[NO_2] = 0.00297\ M$

	$2\ NO_2(g)$	$\rightarrow$	$2\ NO(g)$	+	$O_2(g)$
before reaction (M)	0.01823		0		0
change (M)	-2x		+2x		+x
after 1.00 min (M)	0.01823 - 2x		2x		x

after 1.00 min $[NO_2] = 0.00297\ M = 0.01823 - 2x$

$x = 0.00763\ M = [O_2]$

mass $O_2 = (0.00763\ mol/L)(5.00\ L)(32.00\ g/mol) = 1.22\ g\ O_2$

12.128 (a) N_2O_5, 108.01 amu

$$[N_2O_5]_o = \frac{\left(2.70\ g\ N_2O_5\ x\ \frac{1\ mol\ N_2O_5}{108.01\ g\ N_2O_5}\right)}{2.00\ L} = 0.0125\ mol/L$$

$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o = -(1.7 \times 10^{-3}\ s^{-1})\left(13.0\ min\ x\ \frac{60.0\ s}{1\ min}\right) + \ln (0.0125) = -5.71$$

$[N_2O_5]_t = e^{-5.71} = 3.31 \times 10^{-3}$ mol/L

After 13.0 min, mol $N_2O_5 = (3.31 \times 10^{-3}\ mol/L)(2.00\ L) = 6.62 \times 10^{-3}$ mol N_2O_5

	$N_2O_5(g)$	$\rightarrow$	$2\ NO_2(g)$	+	$1/2\ O_2(g)$
before reaction (mol)	0.0250		0		0
change (mol)	-x		+2x		+1/2x
after reaction (mol)	0.0250 - x		2x		1/2x

After 13.0 min, mol $N_2O_5 = 6.62 \times 10^{-3} = 0.0250 - x$

x = 0.0184 mol

After 13.0 min, $n_{total} = n_{N_2O_5} + n_{NO_2} + n_{O_2} = (6.62 \times 10^{-3}) + 2(0.0184) + 1/2(0.0184)$

$n_{total} = 0.0526$ mol

$55^oC = 328$ K

PV = nRT

$$P_{total} = \frac{nRT}{V} = \frac{(0.0526\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(328\ K)}{2.00\ L} = 0.71\ atm$$

(b) $N_2O_5(g) \rightarrow 2\ NO_2(g) + 1/2\ O_2(g)$

$\Delta H^o_{rxn} = 2\ \Delta H^o_f(NO_2) - \Delta H^o_f(N_2O_5)$

$\Delta H^o_{rxn} = (2\ mol)(33.2\ kJ/mol) - (1\ mol)(11\ kJ/mol) = 55.4\ kJ = 5.54 \times 10^4\ J$

initial rate = $k[N_2O_5]_o = (1.7 \times 10^{-3}\ s^{-1})(0.0125\ mol/L) = 2.125 \times 10^{-5}\ mol/(L \cdot s)$

initial rate absorbing heat = $[2.125 \times 10^{-5}\ mol/(L \cdot s)](2.00\ L)(5.54 \times 10^4\ J/mol) = 2.4\ J/s$

(c)

$$\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o = -(1.7 \times 10^{-3}\ s^{-1})\left(10.0\ min\ x\ \frac{60.0\ s}{1\ min}\right) + \ln (0.0125) = -5.40$$

$[N_2O_5]_t = e^{-5.40} = 4.52 \times 10^{-3}$ mol/L

After 10.0 min, mol $N_2O_5 = (4.52\ x\ 10^{-3}\ mol/L)(2.00\ L) = 9.03 \times 10^{-3}$ mol N_2O_5

	$N_2O_5(g)$	$\rightarrow$	$2\ NO_2(g)$	+	$1/2\ O_2(g)$
before reaction (mol)	0.0250		0		0
change (mol)	-x		+2x		+1/2x
after reaction (mol)	0.0250 - x		2x		1/2x

After 10.0 min, mol $N_2O_5 = 9.03 \times 10^{-3} = 0.0250 - x$

x = 0.0160 mol

heat absorbed = (0.0160 mol)(55.4 kJ/mol) = 0.89 kJ

12.129 $2\ N_2O(g) \rightarrow 2\ N_2(g) + O_2(g)$

P_{O_2} (in exit gas) = 1.0 mm Hg; P_{total} = 1.50 atm = 1140 mm Hg

From the reaction stoichiometry:

P_{N_2} (in exit gas) = 2 P_{O_2} = 2.0 mm Hg

P_{N_2O} (in exit gas) = P_{total} - P_{N_2} - P_{O_2} = 1140 - 2.0 - 1.0 = 1137 mm Hg

Assume P_{N_2O} (initial) = P_{total} = 1140 mm Hg (In assuming a constant total pressure in the tube, we are neglecting the slight change in pressure due to the reaction.)

Volume of tube = $\pi r^2 l = \pi(1.25\ cm)^2(20\ cm) = 98.2\ cm^3 = 0.0982\ L$

Time, t, gases are in the tube = $\frac{\text{volume of tube}}{\text{flow rate}} \times \frac{0.0982\ L}{0.75\ L/min} \times \frac{60\ s}{1\ min} = 7.86\ s$

At time t, $\frac{[N_2O]_t}{[N_2O]_0} = \frac{P_{N_2O}\ (\text{in exit gas})}{P_{N_2O}\ (\text{initial})} = \frac{1137\ mm\ Hg}{1140\ mm\ Hg} = 0.997\ 37$

Because $k = A\,e^{-\frac{E_a}{RT}}$ and $A = 4.2 \times 10^9\ s^{-1}$, k has units of s^{-1}. Therefore, this is a first-order reaction and the appropriate integrated rate law is $\ln \frac{[N_2O]_t}{[N_2O]_0} = -kt$.

$$k = \frac{-\ln \frac{[N_2O]_t}{[N_2O]_0}}{t} = \frac{-\ln (0.997\ 37)}{7.86\ s} = 3.35 \times 10^{-4}\ s^{-1}$$

From the Arrhenius equation, $\ln k = \ln A - \frac{E_a}{RT}$

$$T = \frac{E_a}{(R)[\ln A - \ln k]} = \frac{222\ kJ/mol}{(8.314 \times 10^{-3}\ kJ/(K \bullet mol))[(22.16) - (-8.00)]} = 885\ K$$

12.130 H_2O_2, 34.01 amu

mass H_2O_2 = (0.500 L)(1000 mL/1 L)(1.00 g/ 1 mL)(0.0300) = 15.0 g H_2O_2

mol H_2O_2 = 15.0 g $H_2O_2 \times \frac{1\ mol\ H_2O_2}{34.01\ g\ H_2O_2}$ = 0.441 H_2O_2

$[H_2O_2]_o = \frac{0.441\ mol}{0.500\,L} = 0.882$ mol /L

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.7\ h} = 6.48 \times 10^{-2}/h$

$\ln [H_2O_2]_t = -kt + \ln [H_2O_2]_o$

$\ln [H_2O_2]_t = -(6.48 \times 10^{-2}/h)(4.02\ h) + \ln (0.882)$

$\ln [H_2O_2]_t = -0.386$; $[H_2O_2]_t = e^{-0.386} = 0.680$ mol/L

mol H_2O_2 = (0.680 mol/L)(0.500 L) = 0.340 mol

	$2\ H_2O_2(aq)$	$\rightarrow$	$2\ H_2O(l)$	+	$O_2(g)$
before reaction (mol)	0.441	0	0		
change (mol)	- 2x		+2x		+x
after reaction (mol)	0.441 - 2x		2x		x

After 4.02 h, mol H_2O_2 = 0.340 mol = 0.441 - 2x; solve for x.
2x = 0.101
x = 0.0505 mol = mol O_2

$$P = 738\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg} = 0.971\ atm$$

PV = nRT

$$V = \frac{nRT}{P} = \frac{(0.0505\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(293\ K)}{0.971\ atm} = 1.25\ L$$

$P\Delta V = (0.971\ atm)(1.25\ L) = 1.21\ L \cdot atm$

$$w = -P\Delta V = -1.21\ L \cdot atm = (-1.21\ L \cdot atm)\left(101\ \frac{J}{L \bullet atm}\right) = -122\ J$$

12.131 (a)

	$CH_3CHO(g)$	$\rightarrow$	$CH_4(g)$	+	$CO(g)$
before (atm)	0.500		0		0
change (atm)	-x		+x		+x
after (atm)	0.500 - x		x		x

At 605 s, $P_{total} = P_{CH_3CHO} + P_{CH_4} + P_{CO}$ = (0.500 atm - x) + x + x = 0.808 atm
x = 0.808 atm - 0.500 atm = 0.308 atm

The integrated rate law for a second-order reaction in terms of molar concentrations is $\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$. The ideal gas law, PV = nRT, can be rearranged to show how P is proportional the the molar concentration of a gas.

$P = \frac{n}{V}RT$ (R and T are constant), so $P \propto \frac{n}{V}$ = molar concentration

Because of this relationship, the second-order integrated rate law can be rewritten in terms of partial pressures.

$$\frac{1}{P_t} = kt + \frac{1}{P_o}\ ; \qquad \frac{1}{P_t} - \frac{1}{P_o} = kt\ ; \qquad \frac{\left(\frac{1}{P_t} - \frac{1}{P_o}\right)}{t} = k$$

P is the partial pressure of CH_3CHO.

At t = 0, P_o = 0.500 and at t = 605 s, P_t = 0.500 atm - 0.308 atm = 0.192 atm

$$k = \frac{\left(\frac{1}{0.192\ \text{atm}} - \frac{1}{0.500\ \text{atm}}\right)}{605\ \text{s}} = 5.30 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1}$$

(b) Use the ideal gas law to convert atm^{-1} to M^{-1}.

$$P = \frac{n}{V}RT; \quad \frac{P}{RT} = \frac{n}{V}; \quad \frac{1}{P}RT = \frac{V}{n} = M^{-1}$$

So, multiply k by RT to convert $atm^{-1}\ s^{-1}$ to $M^{-1}\ s^{-1}$.

$k = (5.30 \times 10^{-3}\ atm^{-1}\ s^{-1})RT$

$$k = (5.30 \times 10^{-3}\ \text{atm}^{-1}\ \text{s}^{-1})\left(0.082\ 06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(791\ \text{K}) = 0.344\ \frac{\text{L}}{\text{mol} \bullet \text{s}} = 0.344\ \text{M}^{-1}\ \text{s}^{-1}$$

(c) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$

$\Delta H^o_{rxn} = [\Delta H^o_f(CH_4) + \Delta H^o_f(CO)] - \Delta H^o_f(CH_3CHO)]$

$\Delta H^o_{rxn} = [(1\ mol)(-74.8\ kJ/mol) + (1\ mol)(-110.5\ kJ/mol)] - (1\ mol)(-166.2\ kJ/mol)$

ΔH^o_{rxn} = -19.1 kJ per mole of CH_3CHO that decomposes

PV = nRT

$$\text{mol } CH_3CHO \text{ reacted} = \frac{PV}{RT} = \frac{(0.308\ \text{atm})(1.00\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(791\ \text{K})} = 0.004\ 74\ \text{mol}$$

q = (0.004 74 mol)(19.1 kJ/mol)(1000 J/kJ) = 90.6 J liberated after a reaction time of 605 s

13 Chemical Equilibrium

13.1 (a) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ (b) $K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

13.2 (a) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]} = \dfrac{(5.0 \text{ x } 10^{-2})^2}{(3.0 \text{ x } 10^{-3})^2(3.5 \text{ x } 10^{-3})} = 7.9 \text{ x } 10^4$

(b) $K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2} = \dfrac{(3.0 \text{ x } 10^{-3})^2(3.5 \text{ x } 10^{-3})}{(5.0 \text{ x } 10^{-2})^2} = 1.3 \text{ x } 10^{-5}$

13.3 (a) $K_c = \dfrac{[H^+][C_3H_5O_3^-]}{[C_3H_6O_3]}$

(b) $K_c = \dfrac{[(0.100)(0.0365)]^2}{[0.100 - (0.100)(0.0365)]} = 1.38 \text{ x } 10^{-4}$

13.4 From (1), $K_c = \dfrac{[AB][B]}{[A][B_2]} = \dfrac{(1)(2)}{(1)(2)} = 1$

For a mixture to be at equilibrium, $\dfrac{[AB][B]}{[A][B_2]}$ must be equal to 1.

For (2), $\dfrac{[AB][B]}{[A][B_2]} = \dfrac{(2)(1)}{(2)(1)} = 1$. This mixture is at equilibrium.

For (3), $\dfrac{[AB][B]}{[A][B_2]} = \dfrac{(1)(1)}{(4)(2)} = 0.125$. This mixture is not at equilibrium.

For (4), $\dfrac{[AB][B]}{[A][B_2]} = \dfrac{(2)(2)}{(4)(1)} = 1.0$ This mixture is at equilibrium.

13.5 $K_p = \dfrac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \dfrac{(6.12)(20.3)}{(1.31)(10.0)} = 9.48$

13.6 $2 NO(g) + O_2 - 2 NO_2(g)$; $\Delta n = 2 - 3 = -1$

$K_p = K_c(RT)^{\Delta n}$, $K_c = K_p(1/RT)^{\Delta n}$

at 500 K: $K_p = (6.9 \text{ x } 10^5)[(0.082\ 06)(500)]^{-1} = 1.7 \text{ x } 10^4$

at 1000 K: $K_c = (1.3 \text{ x } 10^{-2})\left(\dfrac{1}{(0.082\ 06)(1000)}\right)^{-1} = 1.1$

13.7 (a) $K_c = \dfrac{[H_2]^3}{[H_2O]^3}$, $K_p = \dfrac{(P_{H_2})^3}{(P_{H_2O})^3}$, $\Delta n = (3) - (3) = 0$ and $K_p = K_c$

(b) $K_c = [H_2]^2[O_2]$, $K_p = (P_{H_2})^2(P_{O_2})$, $\Delta n = (3) - (0) = 3$ and $K_p = K_c(RT)^3$

(c) $K_c = \dfrac{[HCl]^4}{[SiCl_4][H_2]^2}$, $K_p = \dfrac{(P_{HCl})^4}{(P_{SiCl_4})(P_{H_2})^2}$, $\Delta n = (4) - (3) = 1$ and $K_p = K_c(RT)$

(d) $K_c = \dfrac{1}{[Hg_2^{2+}][Cl^-]^2}$

13.8 $K_c = 1.2 \times 10^{-42}$. Because K_c is very small, the equilibrium mixture contains mostly H_2 molecules. H is in periodic group 1A. A very small value of K_c is consistent with strong bonding between 2 H atoms, each with one valence electron.

13.9 The container volume of 5.0 L must be included to calculate molar concentrations.

(a) $Q_c = \dfrac{[NO_2]_t^2}{[NO]_t^2[O_2]_t} = \dfrac{(0.80\ \text{mol}/5.0\ \text{L})^2}{(0.060\ \text{mol}/5.0\ \text{L})^2(1.0\ \text{mol}/5.0\ \text{L})} = 890$

Because $Q_c < K_c$, the reaction is not at equilibrium. The reaction will proceed to the right to reach equilibrium.

(b) $Q_c = \dfrac{[NO_2]_t^2}{[NO]_t^2[O_2]_t} = \dfrac{(4.0\ \text{mol}/5.0\ \text{L})^2}{(5.0 \times 10^{-3}\ \text{mol}/5.0\ \text{L})^2(0.20\ \text{mol}/5.0\ \text{L})} = 1.6 \times 10^7$

Because $Q_c > K_c$, the reaction is not at equilibrium. The reaction will proceed to the left to reach equilibrium.

13.10 $K_c = \dfrac{[AB]^2}{[A_2][B_2]} = 4$; For a mixture to be at equilibrium, $\dfrac{[AB]^2}{[A_2][B_2]}$ must be equal to 4.

For (1), $Q_c = \dfrac{[AB]^2}{[A_2][B_2]} = \dfrac{(6)^2}{(1)(1)} = 36$, $Q_c > K_c$

For (2), $Q_c = \dfrac{[AB]^2}{[A_2][B_2]} = \dfrac{(4)^2}{(2)(2)} = 4$, $Q_c = K_c$

For (3), $Q_c = \dfrac{[AB]^2}{[A_2][B_2]} = \dfrac{(2)^2}{(3)(3)} = 0.44$, $Q_c < K_c$

(a) (2) (b) (1), reverse; (3), forward

13.11 $K_c = \dfrac{[H]^2}{[H_2]} = 1.2 \times 10^{-42}$

(a) $[H] = \sqrt{K_c[H_2]} = \sqrt{(1.2 \times 10^{-42})(0.10)} = 3.5 \times 10^{-22}$ M

(b) H atoms = $(3.5 \times 10^{-22}$ mol/L)(1.0 L)$(6.022 \times 10^{23}$ atoms/mol) = 210 H atoms
H_2 molecules = (0.10 mol/L)(1.0 L)$(6.022 \times 10^{23}$ molecules/mol) = 6.0×10^{22} H_2 molecules

13.12

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
initial (M)	0.150		0.150		0		0
change (M)	-x		-x	+x		+x	

equil (M) 0.150 - x 0.150 - x x x

$$K_c = 4.24 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{x^2}{(0.150 - x)^2}$$

Take the square root of both sides and solve for x.

$$\sqrt{4.24} = \sqrt{\frac{x^2}{(0.150 - x)^2}}; \quad 2.06 = \frac{x}{0.150 - x}; \quad x = 0.101$$

At equilibrium, $[CO_2] = [H_2] = x = 0.101$ M

$[CO] = [H_2O] = 0.150 - x = 0.150 - 0.101 = 0.049$ M

13.13

	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
initial (M)	0.0500		0
change (M)	-x		+2x
equil (M)	0.0500 - x		2x

$$K_c = 4.64 \times 10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.0500 - x)}$$

$4x^2 + (4.64 \times 10^{-3})x - (2.32 \times 10^{-4}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(4.64 \times 10^{-3}) \pm \sqrt{(4.64 \times 10^{-3})^2 - 4(4)(-2.32 \times 10^{-4})}}{2(4)} = \frac{-0.00464 \pm 0.06110}{8}$$

x = -0.008 22 and 0.007 06

Discard the negative solution (-0.008 22) because it leads to a negative concentration of NO_2 and that is impossible.

$[N_2O_4] = 0.0500 - x = 0.0500 - 0.007\ 06 = 0.0429$ M

$[NO_2] = 2x = 2(0.007\ 06) = 0.0141$ M

13.14 $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$$Q_c = \frac{[NO_2]_t^2}{[N_2O_4]_t} = \frac{(0.0300\ \text{mol/L})^2}{(0.0200\ \text{mol/L})} = 0.0450; \quad Q_c > K_c$$

The reaction will approach equilibrium by going from right to left.

	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
initial (M)	0.0200		0.0300
change (M)	+x		-2x
equil (M)	0.0200 + x		0.0300 - 2x

$$K_c = 4.64 \times 10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0300 - 2x)^2}{(0.0200 + x)}$$

$4x^2 - 0.1246x + (8.072 \times 10^{-4}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-0.1246) \pm \sqrt{(-0.1246)^2 - 4(4)(8.072 \times 10^{-4})}}{2(4)} = \frac{0.1246 \pm 0.05109}{8}$$

x = 0.0220 and 0.009 19

Discard the larger solution (0.0220) because it leads to a negative concentration of NO_2,

and that is impossible.
$[N_2O_4] = 0.0200 + x = 0.0200 + 0.009\,19 = 0.0292$ M
$[NO_2] = 0.0300 - 2x = 0.0300 - 2(0.009\,19) = 0.0116$ M

13.15 $K_p = \dfrac{(P_{CO})(P_{H_2})}{(P_{H_2O})} = 2.44$, $Q_p = \dfrac{(1.00)(1.40)}{(1.20)} = 1.17$, $Q_p < K_p$ and the reaction goes to the right to reach equilibrium.

	C(s) +	$H_2O(g)$ _	$CO(g)$ +	$H_2(g)$
initial (atm)		1.20	1.00	1.40
change (atm)		-x	+x	+x
equil (atm)		1.20 - x	1.00 + x	1.40 + x

$$K_p = \frac{(P_{CO})(P_{H_2})}{(P_{H_2O})} = 2.44 = \frac{(1.00 + x)(1.40 + x)}{(1.20 - x)}$$

$x^2 + 4.84x - 1.53 = 0$
Use the quadratic formula to solve for x.

$$x = \frac{-(4.84) \pm \sqrt{(4.84)^2 - 4(1)(-1.53)}}{2(1)} = \frac{-4.84 \pm 5.44}{2}$$

x = -5.14 and 0.300
Discard the negative solution (-5.14) because it leads to negative partial pressures and that is impossible.
$P_{H_2O} = 1.20 - x = 1.20 - 0.300 = 0.90$ atm
$P_{CO} = 1.00 + x = 1.00 + 0.300 = 1.30$ atm
$P_{H_2} = 1.40 + x = 1.40 + 0.300 = 1.70$ atm

13.16 (a) CO(reactant) added, H_2 concentration increases.
(b) CO_2 (product) added, H_2 concentration decreases.
(c) H_2O (reactant) removed, H_2 concentration decreases.
(d) CO_2 (product) removed, H_2 concentration increases.
At equilibrium, $Q_c = K_c = \dfrac{[CO_2][H_2]}{[CO][H_2O]}$. If some CO_2 is removed from the equilibrium mixture, the numerator in Q_c is decreased, which means that $Q_c < K_c$ and the reaction will shift to the right, increasing the H_2 concentration.

13.17 (a) Because there are 2 mol of gas on both sides of the balanced equation, the composition of the equilibrium mixture is unaffected by a change in pressure. The number of moles of reaction products remains the same.
(b) Because there are 2 mol of gas on the left side and 1 mol of gas on the right side of the balanced equation, the stress of an increase in pressure is relieved by a shift in the reaction to the side with fewer moles of gas (in this case, to products). The number of moles of reaction products increases.
(c) Because there is 1 mol of gas on the left side and 2 mol of gas on the right side of the balanced equation, the stress of an increase in pressure is relieved by a shift in the reaction to the side with fewer moles of gas (in this case, to reactants). The number of moles of reaction product decreases.

13.18

13.19 Le Châtelier's principle predicts that a stress of added heat will be relieved by net reaction in the direction that absorbs the heat. Since the reaction is endothermic, the equilibrium will shift from left to right (K_c will increase) with an increase in temperature. Therefore, the equilibrium mixture will contain more of the offending NO, the higher the temperature.

13.20 The reaction is exothermic. As the temperature is increased the reaction shifts from right to left. The amount of ethyl acetate decreases.

$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$

As the temperature is decreased, the reaction shifts from left to right. The product concentrations increase, and the reactant concentrations decrease. This corresponds to an increase in K_c.

13.21 There are more AB(g) molecules at the higher temperature. The equilibrium shifted to the right at the higher temperature, which means the reaction is endothermic.

13.22 (a) A catalyst does not affect the equilibrium composition. The amount of CO remains the same.
(b) The reaction is exothermic. An increase in temperature shifts the reaction toward reactants. The amount of CO increases.
(c) Because there are 3 mol of gas on the left side and 2 mol of gas on the right side of the balanced equation, the stress of an increase in pressure is relieved by a shift in the reaction to the side with fewer moles of gas (in this case, to products). The amount of CO decreases.
(d) An increase in pressure as a result of the addition of an inert gas (with no volume change) does not affect the equilibrium composition. The amount of CO remains the same.
(e) Adding O_2 increases the O_2 concentration and shifts the reaction toward products. The amount of CO decreases.

13.23 (a) Because K_c is so large, k_f is larger than k_r.

(b) $K_c = \frac{k_f}{k_r}$; $\quad k_r = \frac{k_f}{K_c} = \frac{8.5 \times 10^6\ M^{-1}s^{-1}}{3.4 \times 10^{34}} = 2.5 \times 10^{-28}\ M^{-1}\ s^{-1}$

(c) Because the reaction is exothermic, E_a (forward) is less than E_a (reverse). Consequently, as the temperature decreases, k_r decreases more than k_f decreases, and

therefore $K_c = \frac{k_f}{k_r}$ increases.

13.24 $Hb + O_2 \_ Hb(O_2)$
If CO binds to Hb, Hb is removed from the reaction and the reaction will shift to the left resulting in O_2 being released from $Hb(O_2)$. This will decrease the effectiveness of Hb for carrying O_2.

13.25 The equilibrium shifts to the left because at the higher altitude the concentration of O_2 is decreased.

13.26 There are 26 π electrons.

13.27 The partial pressure of O_2 in the atmosphere is 0.2095 atm.
PV = nRT

$$n = \frac{PV}{RT} = \frac{(0.2095\ \text{atm})(0.500\ \text{L})}{\left(0.082\,06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298\ \text{K})} = 4.28 \times 10^{-3}\ \text{mol } O_2$$

$$4.28 \times 10^{-3}\ \text{mol } O_2 \times \frac{6.022 \times 10^{23}\ O_2\ \text{molecules}}{1\ \text{mol } O_2} = 2.58 \times 10^{21}\ O_2\ \text{molecules}$$

Understanding Key Concepts

13.28 (a) (1) and (3) because the number of A and B's are the same in the third and fourth box.

(b) $K_c = \frac{[B]}{[A]} = \frac{6}{4} = 1.5$

(c) Because the same number of molecules appear on both sides of the equation, the volume terms in K_c all cancel. Therefore, we can calculate K_c without including the volume.

13.29 (a) $A_2 + C_2 \_ 2\ AC$ (most product molecules)
(b) $A_2 + B_2 \_ 2\ AB$ (fewest product molecules)

13.30 (a) Only reaction (3), $K_c = \frac{[A][AB]}{[A_2][B]} = \frac{(2)(4)}{(2)(2)} = 2$, is at equilibrium.

(b) $Q_c = \frac{[A][AB]}{[A_2][B]} = \frac{(3)(5)}{(1)(1)} = 15$ for reaction (1). Because $Q_c > K_c$, the reaction will go in the reverse direction to reach equilibrium.

$Q_c = \frac{[A][AB]}{[A_2][B]} = \frac{(1)(3)}{(3)(3)} = 1/3$ for reaction (2). Because $Q_c < K_c$, the reaction will go in the forward direction to reach equilibrium.

13.31 (a) $A_2 + 2\ B \_ 2\ AB$

(b) The number of AB molecules will increase, because as the volume is decreased at constant temperature, the pressure will increase and the reaction will shift to the side of fewer molecules to reduce the pressure.

13.32 When the stopcock is opened, the reaction will go in the reverse direction because there will be initially an excess of AB molecules.

13.33 As the temperature is raised, the reaction proceeds in the reverse direction. This is consistent with an exothermic reaction where "heat" can be considered as a product.

13.34 (a) $AB \rightarrow A + B$
(b) The reaction is endothermic because a stress of added heat (higher temperature) shifts the AB _ A + B equilibrium to the right.
(c) If the volume is increased, the pressure is decreased. The stress of decreased pressure will be relieved by a shift in the equilibrium from left to right, thus increasing the number of A atoms.

13.35 Heat + $BaCO_3(s)$ _ $BaO(s)$ + $CO_2(g)$

(a) (b)

13.36 (a) (b) (c)

13.37 This equilibrium mixture has a $K_c \propto \frac{(2)(2)}{(3)^2}$ and is less than 1. This means that $k_f < k_r$.

Additional Problems
Equilibrium Expressions and Equilibrium Constants

13.38 (a) $K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$ (b) $K_c = \frac{[ClF_3]^2}{[F_2]^3[Cl_2]}$ (c) $K_c = \frac{[HF]^2}{[H_2][F_2]}$

13.39 (a) $K_c = \frac{[CH_3CHO]^2}{[C_2H_4]^2[O_2]}$ (b) $K_c = \frac{[N_2][O_2]}{[NO]^2}$ (c) $K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$

13.40 (a) $K_p = \dfrac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})}$, $\Delta n = 2$ and $K_p = K_c(RT)^2$

(b) $K_p = \dfrac{(P_{ClF_3})^2}{(P_{F_2})^3(P_{Cl_2})}$, $\Delta n = -2$ and $K_p = K_c(RT)^{-2}$

(c) $K_p = \dfrac{(P_{HF})^2}{(P_{H_2})(P_{F_2})}$, $\Delta n = 0$ and $K_p = K_c$

13.41 (a) $K_p = \dfrac{(P_{CH_3CHO})^2}{(P_{C_2H_4})^2(P_{O_2})}$, $\Delta n = -1$ and $K_p = K_c(RT)^{-1}$

(b) $K_p = \dfrac{(P_{N_2})(P_{O_2})}{(P_{NO})^2}$, $\Delta n = 0$ and $K_p = K_c$

(c) $K_p = \dfrac{(P_{NO})^4(P_{H_2O})^6}{(P_{NH_3})^4(P_{O_2})^5}$, $\Delta n = 1$ and $K_p = K_c(RT)$

13.42 $K_c = \dfrac{[C_2H_5OC_2H_5][H_2O]}{[C_2H_5OH]^2}$

13.43 $K_c = \dfrac{[HOCH_2CH_2OH]}{[C_2H_4O][H_2O]}$

13.44 $K_c = \dfrac{[\text{Isocitrate}]}{[\text{Citrate}]}$

13.45 $K_c = \dfrac{[\text{citric acid}]}{[\text{acetic acid}][\text{oxaloacetic acid}]}$

13.46 The two reactions are the reverse of each other.

$K_c(\text{reverse}) = \dfrac{1}{K_c(\text{forward})} = \dfrac{1}{7.5 \times 10^{-9}} = 1.3 \times 10^8$

13.47 The two reactions are the reverse of each other.

$K_p(\text{reverse}) = \dfrac{1}{K_p(\text{forward})} = \dfrac{1}{50.2} = 1.99 \times 10^{-2}$

13.48 $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{(1.5 \times 10^{-2})(3.2 \times 10^{-2})}{(8.3 \times 10^{-3})} = 0.058$

13.49 $K_p = \dfrac{(P_{ClNO})^2}{(P_{NO})^2(P_{Cl_2})} = \dfrac{(1.35)^2}{(0.240)^2(0.608)} = 52.0$

13.50 The container volume of 2.00 L must be included to calculate molar concentrations.
Initial [HI] = 9.30×10^{-3} mol/2.00 L = 4.65×10^{-3} M = 0.004 65 M

	$H_2(g)$	+	$I_2(g)$	_	2 HI(g)
initial (M)	0		0		0.004 65
change (M)	+x		+x		-2x
equil (M)	x		x		0.004 65 - 2x

$x = [H_2] = [I_2] = 6.29 \times 10^{-4}$ M = 0.000 629 M
[HI] = 0.004 65 - 2x = 0.004 65 - 2(0.000 629) = 0.003 39 M

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.003\,39)^2}{(0.000\,629)^2} = 29.0$$

13.51 (a) $K_c = \dfrac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$

(b)

	$CH_3CO_2H(aq)$	_	$H^+(aq)$	+	$CH_3CO_2^-(aq)$
initial (M)	1.0		0		0
change (M)	-0.0042		+0.0042		+0.0042
equil (M)	1.0 - 0.0042		0.0042		0.0042

$$K_c = \frac{(0.0042)(0.0042)}{(1.0 \_\ 0.0042)} = 1.8 \times 10^{-5}$$

13.52 (a) $K_c = \dfrac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$

(b)

	$CH_3CO_2H(soln)$	+	$C_2H_5OH(soln)$	_	$CH_3CO_2C_2H_5(soln)$	+	$H_2O(soln)$
initial (mol)	1.00		1.00		0		0
change (mol)	-x		-x		+x		+x
equil (mol)	1.00 - x		1.00 - x		x		x

x = 0.65 mol; 1.00 - x = 0.35 mol; $K_c = \dfrac{(0.65)^2}{(0.35)^2} = 3.4$

Because there are the same number of molecules on both sides of the equation, the volume terms in K_c cancel. Therefore, we can calculate K_c without including the volume.

13.53 $CH_3CO_2C_2H_5(soln) + H_2O(soln) \_ CH_3CO_2H(soln) + C_2H_5OH(soln)$

$$K_c(\text{hydrolysis}) = \frac{1}{K_c(\text{forward})} = \frac{1}{3.4} = 0.29$$

13.54 $\Delta n = 1$ and $K_p = K_c(RT) = (0.575)(0.082\ 06)(500) = 23.6$

13.55 $2\ SO_2(g) + O_2(g) \_ 2\ SO_3(g)$; $\Delta n = 2 - (2 + 1) = -1$ and $K_p = 3.30$

$$K_c = K_p \left(\frac{1}{RT}\right)^{\Delta n} = (3.30)\left(\frac{1}{(0.082\ 06)(1000)}\right)^{-1} = 271$$

13.56 $K_p = P_{H_2O} = 0.0313$ atm; $\Delta n = 1$

$$K_c = K_p\left(\frac{1}{RT}\right) = (0.0313)\left(\frac{1}{(0.082\ 06)(298)}\right) = 1.28 \times 10^{-3}$$

13.57 $P_{C_{10}H_8} = 0.10\ \text{mm Hg} \times \frac{1\ \text{atm}}{760\ \text{mm Hg}} = 1.3 \times 10^{-4}$ atm

$K_p = P_{C_{10}H_8} = 1.3 \times 10^{-4}$; $\Delta n = 1 - 0 = 1$, $T = 27^oC = 300$ K

$$K_c = K_p\left(\frac{1}{RT}\right)^{\Delta n} = (1.3 \times 10^{-4})\left(\frac{1}{(0.082\ 06)(300)}\right) = 5.3 \times 10^{-6}$$

13.58 (a) $K_c = \frac{[CO_2]^3}{[CO]^3}$, $K_p = \frac{(P_{CO_2})^3}{(P_{CO})^3}$ (b) $K_c = \frac{1}{[O_2]^3}$, $K_p = \frac{1}{(P_{O_2})^3}$

(c) $K_c = [SO_3]$, $K_p = P_{SO_3}$ (d) $K_c = [Ba^{2+}][SO_4^{2-}]$

13.59 (a) $K_c = \frac{[H_2O]^3}{[H_2]^3}$, $K_p = \frac{(P_{H_2O})^3}{(P_{H_2})^3}$ (b) $K_c = \frac{1}{[Ag^+][Cl^-]}$

(c) $K_c = \frac{[HCl]^6}{[H_2O]^3}$, $K_p = \frac{(P_{HCl})^6}{(P_{H_2O})^3}$ (d) $K_c = [CO_2]$, $K_p = P_{CO_2}$

Using the Equilibrium Constant

13.60 (a) Because K_c is very large, the equilibrium mixture contains mostly product.
(b) Because K_c is very small, the equilibrium mixture contains mostly reactants.

13.61 (a) proceeds hardly at all toward completion
(b) goes almost all the way to completion

13.62 (a) Because K_c is very small, the equilibrium mixture contains mostly reactant.
(b) Because K_c is very large, the equilibrium mixture contains mostly product.
(c) Because $K_c = 1.8$, the equilibrium mixture contains an appreciable concentration of both reactants and products.

13.63 (a) Because K_c is very large, the equilibrium mixture contains mostly product.
(b) Because $K_c = 7.5 \times 10^{-3}$, the equilibrium mixture contains an appreciable concentration of both reactants and products.
(c) Because K_c is very small, the equilibrium mixture contains mostly reactant.

13.64 $K_c = 1.2 \times 10^{82}$ is very large. When equilibrium is reached, very little if any ethanol will remain because the reaction goes to completion.

13.65 Because K_c is very small, pure air will contain very little O_3 (ozone) at equilibrium.

$3\ O_2(g) \rightleftharpoons 2\ O_3(g)$; $K_c = \dfrac{[O_3]^2}{[O_2]^3} = 1.7 \times 10^{-56}$; $[O_2] = 8 \times 10^{-3}$ M

$[O_3] = \sqrt{[O_2]^3 \times K_c} = \sqrt{(8 \times 10^{-3})^3 (1.7 \times 10^{-56})} = 9 \times 10^{-32}$ M

13.66 The container volume of 10.0 L must be included to calculate molar concentrations.

$$Q_c = \frac{[CS_2]_t[H_2]_t^4}{[CH_4]_t[H_2S]_t^2} = \frac{(3.0\ \text{mol}/10.0\ \text{L})(3.0\ \text{mol}/10.0\ \text{L})^4}{(2.0\ \text{mol}/10.0\ \text{L})(4.0\ \text{mol}/10.0\ \text{L})^2} = 7.6 \times 10^{-2}; \quad K_c = 2.5 \times 10^{-3}$$

The reaction is not at equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium.

13.67 $$Q_c = \frac{[CO]_t[H_2]_t^3}{[H_2O]_t[CH_4]_t} = \frac{(0.15)(0.20)^3}{(0.035)(0.050)} = 0.69; \quad K_c = 4.7$$

The reaction is not at equilibrium because $Q_c < K_c$. The reaction will proceed from left to right to reach equilibrium.

13.68 $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 0.29$; At equilibrium, $[N_2] = 0.036$ M and $[H_2] = 0.15$ M

$[NH_3] = \sqrt{[N_2] \times [H_2]^3 \times K_c} = \sqrt{(0.036)(0.15)^3(0.29)} = 5.9 \times 10^{-3}$ M

13.69 $K_c = 2.7 \times 10^2 = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$; Because $[SO_3] = [SO_2]$, then $2.7 \times 10^2 = \dfrac{1}{[O_2]}$

$[O_2] = 3.7 \times 10^{-3}$ M

13.70

	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ NO(g)$
initial (M)	1.40		1.40		0
change (M)	-x		-x		+2x
equil (M)	1.40 - x		1.40 - x		2x

$$K_c = 1.7 \times 10^{-3} = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2x)^2}{(1.40 - x)^2}$$

Take the square root of both sides and solve for x.

$$\sqrt{1.7 \times 10^{-3}} = \sqrt{\frac{(2x)^2}{(1.40 - x)^2}}; \quad 4.1 \times 10^{-2} = \frac{2x}{1.40 - x}; \quad x = 2.8 \times 10^{-2}$$

At equilibrium, $[NO] = 2x = 2(2.8 \times 10^{-2}) = 0.056$ M

$[N_2] = [O_2] = 1.40 - x = 1.40 - (2.8 \times 10^{-2}) = 1.37$ M

13.71

	$N_2(g)$	+	$O_2(g)$	$\rightleftharpoons$	$2\ NO(g)$
initial (M)	2.24		0.56		0
change (M)	-x		-x		+2x
equil (M)	2.24 - x		0.56 - x		2x

$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1.7 \times 10^{-3} = \frac{(2x)^2}{(2.24 - x)(0.56 - x)}$

$4x^2 + (4.8 \times 10^{-3})x - (2.1 \times 10^{-3}) = 0$

Use the quadratic formula to solve for x.

$x = \frac{-(4.8 \times 10^{-3}) \pm \sqrt{(4.8 \times 10^{-3})^2 - 4(4)(-2.1 \times 10^{-3})}}{2(4)} = \frac{-0.0048 \pm 0.1834}{8}$

x = -0.0235 and 0.0223

Discard the negative solution (-0.0235) because it gives a negative NO concentration and that is impossible.

$[N_2] = 2.24 - x = 2.24 - 0.0223 = 2.22$ M

$[O_2] = 0.56 - x = 0.56 - 0.0223 = 0.54$ M; $[NO] = 2x = 2(0.0223) = 0.045$ M

13.72

	$PCl_5(g)$	–	$PCl_3(g)$	+	$Cl_2(g)$
initial (M)	0.160		0		0
change (M)	-x		+x		+x
equil (M)	0.160 - x		x		x

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 5.8 \times 10^{-2} = \frac{x^2}{0.160 - x}$

$x^2 + (5.8 \times 10^{-2})x - 0.00928 = 0$

Use the quadratic formula to solve for x.

$x = \frac{-5.8 \times 10^{-2} \pm \sqrt{(5.8 \times 10^{-2})^2 - 4(1)(-0.00928)}}{2(1)} = \frac{-5.8 \times 10^{-2} \pm 0.20}{2}$

x = 0.071 and -0.129

Discard the negative solution (-0.129) because it gives negative concentrations of PCl_3 and Cl_2 and that is impossible.

$[PCl_3] = [Cl_2] = x = 0.071$ M; $[PCl_5] = 0.160 - x = 0.160 - 0.071 = 0.089$ M

13.73 $Q_c = \frac{(0.100)(0.040)}{(0.200)} = 0.020$, $Q_c < K_c$ therefore the reaction proceeds from reactants to products to reach equilibrium.

	$PCl_5(g)$	–	$PCl_3(g)$	+	$Cl_2(g)$
initial (M)	0.200		0.100		0.040
change (M)	-x		+x		+x
equil (M)	0.200 - x		0.100 + x		0.040 + x

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 5.8 \times 10^{-2} = \frac{(0.100 + x)(0.040 + x)}{0.200 - x}$

$x^2 + 0.198x - (7.60 \times 10^{-3}) = 0$

Use the quadratic formula to solve for x.

$x = \frac{-0.198 \pm \sqrt{(0.198)^2 - 4(1)(-7.60 \times 10^{-3})}}{2(1)} = \frac{-0.198 \pm 0.264}{2}$

x = 0.033 and -0.231

Discard the negative solution (-0.231) because it gives negative concentrations of PCl_3 and Cl_2 and that is impossible.
$[PCl_3] = 0.100 + x = 0.100 + 0.033 = 0.133$ M
$[Cl_2] = 0.040 + x = 0.040 + 0.033 = 0.073$ M
$[PCl_5] = 0.200 - x = 0.200 - 0.033 = 0.167$ M

13.74 (a) $K_c = \dfrac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]} = 3.4 = \dfrac{(x)(12.0)}{(4.0)(6.0)}$; x = 6.8 moles $CH_3CO_2C_2H_5$

Note that the volume cancels because the same number of molecules appear on both sides of the chemical equation.

(b)

	CH_3CO_2H(soln)	+ C_2H_5OH(soln)	_ $CH_3CO_2C_2H_5$(soln)	+ H_2O(soln)
initial (mol)	1.00	10.00	0	0
change (mol)	-x	-x	+x	+x
equil (mol)	1.00 - x	10.00 - x	x	x

$K_c = 3.4 = \dfrac{x^2}{(1.00 - x)(10.00 - x)}$

$2.4x^2 - 37.4x + 34 = 0$

Use the quadratic formula to solve for x.

$x = \dfrac{-(-37.4) \pm \sqrt{(-37.4)^2 - 4(2.4)(34)}}{2(2.4)} = \dfrac{37.4 \pm 32.75}{4.8}$

x = 0.969 and 14.6

Discard the larger solution (14.6) because it leads to negative concentrations and that is impossible.

mol $CH_3CO_2H = 1.00 - x = 1.00 - 0.969 = 0.03$ mol
mol $C_2H_5OH = 10.00 - x = 10.00 - 0.969 = 9.03$ mol
mol $CH_3CO_2C_2H_5$ = mol H_2O = x = 0.97 mol

13.75 When equal volumes of two solutions are mixed together, their concentrations are cut in half.

	CH_3Cl(aq)	+ OH^-(aq)	_ CH_3OH(aq)	+ Cl^-(aq)
initial (M)	0.05	0.1	0	0
assume complete reaction (M)	0	0.05	0.05	0.05
assume small back reaction (M)	+x	+x	-x	-x
equil (M)	x	0.05 + x	0.05 - x	0.05 - x

$K_c = \dfrac{[CH_3OH][Cl^-]}{[CH_3Cl][OH^-]} = 10^{16} = \dfrac{(0.05 - x)^2}{x(0.05 + x)}$; Because K_c is very large, x << 0.05.

$10^{16} \approx \dfrac{(0.05)^2}{x(0.05)}$; x = 5 x 10^{-18}

$[CH_3Cl]$ = x = 5 x 10^{-18} M; $[OH^-] = [CH_3OH] = [Cl^-] \approx 0.05$ M

13.76

	ClF_3(g)	_ ClF(g)	+ F_2(g)
initial (atm)	1.47	0	0
change (atm)	-x	+x	+x

equil (atm) 1.47 - x x x

$K_p = \frac{(P_{ClF})(P_{F_2})}{(P_{ClF_3})} = 0.140 = \frac{(x)(x)}{1.47 - x}$; solve for x.

$x^2 + 0.140x - 0.2058 = 0$

Use the quadratic formula to solve for x.

$x = \frac{-(0.140) \pm \sqrt{(0.140)^2 - (4)(1)(-0.2058)}}{2(1)}$

$x = \frac{-0.140 \pm 0.918}{2}$

x = 0.389 and -0.529

Discard the negative solution (-0.529) because it gives negative partial pressures and that is impossible.

$P_{ClF} = P_{F_2} = x = 0.389$ atm

$P_{ClF_3} = 1.47 - x = 1.47 - 0.389 = 1.08$ atm

13.77

	$Fe_2O_3(s)$ + 3 CO(g)	2 Fe(s) +	3 $CO_2(g)$
initial (atm)	0.978		0
change (atm)	-3x		+3x
equil (atm)	0.978 - 3x		3x

$K_p = \frac{(P_{CO_2})^3}{(P_{CO})^3} = 19.9 = \frac{(3x)^3}{(0.978 - 3x)^3}$; take the cube root of both sides and solve for x.

$\sqrt[3]{19.9} = 2.71 = \frac{3x}{(0.978 - 3x)}$

2.65 - 8.13x = 3x

2.65 = 11.13x

x = 2.65/11.13 = 0.238 atm

$P_{CO} = 0.978 - 3x = 0.978 - 3(0.238) = 0.264$ atm

$P_{CO_2} = 3x = 3(0.238) = 0.714$ atm

Le Châtelier's Principle

13.78 (a) Cl^- (reactant) added, AgCl(s) increases
(b) Ag^+ (reactant) added, AgCl(s) increases
(c) Ag^+ (reactant) removed, AgCl(s) decreases
(d) Cl^- (reactant) removed, AgCl(s) decreases

Disturbing the equilibrium by decreasing $[Cl^-]$ increases Q_c $\left(Q_c = \frac{1}{[Ag^+]_t[Cl^-]_t}\right)$ to a value greater than K_c. To reach a new state of equilibrium, Q_c must decrease, which means that the denominator must increase; that is, the reaction must go from right to left, thus decreasing the amount of solid AgCl.

13.79 (a) ClNO (product) added, NO_2 concentration decreases
(b) NO (reactant) added, NO_2 concentration increases
(c) NO (reactant) removed, NO_2 concentration decreases
(d) $ClNO_2$ (reactant) added, NO_2 concentration increases

Adding $ClNO_2$ decreases the value of Q_c $\left(Q_c = \frac{[ClNO][NO_2]}{[ClNO_2][NO]} \right)$. To reach a new state of equilibrium, the reaction must go from left to right, thus increasing the concentration of NO_2.

13.80 (a) Because there are 2 mol of gas on the left side and 3 mol of gas on the right side of the balanced equation, the stress of an increase in pressure is relieved by a shift in the reaction to the side with fewer moles of gas (in this case, to reactants). The number of moles of reaction products decreases.
(b) Because there are 2 mol of gas on both sides of the balanced equation, the composition of the equilibrium mixture is unaffected by a change in pressure. The number of moles of reaction product remains the same.
(c) Because there are 2 mol of gas on the left side and 1 mol of gas on the right side of the balanced equation, the stress of an increase in pressure is relieved by a shift in the reaction to the side with fewer moles of gas (in this case, to products). The number of moles of reaction products increases.

13.81 As the volume increases, the pressure decreases at constant temperature.
(a) Because there is 1 mol of gas on the left side and 2 mol of gas on the right side of the balanced equation, the stress of an increase in volume (decrease in pressure) is relieved by a shift in the reaction to the side with the larger number of moles of gas (in this case, to products).
(b) Because there are 3 mol of gas on the left side and 2 mol of gas on the right side of the balanced equation, the stress of an increase in volume (decrease in pressure) is relieved by a shift in the reaction to the side with the larger number of moles of gas (in this case, to reactants).
(c) Because there are 3 mol of gas on both sides of the balanced equation, the composition of the equilibrium mixture is unaffected by an increase in volume (decrease in pressure). There is no net reaction in either direction.

13.82 $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H^o = -41.2$ kJ
The reaction is exothermic. $[H_2]$ decreases when the temperature is increased.
As the temperature is decreased, the reaction shifts to the right. $[CO_2]$ and $[H_2]$ increase, $[CO]$ and $[H_2O]$ decrease, and K_c increases.

13.83 Because ΔH^o is positive, the reaction is endothermic.
$heat + 3\ O_2(g) \rightleftharpoons 2\ O_3(g)$

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

As the temperature increases, heat is added to the reaction, causing a shift to the right. The $[O_3]$ increases, and the $[O_2]$ decreases. This results in an increase in K_c.

13.84 (a) HCl is a source of Cl^- (product), the reaction shifts left, the equilibrium $[CoCl_4^{2-}]$ increases.
(b) $Co(NO_3)_2$ is a source of $Co(H_2O)_6^{2+}$ (product), the reaction shifts left, the equilibrium $[CoCl_4^{2-}]$ increases.
(c) All concentrations will initially decrease and the reaction will shift to the right, the equilibrium $[CoCl_4^{2-}]$ decreases.
(d) For an exothermic reaction, the reaction shifts to the left when the temperature is increased, the equilibrium $[CoCl_4^{2-}]$ increases.

13.85 (a) $Fe(NO_3)_3$ is a source of Fe^{3+}. Fe^{3+} (reactant) added; the $FeCl^{2+}$ concentration increases.
(b) Cl^- (reactant) removed; the $FeCl^{2+}$ concentration decreases.
(c) An endothermic reaction shifts to the right as the temperature increases; the $FeCl^{2+}$ concentration increases.
(d) A catalyst does not affect the composition of the equilibrium mixture; no change in $FeCl^{2+}$ concentration.

13.86 (a) The reaction is exothermic. The amount of CH_3OH (product) decreases as the temperature increases.

(b) When the volume decreases, the reaction shifts to the side with fewer gas molecules. The amount of CH_3OH increases.
(c) Addition of an inert gas (He) does not affect the equilibrium composition. There is no change.
(d) Addition of CO (reactant) shifts the reaction toward product. The amount of CH_3OH increases.
(e) Addition or removal of a catalyst does not affect the equilibrium composition. There is no change.

13.87 (a) An endothermic reaction shifts to the right as the temperature increases. The amount of acetone increases.
(b) Because there is 1 mol of gas on the left side and 2 mol of gas on the right side of the balanced equation, the stress of an increase in volume (decrease in pressure) is relieved by a shift in the reaction to the side with the larger number of moles of gas (in this case, to products). The amount of acetone increases.
(c) The addition of Ar (an inert gas) with no volume change does not affect the composition of the equilibrium mixture. The amount of acetone does not change.
(d) H_2 (product) added; the amount of acetone decreases.
(e) A catalyst does not affect the composition of the equilibrium mixture. The amount of acetone does not change.

Chemical Equilibrium and Chemical Kinetics

13.88 A + B ⎯ C

$rate_f = k_f[A][B]$ and $rate_r = k_r[C]$; at equilibrium, $rate_f = rate_r$

$k_f[A][B] = k_r[C]$; $\frac{k_f}{k_r} = \frac{[C]}{[A][B]} = K_c$

13.89 An equilibrium mixture that contains large amounts of reactants and small amounts of products has a small K_c. A small K_c has $k_f < k_r$ (c).

13.90 $K_c = \frac{k_f}{k_r} = \frac{0.13}{6.2 \text{ x } 10^{-4}} = 210$

13.91 $K_c = \frac{k_f}{k_r}$; $k_r = \frac{k_f}{K_c} = \frac{6 \text{ x } 10^{-6} \text{ } M^{-1}s^{-1}}{10^{16}} = 6 \text{ x } 10^{-22} \text{ } M^{-1}s^{-1}$

13.92 k_r increases more than k_f, this means that E_a (reverse) is greater than E_a (forward). The reaction is exothermic when E_a (reverse) > E_a (forward).

13.93 k_f increases more than k_r, this means that E_a (forward) is greater than E_a (reverse). The reaction is endothermic when E_a (forward) > E_a (reverse).

General Problems

13.94 (a) $[N_2O_4] = \frac{0.500 \text{ mol}}{4.00 \text{ L}} = 0.125 \text{ M}$

	$N_2O_4(g)$	⎯	$2 NO_2(g)$
initial (M)	0.125		0
change (M)	-(0.793)(0.125)		+(2)(0.793)(0.125)
equil (M)	0.125 - (0.793)(0.125)		(2)(0.793)(0.125)

At equilibrium, $[N_2O_4] = 0.125 - (0.793)(0.125) = 0.0259$ M

$[NO_2] = (2)(0.793)(0.125) = 0.198$ M

$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.198)^2}{(0.0259)} = 1.51$

$\Delta n = 2 - 1 = 1$ and $K_p = K_c(RT)^{\Delta n}$; $K_p = K_c(RT) = (1.51)(0.082\ 06)(400) = 49.6$

(b)

13.95 K_c is very large. The reaction goes essentially to completion.

$K_c = \frac{1}{[CO_2]}$; $[CO_2] = \frac{1}{K_c} = \frac{1}{1.6 \text{ x } 10^{24}} = 6.2 \text{ x } 10^{-25}$ M

13.96 $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 0.291$

At equilibrium, $[N_2] = 1.0 \times 10^{-3}$ M and $[H_2] = 2.0 \times 10^{-3}$ M

$[NH_3] = \sqrt{[N_2] \times [H_2]^3 \times K_c} = \sqrt{(1.0 \times 10^{-3})(2.0 \times 10^{-3})^3(0.291)} = 1.5 \times 10^{-6}$ M

13.97 (a) $K_p = \dfrac{(P_F)^2}{P_{F_2}} = 7.83$ at 1500 K

$P_F = \sqrt{K_p P_{F_2}} = \sqrt{(7.83)(0.200)} = 1.25$ atm

(b)

	$F_2(g)$	_	$2\ F(g)$
initial (atm)	x		0
change (atm)	-y		+2y
equil (atm)	x - y		2y

$2y = 1.25$ so $y = 0.625$

$x - y = 0.200$; $x = 0.200 + y = 0.200 + 0.625 = 0.825$

$f = \dfrac{0.625}{0.825} = 0.758$

(c) The shorter bond in F_2 is expected to be stronger. However, because of the small size of F, repulsion between the lone pairs of the two halogen atoms are much greater in F_2 than in Cl_2.

13.98 $2\ HI(g)$ _ $H_2(g) + I_2(g)$

Calculate K_c. $K_c = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{(0.13)(0.70)}{(2.1)^2} = 0.0206$

$[HI] = \dfrac{0.20\ \text{mol}}{0.5000\ \text{L}} = 0.40$ M

	$2\ HI(g)$	_	$H_2(g)$	+	$I_2(g)$
initial (M)	0.40		0		0
change (M)	-2x		+x		+x
equil (M)	0.40 - 2x		x		x

$K_c = 0.0206 = \dfrac{[H_2][I_2]}{[HI]^2} = \dfrac{x^2}{(0.40 - 2x)^2}$

Take the square root of both sides, and solve for x.

$\sqrt{0.0206} = \sqrt{\dfrac{x^2}{(0.40 - 2x)^2}}$; $0.144 = \dfrac{x}{0.40 - 2x}$; $x = 0.045$

At equilibrium, $[H_2] = [I_2] = x = 0.045$ M; $[HI] = 0.40 - 2x = 0.40 - 2(0.045) = 0.31$ M

13.99 Note the container volume is 5.00 L

$[H_2] = [I_2] = 1.00$ mol/5.00 L = 0.200 M

$[HI] = 2.50$ mol/5.00 L = 0.500 M

	$H_2(g)$	+	$I_2(g)$	_	$2\ HI(g)$
initial (M)	0.200		0.200		0.500
change (M)	-x		-x		+2x

equil (M) 0.200 - x 0.200 - x 0.500 + 2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 129 = \frac{(0.500 + 2x)^2}{(0.200 - x)^2}$$

Take the square root of both sides, and solve for x.

$$\sqrt{129} = \sqrt{\frac{(0.500 + 2x)^2}{(0.200 - x)^2}}; \quad 11.4 = \frac{0.500 + 2x}{0.200 - x}; \quad x = 0.133$$

$[H_2] = [I_2] = 0.200 - x = 0.200 - 0.133 = 0.067$ M

$[HI] = 0.500 + 2x = 0.500 + 2(0.133) = 0.766$ M

13.100 $[H_2O] = \frac{6.00 \text{ mol}}{5.00 \text{ L}} = 1.20$ M

	C(s) +	$H_2O(g)$ −	$CO(g)$ +	$H_2(g)$
initial (M)		1.20	0	0
change (M)		-x	+x	+x
equil (M)		1.20 - x	x	x

$$K_c = \frac{[CO][H_2]}{[H_2O]} = 3.0 \times 10^{-2} = \frac{x^2}{1.20 - x}$$

$x^2 + (3.0 \times 10^{-2})x - 0.036 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(0.030) \pm \sqrt{(0.030)^2 - 4(-0.036)}}{2(1)} = \frac{-0.030 \pm 0.381}{2}$$

x = 0.176 and -0.206

Discard the negative solution (-0.206) because it leads to negative concentrations and that is impossible.

$[CO] = [H_2] = x = 0.18$ M; $[H_2O] = 1.20 - x = 1.20 - 0.18 = 1.02$ M

13.101 (a) Because K_p is larger at the higher temperature, the reaction has shifted toward products at the higher temperature, which means the reaction is endothermic.

(b) (i) Increasing the volume causes the reaction to shift toward the side with more mol of gas (product side). The equilibrium amounts of PCl_3 and Cl_2 increase while that of PCl_5 decresases.

(ii) If there is no volume change, there is no change in equilibrium concentrations.

(iii) Addition of a catalyst does not affect the equilibrium concentrations.

13.102 A decrease in volume (a) and the addition of reactants (c) will affect the composition of the equilibrium mixture, but leave the value of K_c unchanged.

A change in temperature (b) affects the value of K_c.

Addition of a catalyst (d) or an inert gas (e) affects neither the composition of the equilibrium mixture nor the value of K_c.

13.103 (a) Addition of a solid does not affect the equilibrium composition. There is no change in the number of moles of CO_2.

(b) Adding a product causes the reaction to shift toward reactants. The number of moles

of CO_2 decreases.
(c) Decreasing the volume causes the reaction to shift toward the side with fewer mol of gas (reactant side). The number of moles of CO_2 decreases.
(d) The reaction is endothermic. An increase in temperature shifts the reaction toward products. The number of moles of CO_2 increases.

13.104 2 monomer $\rightleftharpoons$ dimer

(a) In benzene, $K_c = 1.51 \times 10^2$

	2 monomer	$\rightleftharpoons$	dimer
initial (M)	0.100		0
change (M)	-2x		+x
equil (M)	0.100 - 2x		x

$$K_c = \frac{[\text{dimer}]}{[\text{monomer}]^2} = 1.51 \times 10^2 = \frac{x}{(0.100 - 2x)^2}$$

$604x^2 - 61.4x + 1.51 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-61.4) \pm \sqrt{(-61.4)^2 - (4)(604)(1.51)}}{2(604)} = \frac{61.4 \pm 11.04}{1208}$$

$x = 0.0600$ and 0.0417

Discard the larger solution (0.0600) because it gives a negative concentration of the monomer and that is impossible.

[monomer] = 0.100 - 2x = 0.100 - 2(0.0417) = 0.017 M; [dimer] = x = 0.0417 M

$$\frac{[\text{dimer}]}{[\text{monomer}]} = \frac{0.0417\ \text{M}}{0.017\ \text{M}} = 2.5$$

(b) In H_2O, $K_c = 3.7 \times 10^{-2}$

	2 monomer	$\rightleftharpoons$	dimer
initial (M)	0.100		0
change (M)	-2x		+x
equil (M)	0.100 - 2x		x

$$K_c = \frac{[\text{dimer}]}{[\text{monomer}]^2} = 3.7 \times 10^{-2} = \frac{x}{(0.100 - 2x)^2}$$

$0.148x^2 - 1.0148x + 0.000\,37 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-1.0148) \pm \sqrt{(-1.0148)^2 - (4)(0.148)(0.00037)}}{2(0.148)} = \frac{1.0148 \pm 1.0147}{0.296}$$

$x = 6.86$ and 3.7×10^{-4}

Discard the larger solution (6.86) because it gives a negative concentration of the monomer and that is impossible.

[monomer] = 0.100 - 2x = 0.100 - 2(3.7×10^{-4}) = 0.099 M; [dimer] = x = 3.7×10^{-4} M

$$\frac{[\text{dimer}]}{[\text{monomer}]} = \frac{3.7 \times 10^{-4}\ \text{M}}{0.099\ \text{M}} = 0.0038$$

(c) K_c for the water solution is so much smaller than K_c for the benzene solution because H_2O can hydrogen bond with acetic acid, thus preventing acetic acid dimer formation. Benzene cannot hydrogen bond with acetic acid.

13.105

	C(s)	+ CO_2(g)	⇌ 2 CO(g)
initial (M)	excess	1.50 mol/20.0 L	0
change (M)		-x	+2x
equil (M)		0.0750 - x	2x

$[CO] = 2x = 7.00 \times 10^{-2}$ M; $x = 0.0350$ M

(a) $[CO_2] = 0.0750 - x = 0.0750 - 0.0350 = 0.0400$ M

(b) $K_c = \dfrac{[CO]^2}{[CO_2]} = \dfrac{(7.00 \times 10^{-2})^2}{(0.0400)} = 0.122$

13.106 (a) $[PCl_5] = 1.000 \text{ mol}/5.000 \text{ L} = 0.2000$ M

	PCl_5(g)	⇌ PCl_3(g)	+ Cl_2(g)
initial (M)	0.2000	0	0
change (M)	-(0.2000)(0.7850)	+(0.2000)(0.7850)	+(0.2000)(0.7850)
equil (M)	0.0430	0.1570	0.1570

$K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{(0.1570)(0.1570)}{(0.0430)} = 0.573$

$\Delta n = 1$ and $K_p = K_c(RT) = (0.573)(0.082\ 06)(500) = 23.5$

(b) $Q_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{(0.150)(0.600)}{(0.500)} = 0.18$

Because $Q_c < K_c$, the reaction proceeds to the right to reach equilibrium.

	PCl_5(g)	⇌ PCl_3(g)	+ Cl_2(g)
initial (M)	0.500	0.150	0.600
change (M)	- x	+x	+x
equil (M)	0.500 - x	0.150 + x	0.600 + x

$K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = 0.573 = \dfrac{(0.150 + x)(0.600 + x)}{(0.500 - x)}$; solve for x.

$x^2 + 1.323x - 0.1965 = 0$

$x = \dfrac{-(1.323) \pm \sqrt{(1.323)^2 - (4)(1)(-0.1965)}}{2(1)} = \dfrac{-1.323 \pm 1.593}{2}$

$x = -1.458$ and 0.135

Discard the negative solution (-1.458) because it will lead to negative concentrations and that is impossible.

$[PCl_5] = 0.500 - x = 0.500 - 0.135 = 0.365$ M

$[PCl_3] = 0.150 + x = 0.150 + 0.135 = 0.285$ M

$[Cl_2] = 0.600 + x = 0.600 + 0.135 = 0.735$ M

13.107 $Q_p = \dfrac{(2.00)(1.50)}{(3.00)} = 1.00$, $Q_p < K_p$ therefore the reaction proceeds from reactants to

products to reach equilibrium.

	$PCl_5(g)$	_	$PCl_3(g)$	+	$Cl_2(g)$
initial (atm)	3.00		2.00		1.50
change (atm)	-x		+x		+x
equil (atm)	3.00 - x		2.00 + x		1.50 + x

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = 1.42 = \frac{(2.00 + x)(1.50 + x)}{3.00 - x}$$

$x^2 + 4.92x - 1.26 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{(-4.92) \pm \sqrt{(4.92)^2 - 4(1)(-1.26)}}{2(1)} = \frac{(-4.92) \pm 5.41}{2}$$

x = 0.245 and -5.165

Discard the negative solution (-5.165) because it gives negative partial pressures and that is impossible.

P_{PCl_5} = 3.00 - x = 3.00 - 0.245 = 2.76 atm

P_{PCl_3} = 2.00 + x = 2.00 + 0.245 = 2.24 atm

P_{Cl_2} = 1.50 + x = 1.50 + 0.245 = 1.74 atm

$P_{total} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$ = 2.76 + 2.24 + 1.74 = 6.74 atm

13.108 (a) $K_c = \frac{[C_2H_6][C_2H_4]}{[C_4H_{10}]}$ $K_p = (P_{C_2H_6})(P_{C_2H_4})OVERP_{C_4H_{10}}$

(b) $K_p = 12$; $\Delta n = 1$; $K_c = K_p\left(\frac{1}{RT}\right) = (12)\left(\frac{1}{(0.082\ 06)(773)}\right) = 0.19$

(c)

	$C_4H_{10}(g)$	_	$C_2H_6(g)$	+	$C_2H_4(g)$
initial (atm)	50		0		0
change (atm)	-x		+x		+x
equil (atm)	50 - x		x		x

$$K_p = 12 = \frac{x^2}{50 - x}; \qquad x^2 + 12x - 600 = 0$$

Use the quadratic formula to solve for x.

$$x = \frac{(-12) \pm \sqrt{(12)^2 - 4(1)(-600)}}{2(1)} = \frac{-12 \pm 50.44}{2}$$

x = -31.22 and 19.22

Discard the negative solution (-31.22) because it leads to negative concentrations and that is impossible.

$$\%\ C_4H_{10}\ \text{converted} = \frac{19.22}{50} \times 100\% = 38\%$$

$P_{total} = P_{C_4H_{10}} + P_{C_2H_6} + P_{C_2H_4}$ = (50 - x) + x + x = (50 - 19) + 19 + 19 = 69 atm

(d) A decrease in volume would decrease the % conversion of C_4H_{10}.

13.109 (a) Because $\Delta n = 0$, $K_p = K_c = 1.0 \times 10^5$

(b) $K_p = 1.0 \times 10^5 = \dfrac{P_{propene}}{P_{cyclopropane}}$; $\quad P_{cyclopropane} = \dfrac{P_{propene}}{1.0 \times 10^5} = \dfrac{5.0 \text{ atm}}{1.0 \times 10^5} = 5.0 \times 10^{-5}$ atm

(c) The ratio of the two concentrations is equal to K_c. The ratio (K_c) cannot be changed by adding cyclopropane. The individual concentrations can change but the ratio of concentrations can't.

Because there is one mole of gas on each side of the balanced equation, the composition of the equilibrium mixture is unaffected by a decrease in volume. The ratio of the two concentrations will not change.

(d) Because K_c is large, $k_f > k_r$.

(e) Because the C–C–C bond angles are 60° and the angles between sp^3 hybrid orbitals are 109.5^o, the hybrid orbitals are not oriented along the bond directions. Their overlap is therefore poor, and the C–C bonds are correspondingly weak.

13.110 (a) $K_p = 3.45$; $\Delta n = 1$; $\quad K_c = K_p\left(\dfrac{1}{RT}\right) = (3.45)\left(\dfrac{1}{(0.082\ 06)(500)}\right) = 0.0840$

(b) $[(CH_3)_3CCl] = 1.00 \text{ mol}/5.00 \text{ L} = 0.200 \text{ M}$

	$(CH_3)_3CCl(g)$	$\rightleftharpoons$	$(CH_3)_2C{=}CH_2(g)$	+	$HCl(g)$
initial (M)	0.200		0		0
change (M)	-x		+x		+x
equil (M)	0.200 - x		x		x

$K_c = 0.0840 = \dfrac{x^2}{0.200 - x}$; $\quad x^2 + 0.0840x - 0.0168 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{(-0.0840) \pm \sqrt{(0.0840)^2 - 4(1)(-0.0168)}}{2(1)} = \frac{-0.0840 \pm 0.272}{2}$$

x = -0.178 and 0.094

Discard the negative solution (-0.178) because it leads to negative concentrations and that is impossible.

$[(CH_3)_2C{=}CCH_2] = [HCl] = x = 0.094$ M

$[(CH_3)_3CCl] = 0.200 - x = 0.200 - 0.094 = 0.106$ M

(c) $K_p = 3.45$

	$(CH_3)_3CCl(g)$	$\rightleftharpoons$	$(CH_3)_2C{=}CH_2(g)$	+	$HCl(g)$
initial (atm)	0		0.400		0.600
change (atm)	+x		-x		-x
equil (atm)	x		0.400 - x		0.600 - x

$K_p = 3.45 = \dfrac{(0.400 - x)(0.600 - x)}{x}$

$x^2 - 4.45x + 0.240 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-4.45) \pm \sqrt{(-4.45)^2 - 4(1)(0.240)}}{2(1)} = \frac{4.45 \pm 4.34}{2}$$

x = 0.055 and 4.40

Discard the larger solution (4.40) because it leads to negative partial pressures and that is impossible.

$P_{\text{t-butyl chloride}} = x = 0.055$ atm; $P_{\text{isobutylene}} = 0.400 - x = 0.400 - 0.055 = 0.345$ atm

$P_{HCl} = 0.600 - x = 0.600 - 0.055 = 0.545$ atm

13.111 (a) The Arrhenius equation gives for the forward and reverse reactions

$$k_f = A_f e^{-E_{a,f}/RT} \quad \text{and} \quad k_r = A_r e^{-E_{a,r}/RT}$$

Addition of a catalyst decreases the activation energies by ΔE_a, so

$$k_f = A_f e^{-(E_{a,f} - \Delta E_a)/RT} = A_f e^{-E_{a,f}/RT} \times e^{\Delta E_a/RT}$$

and

$$k_r = A_r e^{-(E_{a,r} - \Delta E_a)/RT} = A_r e^{-E_{a,r}/RT} \times e^{\Delta E_a/RT}$$

Therefore, the rate constants for both the forward and reverse reactions increase by the same factor, $e^{\Delta E_a/RT}$.

(b) The equilibrium constant is given by $K_c = \frac{k_f}{k_r} = \frac{A_f e^{-E_{a,f}/RT}}{A_r e^{-E_{a,r}/RT}} = \frac{A_f}{A_r} e^{-\Delta E/RT}$

where $\Delta E = E_{a,f} - E_{a,r}$. Addition of a catalyst decreases the activation energies by ΔE_a.

So, $K_c = \frac{k_f}{k_r} = \frac{A_f e^{-E_{a,f}/RT} \times e^{\Delta E_a/RT}}{A_r e^{-E_{a,r}/RT} \times e^{\Delta E_a/RT}} = \frac{A_f}{A_r} e^{-\Delta E/RT}$

K_c is unchanged because of cancellation of $e^{\Delta E_a/RT}$, the factor by which the two rate constants increase.

13.112 The activation energy (E_a) is positive, and for an exothermic reaction, $E_{a,r} > E_{a,f}$.

$k_f = A_f e^{-E_{a,f}/RT}$, $k_r = A_r e^{-E_{a,r}/RT}$

$$K_c = \frac{k_f}{k_r} = \frac{A_f e^{-E_{a,f}/RT}}{A_r e^{-E_{a,r}/RT}} = \frac{A_f}{A_r} e^{(E_{a,r} - E_{a,f})/RT}$$

$(E_{a,r} - E_{a,f})$ is positive, so the exponent is always positive. As the temperature increases, the exponent, $(E_{a,r} - E_{a,f})/RT$, decreases and the value for K_c decreases as well.

13.113 (a) PV = nRT

$$P^o_{Br_2} = \frac{nRT}{V} = \frac{(0.974 \text{ mol})\left(0.082\,06 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(1000 \text{ K})}{1.00 \text{ L}} = 80 \text{ atm}$$

$$P^{o}_{H_2} = \frac{nRT}{V} = \frac{(1.22\ \text{mol})\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(1000\ \text{K})}{1.00\ \text{L}} = 100\ \text{atm}$$

Because K_p is very large, assume first that the reaction goes to completion and then is followed by a small back reaction.

	$H_2(g)$	+	$Br_2(g)$	_	2 HBr(g)
before (atm)	100		80		0
100% reaction (atm)	-80		-80		+2(80)
after (atm)	20		0		160
back reaction (atm)	+x		+x		-2x
after (atm)	20 + x		x		160 - 2x

$P_{H_2} = 20 + x \approx 20$ atm

$P_{HBr} = 160 - 2x \approx 160$ atm

$$K_p = \frac{(P_{HBr})^2}{(P_{H_2})(P_{Br_2})} = 2.1 \times 10^6 = \frac{(160)^2}{(20)(x)}$$

$$P_{Br_2} = x = \frac{(160)^2}{(20)(2.1 \times 10^6)} = 6.1 \times 10^{-4}\ \text{atm}$$

(b) (ii) Adding Br_2 will cause the greatest increase in the pressure of HBr. The very large value of K_p means that the reaction goes essentially to completion. Therefore, the reaction stops when the limiting reactant, Br_2, is essentially consumed. No matter how much H_2 is added or how far the the equilibrium is shifted (by lowering the temperature) to favor the formation of HBr, the amount of HBr will ultimately be limited by the amount of Br_2 present. So more Br_2 must be added in order to produce more HBr.

13.114 (a) $PV = nRT$, $n_{total} = \frac{PV}{RT} = \frac{(0.588\ \text{atm})(1.00\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\ \text{atm}}{\text{K}\bullet\ \text{mol}}\right)(300\ \text{K})} = 0.0239$ mol

	2 NOBr(g)	_	2 NO(g)	+	$Br_2(g)$
initial (mol)	0.0200		0		0
change (mol)	-2x		+2x		+x
equil (mol)	0.0200 - 2x		2x		x

$n_{total} = 0.0239\ \text{mol} = (0.0200 - 2x) + 2x + x = 0.0200 + x$

$x = 0.0239 - 0.0200 = 0.0039$ mol

Because the volume is 1.00 L, the molarity equals the number of moles.

$[NOBr] = 0.0200 - 2x = 0.0200 - 2(0.0039) = 0.0122$ M

$[NO] = 2x = 2(0.0039) = 0.0078$ M

$[Br_2] = x = 0.0039$ M

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(0.0078)^2(0.0039)}{(0.0122)^2} = 1.6 \times 10^{-3}$$

(b) $\Delta n = (3) - (2) = 1$, $K_p = K_c(RT) = (1.6 \times 10^{-3})(0.082\ 06)(300) = 0.039$

13.115 NO_2, 46.01 amu

$$\text{mol } NO_2 = 4.60 \text{ g } NO_2 \times \frac{1 \text{ mol } NO_2}{46.01 \text{ g } NO_2} = 0.100 \text{ mol } NO_2$$

$[NO_2] = 0.100 \text{ mol}/10.0 \text{ L} = 0.0100 \text{ M}$

	$2\ NO_2(g)$	_	$N_2O_4(g)$
initial (M)	0.0100		0
change (M)	-2x		+x
equil (M)	0.0100 - 2x		x

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 4.72 = \frac{x}{(0.0100 - 2x)^2}$$

$18.88x^2 - 1.189x + 0.000\ 472 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-1.189) \pm \sqrt{(-1.189)^2 - 4(18.88)(0.000\ 472)}}{2(18.88)} = \frac{1.189 \pm 1.1739}{37.76}$$

$x = 0.0626$ and 4.00×10^{-4}

Discard the larger solution (0.0626) because it leads to a negative concentration of NO_2 and that is impossible.

$n_{total} = (0.0100 - 2x + x)(10.0 \text{ L}) = (0.0100 - x)(10.0 \text{ L})$

$= [0.0100 \text{ mol/L} - (4.00 \times 10^{-4} \text{ mol/L})](10.0 \text{ L}) = 0.0960 \text{ mol}$

$100^oC = 100 + 273 = 373 \text{ K}$

$$P_{total} = \frac{n_{total}RT}{V} = \frac{(0.0960 \text{ mol})\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(373 \text{ K})}{10.0 \text{ L}} = 0.294 \text{ atm}$$

13.116 (a) $W(s) + 4\ Br(g) \_ WBr_4(g)$

$$K_p = \frac{P_{WBr_4}}{(P_{Br})^4} = 100, \quad P_{WBr_4} = (P_{Br})^4(100) = (0.010 \text{ atm})^4(100) = 1.0 \times 10^{-6} \text{ atm}$$

(b) Because K_p is smaller at the higher temperature, the reaction has shifted toward reactants at the higher temperature, which means the reaction is exothermic.

(c) At 2800 K, $Q_p = \frac{(1.0 \times 10^{-6})}{(0.010)^4} = 100$, $Q_p > K_p$ so the reaction will go from products to reactants, depositing tungsten back onto the filament.

13.117 (a)

	$(NH_4)(NH_2CO_2)(s)$	_	$2\ NH_3(g)$	+	$CO_2(g)$
initial (atm)			0		0
change (atm)			+2x		+x
equil (atm)			2x		x

$P_{total} = 2x + x = 3x = 0.116$ atm
$x = 0.116$ atm$/3 = 0.0387$ atm
$P_{NH_3} = 2x = 2(0.0387 \text{ atm}) = 0.0774$ atm
$P_{CO_2} = x = 0.0387$ atm
$K_p = (P_{NH_3})^2 (P_{CO_2}) = (0.0774)^2(0.0387) = 2.32 \times 10^{-4}$
(b) (i) The total quantity of NH_3 would decrease. When product, CO_2, is added, the equilibrium will shift to the left.
(ii) The total quantity of NH_3 would remain unchanged. Adding a pure solid, $(NH_4)(NH_2CO_2)$, to a heterogeneous equilibrium will not affect the position of the equilibrium.
(iii) The total quantity of NH_3 would increase. When product, CO_2, is removed, the equilibrium will shift to the right.
(iv) The total quantity of NH_3 would increase. When the total volume is increased, the reaction will shift to the side with more total moles of gas, which in this case is the product side.
(v) The total quantity of NH_3 would remain unchanged. Neon is an inert gas which will have no effect on the reaction or on the position of equilibrium.
(vi) The total quantity of NH_3 would increase. Because the reaction is endothermic, an increase in temperature will shift the equilibrium to to the right.

13.118 $2\ NO_2(g) \_ N_2O_4(g)$
$\Delta n = (1) - (2) = -1$ and $K_p = K_c(RT)^{-1} = (216)[(0.082\ 06)(298)]^{-1} = 8.83$

$$K_p = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = 8.83$$

Let $X = P_{N_2O_4}$ and $Y = P_{NO_2}$.

$P_{total} = 1.50$ atm $= X + Y$ and $\frac{X}{Y^2} = 8.83$. Use these two equations to solve for X and Y.

$X = 1.50 - Y$

$$\frac{1.50 \_ Y}{Y^2} = 8.83$$

$8.83Y^2 + Y - 1.50 = 0$
Use the quadratic formula to solve for Y.

$$Y = \frac{\_(1) \pm \sqrt{(1)^2 \_ 4(8.83)(\_1.50)}}{2(8.83)} = \frac{\_1 \pm 7.35}{17.7}$$

$Y = -0.472$ and 0.359
Discard the negative solution (-0.472) because it leads to a negative partial pressure of NO_2 and that is impossible.
$Y = P_{NO_2} = 0.359$ atm
$X = P_{N_2O_4} = 1.50$ atm $- Y = 1.50$ atm $- 0.359$ atm $= 1.14$ atm

13.119 $500^oC = 500 + 273 = 773$ K and $840^oC = 840 + 273 = 1113$ K

Calculate the undissociated pressure of F_2 at 1113 K.

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}; \quad P_2 = \frac{P_1\ T_2}{T_1} = \frac{(0.600\ \text{atm})(1113\ \text{K})}{773\ \text{K}} = 0.864\ \text{atm}$$

	$F_2(g)$	_	$2\ F(g)$
initial (atm)	0.864		0
change (atm)	-x		+2x
equil (atm)	0.864 - x		2x

$P_{total} = (0.864\ \text{atm} - x) + 2x = 0.864\ \text{atm} + x = 0.984\ \text{atm}$

$x = 0.984\ \text{atm} - 0.864\ \text{atm} = 0.120\ \text{atm}$

$P_{F_2} = (0.864\ \text{atm} - x) = (0.864\ \text{atm} - 0.120\ \text{atm}) = 0.744\ \text{atm}$

$P_F = 2x = 2(0.120\ \text{atm}) = 0.240\ \text{atm}$

$$K_p = \frac{(P_F)^2}{P_{F_2}} = \frac{(0.240)^2}{0.744} = 0.0774$$

13.120

	$N_2(g)$	+	$3\ H_2$	_	$2\ NH_3$
initial (mol)	0		0		X
change (mol)	+y		+3y		-2y
equil (mol)	y		3y		X - 2y

$y = 0.200$ mol

Because the volume is 1.00 L, the molarity equals the number of moles.

$[N_2] = y = 0.200$ M; $[H_2] = 3y = 3(0.200) = 0.600$ M

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[NH_3]^2}{(0.200)(0.600)^3} = 4.20, \text{ solve for } [NH_3]_{eq}$$

$$[NH_3]_{eq}^2 = [N_2][H_2]^3(4.20) = (0.200)(0.600)^3(4.20)$$

$$[NH_3]_{eq} = \sqrt{[N_2][H_2]^3(4.20)} = \sqrt{(0.200)(0.600)^3(4.20)} = 0.426\ \text{M}$$

$[NH_3]_{eq} = 0.426\ \text{M} = X - 2(0.200) = [NH_3]_o - 2(0.200)$

$[NH_3]_o = 0.426 + 2(0.200) = 0.826$ M

0.826 mol of NH_3 were placed in the 1.00 L reaction vessel.

Multi-Concept Problems

13.121 (a) H_2O, 18.015 amu; $125.4\ \text{g}\ H_2O \times \frac{1\ \text{mol}\ H_2O}{18.015\ \text{g}\ H_2O} = 6.96\ \text{mol}\ H_2O$

Given that mol CO = mol H_2O = 6.96 mol

$$P_{CO} = P_{H_2O} = \frac{n\,R\,T}{V} = \frac{(6.96\ \text{mol})\left(0.082\ 06\ \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(700\ \text{K})}{10.0\ \text{L}} = 40.0\ \text{atm}$$

	$CO(g)$	+	$H_2O(g)$	_	$CO_2(g)$	+	$H_2(g)$
initial (atm)	40.0		40.0		0		0
equil (atm)	9.80		9.80		40.0 - 9.80 = 30.2		40.0 - 9.80 = 30.2

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(30.2)(30.2)}{(9.80)(9.80)} = 9.50$$

(b) $31.4\ g\ H_2O \times \frac{1\ mol\ H_2O}{18.015\ g\ H_2O} = 1.743\ mol\ H_2O$

$$P_{H_2O} = \frac{n\,R\,T}{V} = \frac{(1.743\ mol)\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(700\ K)}{10.0\ L} = 10.0\ atm$$

P_{H_2O} has been increased by 10.0 atm; a new equilibrium will be established.

	$CO(g)$	+ $H_2O(g)$	_ $CO_2(g)$	+ $H_2(g)$
initial (atm)	9.80	9.80 +10.0	30.2	30.2
change (atm)	-x	-x	+x	+x
equil (atm)	9.80 - x	19.8 - x	30.2 + x	30.2 + x

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = 9.50 = \frac{(30.2 + x)(30.2 + x)}{(9.80 - x)(19.80 - x)}$$

$8.50x^2 - 341.6x + 931.34 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-341.6) \pm \sqrt{(-341.6)^2 - 4(8.50)(931.34)}}{2(8.50)} = \frac{341.6 \pm 291.6}{17.0}$$

x = 37.25 and 2.94

Discard the larger solution (37.25) because it leads to negative partial pressures and that is impossible.

$P_{CO} = 9.80 - x = 9.80 - 2.94 = 6.86\ atm$

$P_{H_2O} = 19.8 - x = 19.8 - 2.94 = 16.9\ atm$

$P_{CO_2} = P_{H_2} = 30.2 + x = 30.2 + 2.94 = 33.1\ atm$

$$n_{H_2} = \frac{P\,V}{R\,T} = \frac{(33.1\ atm)\,(10.0\ L)}{\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(700\ K)} = 5.76\ mol\ H_2$$

$$\frac{5.76\ mol\ H_2}{10.0\ L} \times \frac{1\ L}{1000\ mL} \times \frac{1\ mL}{1\ cm^3} \times \frac{6.022 \times 10^{23}\ H_2\ molecules}{1\ mol\ H_2} = 3.47 \times 10^{20}\ H_2\ molecules/cm^3$$

13.122 (a) CO_2, 44.01 amu; CO, 28.01 amu

$79.2\ g\ CO_2 \times \frac{1\ mol\ CO_2}{44.01\ g\ CO_2} = 1.80\ mol\ CO_2$

	$CO_2(g)$	+ $C(s)$	_ $2\ CO(g)$
initial (mol)	1.80		0
change (mol)	-x		+2x
equil (mol)	1.80 - x		2x

total mass of gas in flask = (16.3 g/L)(5.00 L) = 81.5 g
81.5 = (1.80 - x)(44.01) + (2x)(28.01)
81.5 = 79.22 - 44.01x + 56.02x; 2.28 = 12.01x; x = 2.28/12.01 = 0.19
n_{CO_2} = 1.80 - x = 1.80 - 0.19 = 1.61 mol CO_2; n_{CO} = 2x = 2(0.19) = 0.38 mol CO

$$P_{CO_2} = \frac{n\,R\,T}{V} = \frac{(1.61\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1000\ \text{K})}{5.0\ \text{L}} = 26.4\ \text{atm}$$

$$P_{CO} = \frac{n\,R\,T}{V} = \frac{(0.38\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1000\ \text{K})}{5.0\ \text{L}} = 6.24\ \text{atm}$$

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})} = \frac{(6.24)^2}{(26.4)} = 1.47$$

(b) At 1100K, the total mass of gas in flask = (16.9 g/L)(5.00 L) = 84.5 g
84.5 = (1.80 - x)(44.01) + (2x)(28.01)
84.5 = 79.22 - 44.01x + 56.02x; 5.28 = 12.01x; x = 5.28/12.01 = 0.44
n_{CO_2} = 1.80 - x = 1.80 - 0.44 = 1.36 mol CO_2; n_{CO} = 2x = 2(0.44) = 0.88 mol CO

$$P_{CO_2} = \frac{n\,R\,T}{V} = \frac{(1.36\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1100\ \text{K})}{5.0\ \text{L}} = 24.6\ \text{atm}$$

$$P_{CO} = \frac{n\,R\,T}{V} = \frac{(0.88\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1100\ \text{K})}{5.0\ \text{L}} = 15.9\ \text{atm}$$

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})} = \frac{(15.9)^2}{(24.6)} = 10.3$$

(c) In agreement with Le Châtelier's principle, the reaction is endothermic because K_p increases with increasing temperature.

13.123 CO_2, 44.01 amu; CO, 28.01 amu; $BaCO_3$, 197.34 amu

$$1.77\ \text{g}\ CO_2 \times \frac{1\ \text{mol}\ CO_2}{44.01\ \text{g}\ CO_2} = 0.0402\ \text{mol}\ CO_2$$

	$CO_2(g)$	+	C(s)	⎯	2 CO(g)
initial (mol)	0.0402				0
change (mol)	-x				+2x
equil (mol)	0.0402 - x				2x

$$3.41\ \text{g}\ BaCO_3 \times \frac{1\ \text{mol}\ BaCO_3}{197.34\ \text{g}\ BaCO_3} \times \frac{1\ \text{mol}\ CO_2}{1\ \text{mol}\ BaCO_3} = 0.0173\ \text{mol}\ CO_2$$

mol CO_2 = 0.0173 = 0.0402 - x; x = 0.0229
mol CO = 2x = 2(0.0229) = 0.0458 mol CO

$$P_{CO_2} = \frac{n\,R\,T}{V} = \frac{(0.0173\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1100\ \text{K})}{1.000\ \text{L}} = 1.562\ \text{atm}$$

$$P_{CO} = \frac{n\,R\,T}{V} = \frac{(0.0458\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(1100\ \text{K})}{1.000\ \text{L}} = 4.134\ \text{atm}$$

$$K_p = \frac{(P_{CO})^2}{(P_{CO_2})} = \frac{(4.134)^2}{(1.562)} = 11.0$$

13.124 (a) N_2O_4, 92.01 amu

$$14.58\ \text{g}\ N_2O_4 \times \frac{1\ \text{mol}\ N_2O_4}{92.01\ \text{g}\ N_2O_4} = 0.1585\ \text{mol}\ N_2O_4$$

PV = nRT

$$P_{N_2O_4} = \frac{n\,R\,T}{V} = \frac{(0.1585\ \text{mol})\left(0.082\ 06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(400\ \text{K})}{1.000\ \text{L}} = 5.20\ \text{atm}$$

	$N_2O_4(g)$	_	$2\ NO_2(g)$
initial (atm)	5.20		0
change (atm)	-x		+2x
equil (atm)	5.20 - x		2x

$P_{total} = P_{N_2O_4} + P_{NO_2} = (5.20 - x) + (2x) = 9.15$ atm

5.20 + x = 9.15 atm

x = 3.95 atm

$P_{N_2O_4} = 5.20 - x = 5.20 - 3.95 = 1.25$ atm

$P_{NO_2} = 2x = 2(3.95) = 7.90$ atm

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(7.90)^2}{(1.25)} = 49.9$$

$$\Delta n = 1 \text{ and } K_c = K_p\left(\frac{1}{RT}\right) = \frac{(49.9)}{(0.082\ 06)(400)} = 1.52$$

(b) $\Delta H^o_{rxn} = [2\ \Delta H^o_f(NO_2)] - \Delta H^o_f(N_2O_4)$

$\Delta H^o_{rxn} = [(2\ \text{mol})(33.2\ \text{kJ/mol})] - [(1\text{mol})(9.16\ \text{kJ/mol})] = 57.2\ \text{kJ}$

PV = nRT

$$\text{moles } N_2O_4 \text{ reacted} = n = \frac{PV}{RT} = \frac{(3.95\ \text{atm})(1.000\ \text{L})}{\left(0.082\,06\ \frac{\text{L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\right)(400\ \text{K})} = 0.1203\ \text{mol}\ N_2O_4$$

$q = (57.24\ \text{kJ/mol}\ N_2O_4)(0.1203\ \text{mol}\ N_2O_4) = 6.89\ \text{kJ}$

13.125 $C_{10}H_8(s)$ _ $C_{10}H_8(g)$

(a) $K_c = [C_{10}H_8] = 5.40 \times 10^{-6}$

room volume = 8.0 ft x 10.0 ft x 8.0 ft = 640 ft^2

$$\text{room volume} = 640\ ft^2 \times \left(\frac{12\ in}{1\ ft}\right)^3 \times \left(\frac{2.54\ cm}{1\ in}\right)^3 \times \left(\frac{1.0\ L}{1000\ cm^3}\right) = 18122.8\ L$$

$C_{10}H_8$ molecules = (5.40 x 10^{-6} mol/L)(18122.8 L)(6.022 x 10^{23} molecules/mol)

= 5.89 x 10^{22} $C_{10}H_8$ molecules

(b) $C_{10}H_8$, 128.17 amu

mol $C_{10}H_8$ = (5.40 x 10^{-6} mol/L)(18122.8 L) = 0.0979 mol $C_{10}H_8$

$$\text{mass } C_{10}H_8 = 0.0979\ mol\ C_{10}H_8 \times \frac{128.17\ g\ C_{10}H_8}{1\ mol\ C_{10}H_8} = 12.55\ g\ C_{10}H_8$$

moth ball: r = 12.0 mm/2 = 6.0 mm = 0.60 cm

volume of moth ball = $(4/3)\pi r^3 = (4/3)\pi(0.60cm)^3 = 0.905\ cm^3$

mass of moth ball = ($0.905\ cm^3$/moth ball)(1.16 g/cm^3) = 1.05 g/moth ball

$$\text{number of moth balls} = \frac{12.55\ g\ C_{10}H_8}{1.05\ g\ C_{10}H_8/\text{moth ball}} = 12 \text{ moth balls}$$

13.126 The atmosphere is 21% (0.21) O_2; $P_{O_2} = (0.21)(720\ mm\ Hg) = 0.199$ atm

2 $O_3(g)$ _ 3 $O_2(g)$

$$K_p = \frac{(P_{O_2})^3}{(P_{O_3})^2}; \qquad P_{O_3} = \sqrt{\frac{(P_{O_2})^3}{K_p}} = \sqrt{\frac{(0.199)^3}{1.3 \times 10^{57}}} = 2.46 \times 10^{-30}\ atm$$

$$\text{vol} = 10 \times 10^6\ m^3 \times \left(\frac{100\ cm}{1\ m}\right)^3 \times \frac{1\ L}{1000\ cm^3} = 1.0 \times 10^{10}\ L$$

$$n_{O_3} = \frac{P\,V}{R\,T} = \frac{(2.46 \times 10^{-30}\ atm)(1.0 \times 10^{10}\ L)}{\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)} = 1.0 \times 10^{-21}\ mol\ O_3$$

$$O_3 \text{ molecules} = 1.0 \times 10^{-21}\ mol\ O_3 \times \frac{6.022 \times 10^{23}\ O_3\ molecules}{1\ mol\ O_3} = 6.0 \times 10^2\ O_3 \text{ molecules}$$

13.127 250.0 mL = 0.2500 L

$[CH_3CO_2H] = 0.0300\ mol/0.2500\ L = 0.120\ M$

	2 CH_3CO_2H	_	$(CH_3CO_2H)_2$
initial (M)	0.120		0
change (M)	-2x		+x
equil (M)	0.120 - 2x		x

$$K_c = \frac{[\text{dimer}]}{[\text{monomer}]^2} = 1.51 \times 10^2 = \frac{x}{(0.120 - 2x)^2}$$

$604x^2 - 73.48x + 2.1744 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-73.48) \pm \sqrt{(-73.48)^2 - 4(604)(2.1744)}}{2(604)} = \frac{73.48 \pm 12.08}{1208}$$

x = 0.0708 and 0.0508

Discard the larger solution (0.0708) because it leads to a negative concentration and that is impossible.

[monomer] = 0.120 - 2x = 0.120 - 2(0.0508) = 0.0184 M

[dimer] = x = 0.0508 M

(b) $25^oC = 25 + 273 = 298$ K

$$\Pi = MRT = (0.0184\ M + 0.0508\ M)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\,K) = 1.69\ atm$$

13.128 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$\Delta n = (2) - (1) = 1$ and at 700 K, $K_p = K_c(RT) = (46.9)(0.082\ 06)(700) = 2694$

(a) Because K_p is larger at the higher temperature, the reaction has shifted toward products at the higher temperature, which means the reaction is endothermic. Because the reaction involves breaking two P–Cl bonds and forming just one Cl–Cl bond, it should be endothermic.

(b) PCl_5, 208.24 amu

$$\text{mol } PCl_5 = 1.25\ g\ PCl_5 \times \frac{1\ mol\ PCl_5}{208.24\ g\ PCl_5} = 6.00 \times 10^{-3}\ mol$$

$$PV = nRT, \quad P_{PCl_5} = \frac{nRT}{V} = \frac{(6.00 \times 10^{-3}\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(700\ K)}{0.500\ L} = 0.689\ atm$$

Because K_p is so large, first assume the reaction goes to completion and then allow for a small back reaction.

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
before rxn (atm)	0.689		0		0
100% rxn (atm)	-0.689		+0.689		+0.689
after rxn (atm)	0		0.689		0.689
back rxn (atm)	+x		-x		-x
equil (atm)	x		0.689 - x		0.689 - x

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{P_{PCl_5}} = 2694 = \frac{(0.689 - x)^2}{x} \approx \frac{(0.689)^2}{x}$$

$$x = P_{PCl_5} = \frac{(0.689)^2}{2694} = 1.76 \times 10^{-4}\ atm$$

$$P_{total} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$

$$P_{total} = x + (0.689 - x) + (0.689 - x) = 0.689 + 0.689 - 1.76 \times 10^{-4} = 1.38\ atm$$

$$\% \text{ dissociation} = \frac{(P_{PCl_5})_o - (P_{PCl_5})}{(P_{PCl_5})_o} \times 100\% = \frac{0.689 - (1.76 \times 10^{-4})}{0.689} \times 100\% = 99.97\%$$

(c)
The molecular geometry is trigonal bipyramidal. There is no dipole moment because of a symmetrical distribution of Cl's around the central P.

The molecular geometry is trigonal pyramidal. There is a dipole moment because of the lone pair of electrons on the P and an unsymmetrical distribution of Cl's around the central P.

16 Applications of Aqueous Equilibria

16.1 (a) $HNO_2(aq) + OH^-(aq) \Omega NO_2^-(aq) + H_2O(l)$; NO_2^- (basic anion), pH > 7.00

(b) $H_3O^+(aq) + NH_3(aq) \Omega NH_4^+(aq) + H_2O(l)$; NH_4^+ (acidic cation), pH < 7.00

(c) $OH^-(aq) + H_3O^+(aq) \Omega 2\ H_2O(l)$; pH = 7.00

16.2 (a) $HF(aq) + OH^-(aq) \Omega H_2O(l) + F^-(aq)$

$$K_n = \frac{K_a}{K_w} = \frac{3.5 \times 10^{-4}}{1.0 \times 10^{-14}} = 3.5 \times 10^{10}$$

(b) $H_3O^+(aq) + OH^-(aq) \Omega 2\ H_2O(l)$

$$K_n = \frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14}$$

(c) $HF(aq) + NH_3(aq) \Omega NH_4^+(aq) + F^-(aq)$

$$K_n = \frac{K_a K_b}{K_w} = \frac{(3.5 \times 10^{-4})(1.8 \times 10^{-5})}{1.0 \times 10^{-14}} = 6.3 \times 10^5$$

The tendency to proceed to completion is determined by the magnitude of K_n. The larger the value of K_n, the further does the reaction proceed to completion.

The tendency to proceed to completion is: reaction (c) < reaction (a) < reaction (b)

16.3

	$HCN(aq)$	+ $H_2O(l)$ Ω	$H_3O^+(aq)$	+ $CN^-(aq)$
initial (M)	0.025		~0	0.010
change (M)	−x		+x	+x
equil (M)	0.025 − x		x	0.010 + x

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10} = \frac{x(0.010 + x)}{0.025 - x} \approx \frac{x(0.010)}{0.025}$$

Solve for x. $x = 1.23 \times 10^{-9}$ M $= 1.2 \times 10^{-9}$ M $= [H_3O^+]$

$pH = -\log[H_3O^+] = -\log(1.23 \times 10^{-9}) = 8.91$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.23 \times 10^{-9}} = 8.2 \times 10^{-6}\ M$$

$[Na^+] = [CN^-] = 0.010$ M; [HCN] = 0.025 M

$$\% \text{ dissociation} = \frac{[HCN]_{diss}}{[HCN]_{initial}} \times 100\% = \frac{1.23 \times 10^{-9}\ M}{0.025\ M} \times 100\% = 4.9 \times 10^{-6}\ \%$$

16.4 From $NH_4Cl(s)$, $[NH_4^+]_{initial} = \frac{0.10\ mol}{0.500\ L} = 0.20\ M$

	$NH_3(aq) + H_2O(l)$	Ω	$NH_4^+(aq) + OH^-(aq)$
initial (M)	0.40		0.20 ~0
change (M)	−x		+x +x
equil (M)	0.40 − x		0.20 + x x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(0.20 + x)(x)}{(0.40 - x)} \approx \frac{(0.20)(x)}{(0.40)}$$

Solve for x. $x = [OH^-] = 3.6 \times 10^{-5}\ M$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-5}} = 2.8 \times 10^{-10}\ M$$

$pH = -\log[H_3O^+] = -\log(2.8 \times 10^{-10}) = 9.55$

16.5 Each solution contains the same number of B molecules. The presence of BH^+ from BHCl lowers the percent dissociation of B. Solution (2) contains no BH^+, therefore it has the largest percent dissociation. BH^+ is the conjugate acid of B. Solution (1) has the largest amount of BH^+ and it would be the most acidic solution and have the lowest pH.

16.6 (a) (1) and (3). Both pictures show equal concentrations of HA and A^-.
(b) (3). It contains a higher concentration of HA and A^-.

16.7

	$HF(aq) + H_2O(l)$	Ω	$H_3O^+(aq) + F^-(aq)$
initial (M)	0.25		~0 0.50
change (M)	−x		+x +x
equil (M)	0.25 − x		x 0.50 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 3.5 \times 10^{-4} = \frac{x(0.50 + x)}{0.25 - x} \approx \frac{x(0.50)}{0.25}$$

Solve for x. $x = 1.75 \times 10^{-4}\ M = [H_3O^+]$

For the buffer, $pH = -\log[H_3O^+] = -\log(1.75 \times 10^{-4}) = 3.76$

(a) mol HF = 0.025 mol; mol F^- = 0.050 mol; vol = 0.100 L

	$F^-(aq) + H_3O^+(aq)$	100%	$HF(aq) + H_2O(l)$
before (mol)	0.050 0.002		0.025
change (mol)	−0.002 −0.002		+0.002
after (mol)	0.048 0		0.027

$$[H_3O^+] = K_a \frac{[HF]}{[F^-]} = (3.5 \times 10^{-4})\left(\frac{0.27}{0.48}\right) = 1.97 \times 10^{-4}\ M$$

$pH = -\log[H_3O^+] = -\log(1.97 \times 10^{-4}) = 3.71$

(b) mol HF = 0.025 mol; mol F^- = 0.050 mol; vol = 0.100 L

	HF(aq)	+ OH^-(aq)	$\xrightarrow{100\%}$	F^-(aq)	+ H_2O(l)
before (mol)	0.025	0.004		0.050	
change (mol)	S0.004	S0.004		+0.004	
after (mol)	0.021	0		0.054	

$$[H_3O^+] = K_a \frac{[HF]}{[F^-]} = (3.5 \times 10^{-4})\left(\frac{0.21}{0.54}\right) = 1.36 \times 10^{-4}\ M$$

$$pH = -\log[H_3O^+] = -\log(1.36 \times 10^{-4}) = 3.87$$

16.8

	HF(aq)	+ H_2O(l)	Ω	H_3O^+(aq)	+ F^-(aq)
initial (M)	0.050			~0	0.100
change (M)	Sx			+x	+x
equil (M)	0.050 S x			x	0.100 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 3.5 \times 10^{-4} = \frac{x(0.100 + x)}{0.050 - x} \approx \frac{x(0.100)}{0.050}$$

Solve for x. $x = [H_3O^+] = 1.75 \times 10^{-4}$ M

$pH = -\log[H_3O^+] = -\log(1.75 \times 10^{-4}) = 3.76$

mol HF = 0.050 mol/L x 0.100 L = 0.0050 mol HF

mol F^- = 0.100 mol/L x 0.100 L = 0.0100 mol F^-

mol HNO_3 = mol H_3O^+ = 0.002 mol

Neutralization reaction:	F^-(aq)	+ H_3O^+(aq)	$\xrightarrow{100\%}$	HF(aq)	+ H_2O(l)
before reaction (mol)	0.0100	0.002		0.0050	
change (mol)	S0.002	S0.002		+0.002	
after reaction (mol)	0.008	0		0.007	

$$[HF] = \frac{0.007\ mol}{0.100\ L} = 0.07\ M; \qquad [F^-] = \frac{0.008\ mol}{0.100\ L} = 0.08\ M$$

$$[H_3O^+] = K_a \frac{[HF]}{[F^-]} = (3.5 \times 10^{-4})\frac{(0.07)}{(0.08)} = 3 \times 10^{-4}\ M$$

$pH = -\log[H_3O^+] = -\log(3 \times 10^{-4}) = 3.5$

This solution has less buffering capacity than the solution in Problem 16.7 because it contains less HF and F^- per 100 mL. Note that the change in pH is greater than that in Problem 16.7.

16.9 When equal volumes of two solutions are mixed together, the concentration of each solution is cut in half.

$$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$$

For HCO_3^-, $K_a = 5.6 \times 10^{-11}$, $pK_a = -\log K_a = -\log(5.6 \times 10^{-11}) = 10.25$

$$pH = 10.25 + \log\left(\frac{0.050}{0.10}\right) = 10.25 - 0.30 = 9.95$$

16.10 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$$

For HCO_3^-, $K_a = 5.6 \times 10^{-11}$, $pK_a = -\log K_a = -\log(5.6 \times 10^{-11}) = 10.25$

$$10.40 = 10.25 + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}; \qquad \log\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10.40 - 10.25 = 0.15$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{0.15} = 1.4$$

To obtain a buffer solution with pH 10.40, make the Na_2CO_3 concentration 1.4 times the concentration of $NaHCO_3$.

16.11 Look for an acid with pK_a near the required pH of 7.50.
$K_a = 10^{-pH} = 10^{-7.50} = 3.2 \times 10^{-8}$
Suggested buffer system: HOCl ($K_a = 3.5 \times 10^{-8}$) and NaOCl.

16.12 (a) serine is 66% dissociated at $pH = 9.15 + \log\left(\frac{66}{34}\right) = 9.44$

(b) serine is 5% dissociated at $pH = 9.15 + \log\left(\frac{5}{95}\right) = 7.87$

16.13 (a) mol HCl = mol H_3O^+ = 0.100 mol/L x 0.0400 L = 0.004 00 mol
mol NaOH = mol OH^- = 0.100 mol/L x 0.0350 L = 0.003 50 mol

Neutralization reaction:	$H_3O^+(aq)$ +	$OH^-(aq)$	2 $H_2O(l)$
before reaction (mol)	0.004 00	0.003 50	
change (mol)	−0.003 50	−0.003 50	
after reaction (mol)	0.000 50	0	

$$[H_3O^+] = \frac{0.000\,50 \text{ mol}}{(0.0400 \text{ L} + 0.0350 \text{ L})} = 6.7 \times 10^{-3} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(6.7 \times 10^{-3}) = 2.17$

(b) mol HCl = mol H_3O^+ = 0.100 mol/L x 0.0400 L = 0.004 00 mol
mol NaOH = mol OH^- = 0.100 mol/L x 0.0450 L = 0.004 50 mol

Neutralization reaction:	$H_3O^+(aq)$ +	$OH^-(aq)$	2 $H_2O(l)$
before reaction (mol)	0.004 00	0.004 50	
change (mol)	−0.004 00	−0.004 00	
after reaction (mol)	0	0.000 50	

$$[OH^-] = \frac{0.000\,50 \text{ mol}}{(0.0400 \text{ L} + 0.0450 \text{ L})} = 5.9 \times 10^{-3} \text{ M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-3}} = 1.7 \times 10^{-12} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(1.7 \times 10^{-12}) = 11.77$

The results obtained here are consistent with the pH data in Table 16.1

16.14 (a) mol NaOH = mol OH^- = 0.100 mol/L x 0.0400 L = 0.004 00 mol
mol HCl = mol H_3O^+ = 0.0500 mol/L x 0.0600 L = 0.003 00 mol

Neutralization reaction:	$H_3O^+(aq)$ +	$OH^-(aq)$	2 $H_2O(l)$
before reaction (mol)	0.003 00	0.004 00	
change (mol)	−0.003 00	−0.003 00	

after reaction (mol) 0 0.001 00

$$[OH^{-}] = \frac{0.001\,00\ \text{mol}}{(0.0400\ \text{L} + 0.0600\ \text{L})} = 1.0 \times 10^{-2}\ \text{M}$$

$$[H_3O^{+}] = \frac{K_w}{[OH^{-}]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\ \text{M}$$

$pH = -\log[H_3O^{+}] = -\log(1.0 \times 10^{-12}) = 12.00$

(b) mol NaOH = mol OH^{-} = 0.100 mol/L x 0.0400 L = 0.004 00 mol

mol HCl = mol H_3O^{+} = 0.0500 mol/L x 0.0802 L = 0.004 01 mol

Neutralization reaction:	$H_3O^{+}(aq)$ +	$OH^{-}(aq)$	$2\ H_2O(l)$
before reaction (mol)	0.004 01	0.004 00	
change (mol)	−0.004 00	−0.004 00	
after reaction (mol)	0.000 01	0	

$$[H_3O^{+}] = \frac{0.000\,01\ \text{mol}}{(0.0400\ \text{L} + 0.0802\ \text{L})} = 8.3 \times 10^{-5}\ \text{M}$$

$pH = -\log[H_3O^{+}] = -\log(8.3 \times 10^{-5}) = 4.08$

(c) mol NaOH = mol OH^{-} = 0.100 mol/L x 0.0400 L = 0.004 00 mol

mol HCl = mol H_3O^{+} = 0.0500 mol/L x 0.1000 L = 0.005 00 mol

Neutralization reaction:	$H_3O^{+}(aq)$ +	$OH^{-}(aq)$	$2\ H_2O(l)$
before reaction (mol)	0.005 00	0.004 00	
change (mol)	−0.004 00	−0.004 00	
after reaction (mol)	0.001 00	0	

$$[H_3O^{+}] = \frac{0.001\,00\ \text{mol}}{(0.0400\ \text{L} + 0.1000\ \text{L})} = 7.1 \times 10^{-3}\ \text{M}$$

$pH = -\log[H_3O^{+}] = -\log(7.1 \times 10^{-3}) = 2.15$

16.15 (a) (3), only HA present (b) (1), HA and A^{-} present
(c) (4), only A^{-} present (d) (2), A^{-} and OH^{-} present

16.16 $$\text{mol NaOH required} = \left(\frac{0.016\ \text{mol HOCl}}{\text{L}}\right)(0.100\ \text{L})\left(\frac{1\ \text{mol NaOH}}{1\ \text{mol HOCl}}\right) = 0.0016\ \text{mol}$$

$$\text{vol NaOH required} = (0.0016\ \text{mol})\left(\frac{1\ \text{L}}{0.0400\ \text{mol}}\right) = 0.040\ \text{L} = 40\ \text{mL}$$

40 mL of 0.0400 M NaOH are required to reach the equivalence point.

(a) mmol HOCl = 0.016 mmol/mL x 100.0 mL = 1.6 mmol

mmol NaOH = mmol OH^{-} = 0.0400 mmol/mL x 10.0 mL = 0.400 mmol

Neutralization reaction:	$HOCl(aq)$ +	$OH^{-}(aq)$	$OCl^{-}(aq)$ +	$H_2O(l)$
before reaction (mmol)	1.6	0.400	0	
change (mmol)	−0.400	−0.400	+0.400	
after reaction (mmol)	1.2	0	0.400	

$$[HOCl] = \frac{1.2\ \text{mmol}}{(100.0\ \text{mL} + 10.0\ \text{mL})} = 1.09 \times 10^{-2}\ \text{M}$$

$$[OCl^{-}] = \frac{0.400\ \text{mmol}}{(100.0\ \text{mL} + 10.0\ \text{mL})} = 3.64 \times 10^{-3}\ \text{M}$$

	$HOCl(aq)$ + $H_2O(l)$ Ω	$H_3O^+(aq)$ +	$OCl^-(aq)$
initial (M)	0.0109	~0	0.003 64
change (M)	Sx	+x	+x
equil (M)	0.0109 S x	x	0.003 64 + x

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = 3.5 \times 10^{-8} = \frac{x(0.003\,64 + x)}{0.0109 - x} \approx \frac{x(0.003\,64)}{0.0109}$$

Solve for x. $x = [H_3O^+] = 1.05 \times 10^{-7}$ M

$pH = -\log[H_3O^+] = -\log(1.05 \times 10^{-7}) = 6.98$

(b) Halfway to the equivalence point, $[OCl^-] = [HOCl]$

$pH = pK_a = -\log K_a = -\log(3.5 \times 10^{-8}) = 7.46$

(c) At the equivalence point the solution contains the salt, NaOCl.

mol NaOCl = initial mol HOCl = 0.0016 mol = 1.6 mmol

$$[OCl^-] = \frac{1.6 \text{ mmol}}{(100.0 \text{ mL} + 40.0 \text{ mL})} = 1.1 \times 10^{-2} \text{ M}$$

For OCl^-, $K_b = \dfrac{K_w}{K_a \text{ for HOCl}} = \dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}$

	$OCl^-(aq)$ + $H_2O(l)$ Ω	$HOCl(aq)$ +	$OH^-(aq)$
initial (M)	0.011	0	~0
change (M)	Sx	+x	+x
equil (M)	0.011 S x	x	x

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]} = 2.9 \times 10^{-7} = \frac{x^2}{0.011 - x} \approx \frac{x^2}{0.011}$$

Solve for x. $x = [OH^-] = 5.65 \times 10^{-5}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.65 \times 10^{-5}} = 1.77 \times 10^{-10} = 1.8 \times 10^{-10} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(1.77 \times 10^{-10}) = 9.75$

16.17 From Problem 16.16, pH = 9.75 at the equivalence point.
Use thymolphthalein (pH 9.4 S 10.6). Bromthymol blue is unacceptable because it changes color halfway to the equivalence point.

16.18 (a) mol NaOH required to reach first equivalence point

$$= \left(\frac{0.0800 \text{ mol } H_2SO_3}{\text{L}}\right)(0.0400 \text{ L})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } H_2SO_3}\right) = 0.003\,20 \text{ mol}$$

vol NaOH required to reach first equivalence point

$$= (0.003\,20 \text{ mol})\left(\frac{1 \text{ L}}{0.160 \text{ mol}}\right) = 0.020 \text{ L} = 20.0 \text{ mL}$$

20.0 mL is enough NaOH solution to reach the first equivalence point for the titration of the diprotic acid, H_2SO_3.

For H_2SO_3,

$K_{a1} = 1.5 \times 10^{-2}$, $pK_{a1} = -\log K_{a1} = -\log(1.5 \times 10^{-2}) = 1.82$

$K_{a2} = 6.3 \times 10^{-8}$, $pK_{a2} = -\log K_{a2} = -\log(6.3 \times 10^{-8}) = 7.20$

At the first equivalence point, $pH = \dfrac{pK_{a1} + pK_{a2}}{2} = \dfrac{1.82 + 7.20}{2} = 4.51$

(b) mol NaOH required to reach second equivalence point

$$= \left(\frac{0.0800 \text{ mol } H_2SO_3}{\text{L}}\right)(0.0400 \text{ L})\left(\frac{2 \text{ mol NaOH}}{1 \text{ mol } H_2SO_3}\right) = 0.006\,40 \text{ mol}$$

vol NaOH required to reach second equivalence point

$$= (0.006\,40 \text{ mol})\left(\frac{1 \text{ L}}{0.160 \text{ mol}}\right) = 0.040 \text{ L} = 40.0 \text{ mL}$$

30.0 mL is enough NaOH solution to reach halfway to the second equivalent point.

Halfway to the second equivalence point

$pH = pK_{a2} = -\log K_{a2} = -\log(6.3 \times 10^{-8}) = 7.20$

(c) mmol HSO_3^- = 0.0800 mmol/mL x 40.0 mL = 3.20 mmol

volume NaOH added after first equivalence point = 35.0 mL − 20.0 mL = 15.0 mL

mmol NaOH = mmol OH^- = 0.160 mmol/L x 15.0 mL = 2.40 mmol

Neutralization reaction:	$HSO_3^-(aq)$	+ $OH^-(aq)$	⇌	$SO_3^{2-}(aq)$	+ $H_2O(l)$
before reaction (mmol)	3.20	2.40		0	
change (mmol)	−2.40	−2.40		+2.40	
after reaction (mmol)	0.80	0		2.40	

$$[HSO_3^-] = \frac{0.80 \text{ mmol}}{(40.0 \text{ mL} + 35.0 \text{ mL})} = 0.0107 \text{ M}$$

$$[SO_3^{2-}] = \frac{2.40 \text{ mmol}}{(40.0 \text{ mL} + 35.0 \text{ mL})} = 0.0320 \text{ M}$$

	$HSO_3^-(aq)$	+ $H_2O(l)$	⇌	$H_3O^+(aq)$	+ $SO_3^{2-}(aq)$
initial (M)	0.0107		~0	0.0320	
change (M)	−x		+x	+x	
equil (M)	0.0107 − x		x	0.0320 + x	

$$K_a = \frac{[H_3O^+][SO_3^{2-}]}{[HSO_3^-]} = 6.3 \times 10^{-8} = \frac{x(0.0320 + x)}{0.0107 - x} \approx \frac{x(0.0320)}{0.0107}$$

Solve for x. $x = [H_3O^+] = 2.1 \times 10^{-8}$ M

$pH = -\log[H_3O^+] = -\log(2.1 \times 10^{-8}) = 7.68$

16.19 Let H_2A^+ = valine cation

(a) mol NaOH required to reach first equivalence point

$$= \left(\frac{0.0250 \text{ mol } H_2A^+}{\text{L}}\right)(0.0400 \text{ L})\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } H_2A^+}\right) = 0.001\,00 \text{ mol}$$

vol NaOH required to reach first equivalence point

$$= (0.001\ 00\ \text{mol})\left(\frac{1\ \text{L}}{0.100\ \text{mol}}\right) = 0.0100\ \text{L} = 10.0\ \text{mL}$$

10.0 mL is enough NaOH solution to reach the first equivalence point for the titration of the diprotic acid, H_2A^+.

For H_2A^+,

$K_{a1} = 4.8 \times 10^{-3}$, $pK_{a1} = -\log K_{a1} = -\log(4.8 \times 10^{-3}) = 2.32$

$K_{a2} = 2.4 \times 10^{-10}$, $pK_{a2} = -\log K_{a2} = -\log(2.4 \times 10^{-10}) = 9.62$

At the first equivalence point, $\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \frac{2.32 + 9.62}{2} = 5.97$

(b) mol NaOH required to reach second equivalence point

$$= \left(\frac{0.0250\ \text{mol}\ H_2A^+}{\text{L}}\right)(0.0400\ \text{L})\left(\frac{2\ \text{mol NaOH}}{1\ \text{mol}\ H_2A^+}\right) = 0.002\ 00\ \text{mol}$$

vol NaOH required to reach second equivalence point

$$= (0.002\ 00\ \text{mol})\left(\frac{1\ \text{L}}{0.100\ \text{mol}}\right) = 0.0200\ \text{L} = 20.0\ \text{mL}$$

15.0 mL is enough NaOH solution to reach halfway to the second equivalent point.

Halfway to the second equivalence point

$\text{pH} = \text{p}K_{a2} = -\log K_{a2} = -\log(2.4 \times 10^{-10}) = 9.62$

(c) 20.0 mL is enough NaOH to reach the second equivalence point.

At the second equivalence point

mmol A^s = (0.0250 mmol/mL)(40.0 mL) = 1.00 mmol A^s

solution volume = 40.0 mL + 20.0 mL = 60.0 mL

$$[A^s] = \frac{1.00\ \text{mmol}}{60.0\ \text{mL}} = 0.0167\ \text{M}$$

	$A^s(aq)$ + $H_2O(l)$ Ω	$HA(aq)$ +	$OH^s(aq)$
initial (M)	0.0167	0	~0
change (M)	Sx	+x	+x
equil (M)	0.0167 S x	x	x

$$K_b = \frac{K_w}{K_a\ \text{for HA}} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{2.4 \times 10^{-10}} = 4.17 \times 10^{s5}$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = 4.17 \times 10^{-5} = \frac{x^2}{0.0167 - x}$$

$x^2 + (4.17 \times 10^{s5})x\ \text{S}\ (6.964 \times 10^{s7}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(4.17 \times 10^{-5}) \pm \sqrt{(4.17 \times 10^{-5})^2 - (4)(1)(-6.964 \times 10^{-7})}}{2(1)} = \frac{(-4.17 \times 10^{-5}) \pm (1.67 \times 10^{-3})}{2}$$

$x = 8.14 \times 10^{s4}$ and S8.56×10^{s4}

Of the two solutions for x, only the positive value has physical meaning because x is the $[OH^s]$.

$x = [OH^-] = 8.14 \times 10^{-4}$ M

$[H_3O^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{8.14 \times 10^{-4}} = 1.23 \times 10^{-11}$ M

$pH = -\log[H_3O^+] = -\log(1.23 \times 10^{-11}) = 10.91$

16.20 (a) $K_{sp} = [Ag^+][Cl^-]$ (b) $K_{sp} = [Pb^{2+}][I^-]^2$
(c) $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$ (d) $K_{sp} = [Cr^{3+}][OH^-]^3$

16.21 $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (2.01 \times 10^{-8})^3(1.6 \times 10^{-5})^2 = 2.1 \times 10^{-33}$

16.22 $[Ba^{2+}] = [SO_4^{2-}] = 1.05 \times 10^{-5}$ M; $K_{sp} = [Ba^{2+}][SO_4^{2-}] = (1.05 \times 10^{-5})^2 = 1.10 \times 10^{-10}$

16.23 (a)

	$AgCl(s)$	Ω	$Ag^+(aq)$	+	$Cl^-(aq)$
equil (M)			x		x

$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} = (x)(x)$

molar solubility = $x = \sqrt{K_{sp}} = 1.3 \times 10^{-5}$ mol/L

AgCl, 143.32 amu

$$\text{solubility} = \frac{\left(1.3 \times 10^{-5} \text{ mol} \times \frac{143.32 \text{ g}}{1 \text{ mol}}\right)}{1 \text{ L}} = 0.0019 \text{ g/L}$$

(b)

	$Ag_2CrO_4(s)$	Ω	$2\,Ag^+(aq)$	+	$CrO_4^{2-}(aq)$
equil (M)			2x		x

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 1.1 \times 10^{-12} = (2x)^2(x) = 4x^3$

molar solubility = $x = \sqrt[3]{\dfrac{1.1 \times 10^{-12}}{4}} = 6.5 \times 10^{-5}$ mol/L

Ag_2CrO_4, 331.73 amu

$$\text{solubility} = \frac{\left(6.5 \times 10^{-5} \text{ mol} \times \frac{331.73 \text{ g}}{1 \text{ mol}}\right)}{1 \text{ L}} = 0.022 \text{ g/L}$$

Ag_2CrO_4 has both the higher molar and gram solubility, despite its smaller value of K_{sp}.

16.24 Let the number of ions be proportional to its concentration.
For AgX, $K_{sp} = [Ag^+][X^-]$ % (4)(4) = 16
For AgY, $K_{sp} = [Ag^+][Y^-]$ % (1)(9) = 9
For AgZ, $K_{sp} = [Ag^+][Z^-]$ % (3)(6) = 18
(a) AgZ (b) AgY

16.25 $[Mg^{2+}]_0$ is from 0.10 M $MgCl_2$.

	$MgF_2(s)$	Ω	$Mg^{2+}(aq)$	+	$2\,F^-(aq)$
initial (M)			0.10		0
change (M)			+x		+2x
equil (M)			0.10 + x		2x

$K_{sp} = 7.4 \times 10^{s11} = [Mg^{2+}][F^{s}]^2 = (0.10 + x)(2x)^2 \approx (0.10)(4x^2)$
$x = 1.4 \times 10^{s5}$, molar solubility = $x = 1.4 \times 10^{s5}$ M

16.26 Compounds that contain basic anions are more soluble in acidic solution than in pure water. AgCN, $Al(OH)_3$, and ZnS all contain basic anions.

16.27 $[Cu^{2+}] = (5.0 \times 10^{s3} \text{ mol})/(0.500 \text{ L}) = 0.010$ M

	$Cu^{2+}(aq)$	+	$4\ NH_3(aq)$	Ω	$Cu(NH_3)_4^{2+}(aq)$
before reaction (M)	0.010		0.40		0
assume 100 % reaction (M)	S0.010		S 4(0.010)		+0.010
after reaction (M)	0		0.36		0.010
assume small back reaction (M)	+x		+4x		Sx
equil (M)	x		0.36 + 4x		0.010 S x

$$K_f = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4} = 5.6 \times 10^{11} = \frac{(0.010 - x)}{(x)(0.36 + 4x)^4} \approx \frac{0.010}{x(0.36)^4}$$

Solve for x. $x = [Cu^{2+}] = 1.1 \times 10^{s12}$ M

16.28

$AgBr(s)$ Ω $Ag^+(aq) + Br^s(aq)$ $K_{sp} = 5.4 \times 10^{s13}$
$Ag^+(aq) + 2\ S_2O_3^{2s} \mid Ag(S_2O_3)_2^{3s}(aq)$ $K_f = 4.7 \times 10^{13}$
dissolution reaction $AgBr(s) + 2\ S_2O_3^{2s}(aq)$ Ω $Ag(S_2O_3)_2^{3s}(aq) + Br^s(aq)$

$K = (K_{sp})(K_f) = (5.4 \times 10^{s13})(4.7 \times 10^{13}) = 25.4$

	$AgBr(s) + 2\ S_2O_3^{2s}(aq)$ Ω	$Ag(S_2O_3)_2^{3s}(aq)$ +	$Br^s(aq)$
initial (M)	0.10	0	0
change (M)	S2x	x	x
equil (M)	0.10 S 2x	x	x

$$K = \frac{[Ag(S_2O_3)_2^{3-}][Br^-]}{[S_2O_3^{2-}]^2} = 25.4 = \frac{x^2}{(0.10 - 2x)^2}$$

Take the square root of both sides and solve for x.

$$\sqrt{25.4} = \sqrt{\frac{x^2}{(0.10 - 2x)^2}}; \quad 5.04 = \frac{x}{0.10 - 2x}; \quad x = \text{molar solubility} = 0.045 \text{ mol/L}$$

16.29 On mixing equal volumes of two solutions, the concentrations of both solutions are cut in half.
For $BaCO_3$, $K_{sp} = 2.6 \times 10^{s9}$
(a) $IP = [Ba^{2+}][CO_3^{2s}] = (1.5 \times 10^{s3})(1.0 \times 10^{s3}) = 1.5 \times 10^{s6}$
$IP > K_{sp}$; a precipitate of $BaCO_3$ will form.
(b) $IP = [Ba^{2+}][CO_3^{2s}] = (5.0 \times 10^{s6})(2.0 \times 10^{s5}) = 1.0 \times 10^{s10}$
$IP < K_{sp}$; no precipitate will form.

16.30 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[NH_3]}{[NH_4^+]}$$

For NH_4^+, $K_a = 5.6 \times 10^{s10}$, $pK_a = S\log K_a = S\log(5.6 \times 10^{s10}) = 9.25$

$$pH = 9.25 + \log \frac{(0.20)}{(0.20)} = 9.25; \quad [H_3O^+] = 10^{spH} = 10^{s9.25} = 5.6 \times 10^{s10}\ M$$

$$[OH^s] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.8 \times 10^{s5}\ M$$

$$[Fe^{2+}] = [Mn^{2+}] = \frac{(25\ mL)(1.0 \times 10^{-3}\ M)}{250\ mL} = 1.0 \times 10^{s4}\ M$$

For $Mn(OH)_2$, $K_{sp} = 2.1 \times 10^{s13}$

$IP = [Mn^{2+}][OH^s]^2 = (1.0 \times 10^{s4})(1.8 \times 10^{s5})^2 = 3.2 \times 10^{s14}$

$IP < K_{sp}$; no precipitate will form.

For $Fe(OH)_2$, $K_{sp} = 4.9 \times 10^{s17}$

$IP = [Fe^{2+}][OH^s]^2 = (1.0 \times 10^{s4})(1.8 \times 10^{s5})^2 = 3.2 \times 10^{s14}$

$IP > K_{sp}$; a precipitate of $Fe(OH)_2$ will form.

16.31 $MS(s) + 2\ H_3O^+(aq)\ \Omega\ M^{2+}(aq) + H_2S(aq) + 2\ H_2O(l)$

$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2}$$

For ZnS, $K_{spa} = 3 \times 10^{s2}$; for CdS, $K_{spa} = 8 \times 10^{s7}$

$[Cd^{2+}] = [Zn^{2+}] = 0.005$ M

Because the two cation concentrations are equal, Q_c is the same for both.

$$Q_c = \frac{[M^{2+}]_t[H_2S]_t}{[H_3O^+]_t^2} = \frac{(0.005)(0.10)}{(0.3)^2} = 6 \times 10^{s3}$$

$Q_c > K_{spa}$ for CdS; CdS will precipitate. $Q_c < K_{spa}$ for ZnS; Zn^{2+} will remain in solution.

16.32 This protein has both acidic and basic sites. H_3PO_4-$H_2PO_4^s$ is an acidic buffer. It protonates the basic sites in the protein making them positive and the protein migrates towards the negative electrode. H_3BO_3-$H_2BO_3^s$ is a basic buffer. At basic pH's, the acidic sites in the protein are dissociated making them negative and the protein migrates towards the positive electrode.

16.33 To increase the rate at which the proteins migrates toward the negative electrode, increase the number of basic sites that are protonated by lowering the pH. Decrease the $[HPO_4^{2s}]/[H_2PO_4^s]$ ratio (less HPO_4^{2s}, more $H_2PO_4^s$) to lower the pH.

Understanding Key Concepts

16.34 A buffer solution contains a conjugate acid-base pair in about equal concentrations.

(a) (1), (3), and (4)

(b) (4) because it has the highest buffer concentration.

16.35 (a) (2) has the highest pH, $[A^s] > [HA]$
(3) has the lowest pH, $[HA] > [A^s]$

(b) (c)

16.36 (4); only A^s and water should be present

16.37 (a) (1) corresponds to (iii); (2) to (i); (3) to (iv); and (4) to (ii)
(b) Solution (3) has the highest pH; solution (2) has the lowest pH.

16.38 (a) (i) (1), only B present (ii) (4), equal amounts of B and BH^+ present
(iii) (3), only BH^+ present (iv) (2), BH^+ and H_3O^+ present
(b) The pH is less than 7 because BH^+ is an acidic cation.

16.39 (2) is supersaturated; (3) is unsaturated; (4) is unsaturated

16.40 Let the number of ions be proportional to its concentration.
For Ag_2CrO_4, $K_{sp} = [Ag^+]^2[CrO_4^{2s}]$ % $(4)^2(2) = 32$
For (2), IP $= [Ag^+]^2[CrO_4^{2s}]$ % $(2)^2(4) = 16$
For (3), IP $= [Ag^+]^2[CrO_4^{2s}]$ % $(6)^2(2) = 72$
For (4), IP $= [Ag^+]^2[CrO_4^{2s}]$ % $(2)^2(6) = 24$
A precipitate will form when IP > K_{sp}. A precipitate will form only in (3).

16.41 (a) The lower curve represents the titration of a strong acid; the upper curve represents the titration of a weak acid.
(b) pH = 7 for titration of the strong acid; pH = 10 for titration of the weak acid.
(c) Halfway to the equivalence point, the pH = $pK_a \sim 6.3$.

Additional Problems
Neutralization Reactions

16.42 (a) $HI(aq) + NaOH(aq) \mid H_2O(l) + NaI(aq)$
net ionic equation: $H_3O^+(aq) + OH^s(aq) \mid 2\ H_2O(l)$
The solution at neutralization contains a neutral salt (NaI); pH = 7.00.

(b) $2\ HOCl(aq) + Ba(OH)_2(aq) \mid 2\ H_2O(l) + Ba(OCl)_2(aq)$

net ionic equation: $HOCl(aq) + OH^{s}(aq) \mid H_2O(l) + OCl^{s}(aq)$
The solution at neutralization contains a basic anion (OCl^{s}); pH > 7.00
(c) $HNO_3(aq) + C_6H_5NH_2(aq) \mid C_6H_5NH_3NO_3(aq)$
net ionic equation: $H_3O^{+}(aq) + C_6H_5NH_2(aq) \mid H_2O(l) + C_6H_5NH_3^{+}(aq)$
The solution at neutralization contains an acidic cation ($C_6H_5NH_3^{+}$); pH < 7.00.
(d) $C_6H_5CO_2H(aq) + KOH(aq) \mid H_2O(l) + C_6H_5CO_2K(aq)$
net ionic equation: $C_6H_5CO_2H(aq) + OH^{s}(aq) \mid H_2O(l) + C_6H_5CO_2^{s}(aq)$
The solution at neutralization contains a basic anion ($C_6H_5CO_2^{s}$); pH > 7.00.

16.43 (a) $HNO_2(aq) + CsOH(aq) \mid H_2O(l) + CsNO_2(aq)$
net ionic equation: $HNO_2(aq) + OH^{s}(aq) \mid H_2O(l) + NO_2^{s}(aq)$
The solution at neutralization contains a basic anion (NO_2^{s}); pH > 7.00
(b) $HBr(aq) + NH_3(aq) \mid NH_4Br(aq)$
net ionic equation: $H_3O^{+}(aq) + NH_3(aq) \mid H_2O(l) + NH_4^{+}(aq)$
The solution at neutralization contains an acidic cation (NH_4^{+}); pH < 7.00
(c) $HClO_4(aq) + KOH(aq) \mid H_2O(l) + KClO_4(aq)$
net ionic equation: $H_3O^{+}(aq) + OH^{s}(aq) \mid 2\ H_2O(l)$
The solution at neutralization contains a neutral salt ($KClO_4$); pH = 7.00
(d) $HOBr(aq) + NH_3(aq) \mid NH_4OBr(aq)$
net ionic equation: $HOBr(aq) + NH_3(aq) \mid NH_4^{+}(aq) + OBr^{s}(aq)$
The solution at neutralization contains the salt NH_4OBr.
$K_a(NH_4^{+}) = 5.6 \times 10^{s10}$ and $K_b(OBr^{s}) = 5.0 \times 10^{s5}$; $K_b(OBr^{s}) > K_a(NH_4^{+})$; pH > 7.00

16.44 (a) Strong acid - strong base reaction $K_n = \frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14}$

(b) Weak acid - strong base reaction $K_n = \frac{K_a}{K_w} = \frac{3.5 \times 10^{-8}}{1.0 \times 10^{-14}} = 3.5 \times 10^{6}$

(c) Strong acid - weak base reaction $K_n = \frac{K_b}{K_w} = \frac{4.3 \times 10^{-10}}{1.0 \times 10^{-14}} = 4.3 \times 10^{4}$

(d) Weak acid - strong base reaction $K_n = \frac{K_a}{K_w} = \frac{6.5 \times 10^{-5}}{1.0 \times 10^{-14}} = 6.5 \times 10^{9}$

(c) < (b) < (d) < (a)

16.45 (d) Weak acid - strong base reaction $K_n = \frac{K_a}{K_w} = \frac{4.5 \times 10^{-4}}{1.0 \times 10^{-14}} = 4.5 \times 10^{10}$

(c) Strong acid - weak base reaction $K_n = \frac{K_b}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^{9}$

(a) Strong acid - strong base reaction $K_n = \frac{1}{K_w} = \frac{1}{1.0 \times 10^{-14}} = 1.0 \times 10^{14}$

(d) Weak acid - weak base reaction $K_n = \frac{K_a K_b}{K_w} = \frac{(2.0 \times 10^{-9})(1.8 \times 10^{-5})}{1.0 \times 10^{-14}} =$ 3.6

(d) < (b) < (a) < (c)

16.46 (a) After mixing, the solution contains the basic salt, NaF; pH > 7.00
(b) After mixing, the solution contains the neutral salt, NaCl; pH = 7.00
Solution (a) has the higher pH.

16.47 (a) After mixing, the solution contains the neutral salt, $NaClO_4$; pH = 7.00
(b) After mixing, the solution contains the acidic salt, NH_4ClO_4; pH < 7.00
Solution (b) has the lower pH.

16.48 Weak acid - weak base reaction $K_n = K_aK_b \text{ over } K_w = \frac{(1.3 \times 10^{-10})(1.8 \times 10^{-9})}{1.0 \times 10^{-14}} = 2.3 \times 10^{s5}$

K_n is small so the neutralization reaction does not proceed very far to completion.

16.49 Weak acid - weak base reaction $K_n = \frac{K_aK_b}{K_w} = \frac{(8.0 \times 10^{-5})(4.3 \times 10^{-10})}{1.0 \times 10^{-14}} = 3.4$

Because K_n is close to 1, there will be an appreciable amount of aniline present at equilibrium.

The CommonSIon Effect

16.50 $HNO_2(aq) + H_2O(l) \; \Omega \; H_3O^+(aq) + NO_2^s(aq)$
(a) $NaNO_2$ is a source of NO_2^s (reaction product). The equilibrium shifts towards reactants, and the percent dissociation of HNO_2 decreases.
(c) HCl is a source of H_3O^+ (reaction product). The equilibrium shifts towards reactants, and the percent dissociation of HNO_2 decreases.
(d) $Ba(NO_2)_2$ is a source of NO_2^s (reaction product). The equilibrium shifts towards reactants, and the percent dissociation of HNO_2 decreases.

16.51 $NH_3(aq) + H_2O(l) \; \Omega \; NH_4^+(aq) + OH^s(aq)$
(a) KOH is a strong base, and it increases the $[OH^s]$. The pH increases.
(b) NH_4NO_3 is a source of NH_4^+ (reaction product). The equilibrium shifts towards reactants, and the $[OH^s]$ decreases. The pH decreases.
(c) NH_4Br is a source of NH_4^+ (reaction product). The equilibrium shifts towards reactants, and the $[OH^s]$ decreases. The pH decreases.
(d) KBr does not affect the pH of the solution.

16.52 (a) $HF(aq) + H_2O(l) \; \Omega \; H_3O^+(aq) + F^s(aq)$
LiF is a source of F^s (reaction product). The equilibrium shifts toward reactants, and the $[H_3O^+]$ decreases. The pH increases.
(b) Because HI is a strong acid, addition of KI, a neutral salt, does not change the pH.
(c) $NH_3(aq) + H_2O(l) \; \Omega \; NH_4^+(aq) + OH^s(aq)$
NH_4Cl is a source of NH_4^+ (reaction product). The equilibrium shifts toward reactants,

and the $[OH^S]$ decreases. The pH decreases.

16.53 (a) $NH_3(aq) + H_2O(l) \Omega NH_4^+(aq) + OH^S(aq)$
NH_4Cl is a source of NH_4^+ (reaction product). The equilibrium shifts toward reactants, and the $[OH^S]$ decreases. The pH decreases.
(b) $HCO_3^S(aq) + H_2O(l) \Omega H_3O^+(aq) + CO_3^{2S}(aq)$
Na_2CO_3 is a source of CO_3^{2S} (reaction product). The equilibrium shifts toward reactants, and the $[H_3O^+]$ decreases. The pH increases.
(c) Because NaOH is a strong base, addition of $NaClO_4$, a neutral salt, does not change the pH.

16.54 For 0.25 M HF and 0.10 M NaF

	$HF(aq) + H_2O(l)$	Ω	$H_3O^+(aq) + F^S(aq)$
initial (M)	0.25		~0 0.10
change (M)	Sx		+x +x
equil (M)	0.25 S x		x 0.10 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 3.5 \times 10^{-4} = \frac{x(0.10 + x)}{0.25 - x} \approx \frac{x(0.10)}{0.25}$$

Solve for x. $x = [H_3O^+] = 8.8 \times 10^{S4}$ M
$pH = S\log[H_3O^+] = S\log(8.8 \times 10^{S4}) = 3.06$

16.55 On mixing equal volumes of two solutions, both concentrations are cut in half.
$[CH_3NH_2] = 0.10$ M; $[CH_3NH_3Cl] = 0.30$ M

	$CH_3NH_2(aq) + H_2O(l)$	Ω	$CH_3NH_3^+(aq) + OH^S(aq)$
initial (M)	0.10		0.30 ~0
change (M)	Sx		+x +x
equil (M)	0.10 S x		0.30 + x x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 3.7 \times 10^{-4} = \frac{(0.30 + x)x}{0.10 - x} \approx \frac{(0.30)x}{0.10}$$

Solve for x. $x = [OH^S] = 1.2 \times 10^{S4}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-4}} = 8.1 \times 10^{S11} \text{ M}$$

$pH = S\log[H_3O^+] = S\log(8.1 \times 10^{S11}) = 10.09$

16.56 For 0.10 M HN_3:

	$HN_3(aq) + H_2O(l)$	Ω	$H_3O^+(aq) + N_3^S(aq)$
initial (M)	0.10		~0 0
change (M)	Sx		+x +x
equil (M)	0.10 S x		x x

$$K_a = \frac{[H_3O^+][N_3^-]}{[HN_3]} = 1.9 \times 10^{-5} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

Solve for x. $x = 1.4 \times 10^{S3}$ M

$$\% \text{ dissociation} = \frac{[HN_3]_{diss}}{[HN_3]_{initial}} \times 100\% = \frac{1.4 \times 10^{-3}\ M}{0.10\ M} \times 100\% = 1.4\%$$

For 0.10 M HN_3 in 0.10 M HCl:

	$HN_3(aq)$ + $H_2O(l)$ Ω	$H_3O^+(aq)$ +	$N_3^-(aq)$
initial (M)	0.10	0.10	0
change (M)	Sx	+x	+x
equil (M)	0.10 S x	0.10 + x	x

$$K_a = \frac{[H_3O^+][N_3^-]}{[HN_3]} = 1.9 \times 10^{-5} = \frac{(0.10 + x)(x)}{0.10 - x} \approx \frac{(0.10)(x)}{0.10} = x$$

Solve for x. $x = 1.9 \times 10^{-5}$ M

$$\% \text{ dissociation} = \frac{[HN_3]_{diss}}{[HN_3]_{initial}} \times 100\% = \frac{1.9 \times 10^{-5}\ M}{0.10\ M} \times 100\% = 0.019\%$$

The % dissociation is less because of the common ion (H_3O^+) effect.

16.57

	$NH_3(aq)$ + $H_2O(l)$ Ω	$NH_4^+(aq)$ +	$OH^-(aq)$
initial (M)	0.30	0	~0
change (M)	Sx	+x	+x
equil (M)	0.30 S x	x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{x^2}{0.30 - x} \approx \frac{x^2}{0.30}$$

Solve for x. $x = [OH^-] = 2.3 \times 10^{-3}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-3}} = 4.3 \times 10^{-12}\ M$$

$pH = -\log[H_3O^+] = -\log(4.3 \times 10^{-12}) = 11.37$

Add 4.0 g of NH_4NO_3.

NH_4NO_3, 80.04 amu; $[NH_4^+]$ = molarity of NH_4NO_3 = $\dfrac{\left(4.0\ g \times \dfrac{1\ mol}{80.04\ g}\right)}{0.100\ L} = 0.50\ M$

	$NH_3(aq)$ + $H_2O(l)$ Ω	$NH_4^+(aq)$ +	$OH^-(aq)$
initial (M)	0.30	0.50	~0
change (M)	Sx	+x	+x
equil (M)	0.30 S x	0.50 + x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(0.50 + x)\,x}{0.30 - x} \approx \frac{(0.50)\,x}{0.30}$$

Solve for x. $x = [OH^-] = 1.1 \times 10^{-5}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-5}} = 9.1 \times 10^{-10}\ M$$

$pH = -\log[H_3O^+] = -\log(9.1 \times 10^{-10}) = 9.04$

The % dissociation decreases because of the common ion effect.

Buffer Solutions

16.58 Solutions (a), (c) and (d) are buffer solutions. Neutralization reactions for (c) and (d) result in solutions with equal concentrations of HF and F^-.

16.59 Solutions (b), (c) and (d) are buffer solutions. Neutralization reactions for (b) and (d) result in solutions with equal concentrations of NH_3 and NH_4^+.

16.60 Both solutions buffer at the same pH because in both cases the $[NO_2^-]/[HNO_2] = 1$. Solution (a), however, has a higher concentration of both HNO_2 and NO_2^-, and therefore it has the greater buffer capacity.

16.61 Both solutions buffer at the same pH because in both cases the $[NH_3]/[NH_4^+] = 1.5$. Solution (b), however, has a higher concentration of both NH_3 and NH_4^+, and therefore it has the greater buffer capacity.

16.62 When blood absorbs acid, the equilibrium shifts to the left, decreasing the pH, but not by much because the $[HCO_3^-]/[H_2CO_3]$ ratio remains nearly constant. When blood absorbs base, the equilibrium shifts to the right, increasing the pH, but not by much because the $[HCO_3^-]/[H_2CO_3]$ ratio remains nearly constant.

16.63 $H_2PO_4^-(aq) + H_2O(l) \Omega H_3O^+(aq) + HPO_4^{2-}(aq)$

For $H_2PO_4^-$, $K_{a2} = 6.2 \times 10^{-8}$, $pK_{a2} = -\log K_{a2} = 7.21$

$$pH = 7.4 = pK_{a2} + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.21 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

To maintain pH near 7.4, need $\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.19$ and $\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{0.19} = 1.5$

The principal buffer reactions are:

$H_3O^+(aq) + HPO_4^{2-}(aq) \mid H_2PO_4^-(aq) + H_2O(l)$

$OH^-(aq) + H_2PO_4^-(aq) \mid HPO_4^{2-}(aq) + H_2O(l)$

16.64 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[CN^-]}{[HCN]}$$

For HCN, $K_a = 4.9 \times 10^{-10}$, $pK_a = -\log K_a = -\log(4.9 \times 10^{-10}) = 9.31$

$$pH = 9.31 + \log\left(\frac{0.12}{0.20}\right) = 9.09$$

The pH of a buffer solution will not change on dilution because the acid and base concentrations will change by the same amount and their ratio will remain the same.

16.65 $NaHCO_3$, 84.01 amu; Na_2CO_3, 105.99 amu

$$[HCO_3^-] = \text{molarity of } NaHCO_3 = \frac{\left(4.2\text{ g} \times \frac{1\text{ mol}}{84.01\text{ g}}\right)}{0.20\text{ L}} = 0.25\text{ M}$$

$[CO_3^{2s}]$ = molarity of $Na_2CO_3 = \dfrac{\left(5.3\ g\ x\ \dfrac{1\ mol}{105.99\ g}\right)}{0.20\ L} = 0.25\ M$

$pH = pK_a + \log \dfrac{[base]}{[acid]} = pK_a + \log \dfrac{[CO_3^{2-}]}{[HCO_3^-]}$

For HCO_3^s, $K_{a2} = 5.6 \times 10^{s11}$, $p K_{a2} = \_\log K_{a2} = S\log(5.6 \times 10^{s11}) = 10.25$

$pH = 10.25 + \log \dfrac{[0.25]}{[0.25]} = 10.25$

The pH of a buffer solution will not change on dilution because the acid and base concentrations will change by the same amount and their ratio will remain the same.

16.66 $pH = pK_a + \log \dfrac{[base]}{[acid]} = pK_a + \log \dfrac{[NH_3]}{[NH_4^+]}$

For NH_4^+, $K_a = 5.6 \times 10^{s10}$, $pK_a = S\log K_a = S\log(5.6 \times 10^{s10}) = 9.25$

For the buffer: $pH = 9.25 + \log \dfrac{(0.200)}{(0.200)} = 9.25$

(a) add 0.0050 mol NaOH, $[OH^s] = 0.0050\ mol/0.500\ L = 0.010\ M$

	$NH_4^+(aq)$	+ $OH^s(aq)$	Ω $NH_3(aq)$	+ $H_2O(l)$
before reaction (M)	0.200	0.010	0.200	
change (M)	S0.010	S0.010	+0.010	
after reaction (M)	0.200 S 0.010	0	0.200 + 0.010	

$pH = 9.25 + \log \dfrac{[NH_3]}{[NH_4^+]} = 9.25 + \log \dfrac{(0.200\ +\ 0.010)}{(0.200\ \_\ 0.010)} = 9.29$

(b) add 0.020 mol HCl, $[H_3O^+] = 0.020\ mol/0.500\ L = 0.040\ M$

	$NH_3(aq)$	+ $H_3O^+(aq)$	Ω $NH_4^+(aq)$	+ $H_2O(l)$
before reaction (M)	0.200	0.040	0.200	
change (M)	S0.040	S0.040	+0.040	
after reaction (M)	0.200 S 0.040	0	0.200 + 0.040	

$pH = 9.25 + \log \dfrac{[NH_3]}{[NH_4^+]} = 9.25 + \log \dfrac{(0.200\ \_\ 0.040)}{(0.200\ +\ 0.040)} = 9.07$

16.67 $pH = pK_a + \log \dfrac{[base]}{[acid]} = pK_a + \log \dfrac{[SO_3^{2-}]}{[HSO_3^-]}$

For HSO_3^s, $K_a = 6.3 \times 10^{s8}$, $pK_a = S\log K_a = S\log(6.3 \times 10^{s8}) = 7.20$

For the buffer: $pH = 7.20 + \log \dfrac{(0.300)}{(0.500)} = 6.98$

(a) add (0.0050 L)(0.20 mol/L) = 0.0010 mol HCl = 0.0010 mol H_3O^+

mol HSO_3^s = (0.300 L)(0.500 mol/L) = 0.150 mol

mol SO_3^{2s} = (0.300 L)(0.300 mol/L) = 0.0900 mol

	$SO_3^{2s}(aq)$	+ $H_3O^+(aq)$	Ω $HSO_3^s(aq)$	+ $H_2O(l)$
before reaction (mol)	0.0900	0.0010	0.150	

change (mol)	S0.0010	S0.0010	+0.0010
after reaction (mol)	0.0900 S 0.0010	0	0.150 + 0.0010

$$pH = 7.20 + \log\frac{[SO_3^{2-}]}{[HSO_3^-]} = 7.20 + \log\frac{(0.0900\ \_\ 0.0010)}{(0.150\ +\ 0.0010)} = 6.97$$

(b) add (0.0050 L)(0.10 mol/L) = 0.00050 mol NaOH = 0.00050 mol OH^S

$$HSO_3^S(aq) + OH^S(aq)\ \Omega\ SO_3^{2S}(aq) + H_2O(l)$$

before reaction (mol)	0.150	0.00050	0.0900
change (mol)	S0.00050	S0.00050	+0.00050
after reaction (mol)	0.150 S 0.00050	0	0.0900 + 0.00050

$$pH = 7.20 + \log\frac{[SO_3^{2-}]}{[HSO_3^-]} = 7.20 + \log\frac{(0.0900\ +\ 0.00050)}{(0.150\ \_\ 0.00050)} = 6.98$$

16.68

	Acid	K_a	$pK_a = S\log K_a$
(a)	H_3BO_3	5.8×10^{S10}	9.24
(b)	HCO_2H	1.8×10^{S4}	3.74
(c)	HOCl	3.5×10^{S8}	7.46

The stronger the acid (the larger the K_a), the smaller is the pK_a.

16.69 (a) $K_a = 10^{-pK_a} = 10^{S5.00} = 1.0 \times 10^{S5}$ (b) $K_a = 10^{-pK_a} = 10^{S8.70} = 2.0 \times 10^{S9}$

(b) is the weaker acid

16.70 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[HCO_2^-]}{[HCO_2H]}$$

For HCO_2H, $K_a = 1.8 \times 10^{S4}$; $pK_a = S\log K_a = S\log(1.8 \times 10^{S4}) = 3.74$

$$pH = 3.74 + \log\frac{(0.50)}{(0.25)} = 4.04$$

16.71 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

For H_2CO_3, $K_a = 4.3 \times 10^{S7}$; $pK_a = S\log K_a = S\log(4.3 \times 10^{S7}) = 6.37$

$$7.40 = 6.37 + \log\frac{[HCO_3^-]}{[H_2CO_3]}; \quad 1.03 = \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.03} = 10.7; \qquad \frac{[H_2CO_3]}{[HCO_3^-]} = 0.093$$

16.72 $$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[NH_3]}{[NH_4^+]}$$

For NH_4^+, $K_a = 5.6 \times 10^{S10}$; $pK_a = S\log K_a = S\log(5.6 \times 10^{S10}) = 9.25$

$$9.80 = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}; \qquad 0.550 = \log\frac{[NH_3]}{[NH_4^+]}; \qquad \frac{[NH_3]}{[NH_4^+]} = 10^{0.55} = 3.5$$

The volume of the 1.0 M NH_3 solution should be 3.5 times the volume of the 1.0 M NH_4Cl solution so that the mixture will buffer at pH 9.80.

16.73 $pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$

For CH_3CO_2H, $K_a = 1.8 \times 10^{-5}$; $pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$

$4.44 = 4.74 + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$; $\quad -0.30 = \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$

$\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{-0.30} = 0.50$

The solution should have 0.50 mol of $CH_3CO_2^-$ per mole of CH_3CO_2H. For example, you could dissolve 41g of CH_3CO_2Na in 1.00 L of 1.00 M CH_3CO_2H.

16.74 H_3PO_4, $K_{a1} = 7.5 \times 10^{-3}$; $pK_{a1} = -\log K_{a1} = 2.12$

$H_2PO_4^-$, $K_{a2} = 6.2 \times 10^{-8}$; $pK_{a2} = -\log K_{a2} = 7.21$

HPO_4^{2-}, $K_{a3} = 4.8 \times 10^{-13}$; $pK_{a3} = -\log K_{a3} = 12.32$

The buffer system of choice for pH 7.00 is (b) $H_2PO_4^-$ - HPO_4^{2-} because the pK_a for $H_2PO_4^-$ (7.21) is closest to 7.00.

16.75 HSO_4^-, $K_{a2} = 1.2 \times 10^{-2}$; $pK_{a2} = -\log K_{a2} = 1.92$

HOCl, $K_a = 3.5 \times 10^{-8}$; $pK_a = -\log K_a = 7.56$

$C_6H_5CO_2H$, $K_a = 6.5 \times 10^{-5}$; $pK_a = -\log K_a = 4.19$

The buffer system of choice for pH = 4.50 is (c) $C_6H_5CO_2H$ - $C_6H_5CO_2^-$ because the pK_a for $C_6H_5CO_2H$ (4.19) is closest to 4.50.

pH Titration Curves

16.76 (a) (0.060 L)(0.150 mol/L)(1000 mmol/mol) = 9.00 mmol HNO_3

(b) vol NaOH = (9.00 mmol HNO_3)$\left(\frac{1 \text{ mmol NaOH}}{1 \text{ mmol } HNO_3}\right)\left(\frac{1 \text{ mL NaOH}}{0.450 \text{ mmol NaOH}}\right)$ = 20.0 mL NaOH

(c) At the equivalence point the solution contains the neutral salt $NaNO_3$. The pH is 7.00.

(d)

16.77

mmol NaOH = (50.0 mL)(1.0 mmol/mL) = 50 mmol
mmol HCl = mmol NaOH = 50 mmol

$$\text{vol HCl} = (50 \text{ mmol})\left(\frac{1.0 \text{ mL}}{1.0 \text{ mmol}}\right) = 50 \text{ mL}$$

50 mL of 1.0 M HCl is needed to reach the equivalence point.

16.78 mmol OH^- = (20.0 mL)(0.150 mmol/mL) = 3.00 mmol
mmol acid present = mmol OH^- added = 3.00 mmol

$$[\text{acid}] = \frac{3.00 \text{ mmol}}{60.0 \text{ mL}} = 0.0500 \text{ M}$$

16.79 mmol OH^- = (60.0 mL)(0.240 mmol/mL) = 14.4 mmol

$$\text{mmol acid present} = 14.4 \text{ mmol } OH^- \times \frac{1 \text{ mmol acid}}{2 \text{ mmol } OH^-} = 7.20 \text{ mmol acid}$$

$$[\text{acid}] = \frac{7.20 \text{ mmol}}{25.0 \text{ mL}} = 0.288 \text{ M}$$

16.80 $HBr(aq) + NaOH(aq) \mid Na^+(aq) + Br^-(aq) + H_2O(l)$
(a) $[H_3O^+] = 0.120$ M; pH = $-\log[H_3O^+] = -\log(0.120) = 0.92$
(b) (50.0 mL)(0.120 mmol/mL) = 6.00 mmol HBr
(20.0 mL)(0.240 mmol/mL) = 4.80 mmol NaOH
6.00 mmol HBr − 4.80 mmol NaOH = 1.20 mmol HBr after neutralization

$$[H_3O^+] = \frac{1.20 \text{ mmol}}{(50.0 \text{ mL} + 20.0 \text{ mL})} = 0.0171 \text{ M}$$

pH = $-\log[H_3O^+] = -\log(0.0171) = 1.77$
(c) (24.9 mL)(0.240 mmol/mL) = 5.98 mmol NaOH
6.00 mmol HBr − 5.98 mmol NaOH = 0.02 mmol HBr after neutralization

$$[H_3O^+] = \frac{0.02 \text{ mmol}}{(50.0 \text{ mL} + 24.9 \text{ mL})} = 3 \times 10^{-4} \text{ M}$$

pH = $-\log[H_3O^+] = -\log(3 \times 10^{-4}) = 3.5$

(d) The titration reaches the equivalence point when 25.0 mL of 0.240 M NaOH is added. At the equivalence point the solution contains the neutral salt NaBr. The pH is 7.00.

(e) (25.1 mL)(0.240 mmol/mL) = 6.024 mmol NaOH

6.024 mmol NaOH S 6.00 mmol HBr = 0.024 mmol NaOH after neutralization

$$[OH^-] = \frac{0.024\ \text{mmol}}{(50.0\ \text{mL} + 25.1\ \text{mL})} = 3.2 \times 10^{-4}\ \text{M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.2 \times 10^{-4}} = 3.1 \times 10^{-11}\ \text{M}$$

pH = S$\log[H_3O^+]$ = S$\log(3.1 \times 10^{-11})$ = 10.5

(f) (40.0 mL)(0.240 mmol/mL) = 9.60 mmol NaOH

9.60 mmol NaOH S 6.00 mmol HBr = 3.60 mmol NaOH after neutralization

$$[OH^-] = \frac{3.60\ \text{mmol}}{(50.0\ \text{mL} + 40.0\ \text{mL})} = 0.040\ \text{M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.040} = 2.5 \times 10^{-13}\ \text{M}$$

pH = S$\log[H_3O^+]$ = S$\log(2.5 \times 10^{-13})$ = 12.60

16.81 $Ba(OH)_2(aq) + 2\ HNO_3(aq) \rightarrow Ba^{2+}(aq) + 2\ NO_3^-(aq) + 2\ H_2O(l)$

(a) $[OH^-] = 2(0.150\ \text{M}) = 0.300\ \text{M}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.300} = 3.33 \times 10^{-14}\ \text{M}$$

pH = S$\log[H_3O^+]$ = S$\log(3.33 \times 10^{-14})$ = 13.48

(b) (40.0 mL)(0.150 mmol/mL) = 6.00 mmol $Ba(OH)_2$

$$6.00\ \text{mmol Ba(OH)}_2 \times \frac{2\ \text{mmol OH}^-}{1\ \text{mmol Ba(OH)}_2} = 12.0\ \text{mmol OH}^-$$

(10.0 mL)(0.400 mmol/mL) = 4.00 mmol HNO_3

12.0 mmol OH^- S 4.00 mmol HNO_3 = 8.00 mmol OH^- after neutralization

$$[OH^-] = \frac{8.00\ \text{mmol}}{(40.0\ \text{mL} + 10.0\ \text{mL})} = 0.160\ \text{M}$$

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \text{ x } 10^{-14}}{0.160} = 6.25 \text{ x } 10^{S14}$ M

pH = S$\log[H_3O^+]$ = S$\log(6.25 \text{ x } 10^{S14})$ = 13.20

(c) (20.0 mL)(0.400 mmol/mL) = 8.00 mmol HNO_3

12.0 mmol OH^S S 8.00 mmol HNO_3 = 4.00 mmol OH^S after neutralization

$[OH^S] = \frac{4.00 \text{ mmol}}{(40.0 \text{ mL} + 20.0 \text{ mL})} = 0.0667$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \text{ x } 10^{-14}}{0.0667} = 1.50 \text{ x } 10^{S13}$ M

pH = S$\log[H_3O^+]$ = S$\log(1.50 \text{ x } 10^{S13})$ = 12.82

(d) The titration reaches the equivalence point when 30.0 mL of 0.400 M HNO_3 is added. At the equivalence point the solution contains the neutral salt $Ba(NO_3)_2$. The pH is 7.00.

(e) (40.0 mL)(0.400 mmol/mL) = 16.0 mmol HNO_3

16.0 mmol HNO_3 S 12.0 mmol OH^S = 4.00 mmol H_3O^+ after neutralization

$[H_3O^+] = \frac{4.00 \text{ mmol}}{(40.0 \text{ mL} + 40.0 \text{ mL})} = 0.0500$ M

pH = S$\log[H_3O^+]$ = S$\log(0.0500)$ = 1.30

16.82 mmol HF = (40.0 mL)(0.250 mmol/mL) = 10.0 mmol

mmol NaOH required = mmol HF = 10.0 mmol

mL NaOH required = $(10.0 \text{ mmol})\left(\frac{1.00 \text{ mL}}{0.200 \text{ mmol}}\right) = 50.0 \text{ mL}$

50.0 mL of 0.200 M NaOH is required to reach the equivalence point.
For HF, $K_a = 3.5 \times 10^{-4}$; $pK_a = -\log K_a = -\log(3.5 \times 10^{-4}) = 3.46$
(a) mmol HF = 10.0 mmol
mmol NaOH = (0.200 mmol/mL)(10.0 mL) = 2.00 mmol

Neutralization reaction:	$HF(aq)$ +	$OH^-(aq)$ ⏐	$F^-(aq)$ +	$H_2O(l)$
before reaction (mmol)	10.0	2.00	0	
change (mmol)	−2.00	−2.00	+2.00	
after reaction (mmol)	8.0	0	2.00	

$$[HF] = \frac{8.0 \text{ mmol}}{(40.0 \text{ mL} + 10.0 \text{ mL})} = 0.16 \text{ M}; \quad [F^-] = \frac{2.00 \text{ mmol}}{(40.0 \text{ mL} + 10.0 \text{ mL})} = 0.0400 \text{ M}$$

	$HF(aq)$ +	$H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$F^-(aq)$
initial (M)	0.16		~0	0.0400
change (M)	−x		+x	+x
equil (M)	0.16 − x		x	0.0400 + x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 3.5 \times 10^{-4} = \frac{x(0.0400 + x)}{0.16 - x} \approx \frac{x(0.0400)}{0.16}$$

Solve for x. $x = [H_3O^+] = 1.4 \times 10^{-3}$ M
$pH = -\log[H_3O^+] = -\log(1.4 \times 10^{-3}) = 2.85$
(b) Halfway to the equivalence point,
$pH = pK_a = -\log K_a = -\log(3.5 \times 10^{-4}) = 3.46$
(c) At the equivalence point only the salt NaF is in solution.

$$[F^-] = \frac{10.0 \text{ mmol}}{(40.0 \text{ mL} + 50.0 \text{ mL})} = 0.111 \text{ M}$$

	$F^-(aq)$ +	$H_2O(l)$ ⇌	$HF(aq)$ +	$OH^-(aq)$
initial (M)	0.111		0	~0
change (M)	−x		+x	+x
equil (M)	0.111 − x		x	x

For F^-, $K_b = \dfrac{K_w}{K_a \text{ for HF}} = \dfrac{1.0 \times 10^{-14}}{3.5 \times 10^{-4}} = 2.9 \times 10^{-11}$

$$K_b = \frac{[HF][OH^-]}{[F^-]} = 2.9 \times 10^{-11} = \frac{x^2}{0.111 - x} \approx \frac{x^2}{0.111}$$

Solve for x. $x = [OH^-] = 1.8 \times 10^{-6}$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-6}} = 5.6 \times 10^{-9} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(5.6 \times 10^{-9}) = 8.25$
(d) mmol HF = 10.0 mmol
mol NaOH = (0.200 mmol/mL)(80.0 mL) = 16.0 mmol

Neutralization reaction:	$HF(aq)$ +	$OH^-(aq)$ ⏐	$F^-(aq)$ +	$H_2O(l)$
before reaction (mmol)	10.0	16.0	0	
change (mmol)	−10.0	−10.0	+10.0	
after reaction (mmol)	0	6.0	10.0	

After the equivalence point, the pH of the solution is determined by the $[OH^-]$.

$$[OH^-] = \frac{6.0\ \text{mmol}}{(40.0\ \text{mL} + 80.0\ \text{mL})} = 5.0 \times 10^{-2}\ \text{M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(2.0 \times 10^{-13}) = 12.70$$

16.83 mmol CH_3NH_2 = (100.0 mL)(0.100 mmol/mL) = 10.0 mmol

mmol HNO_3 required = mmol CH_3NH_2 = 10.0 mmol

$$\text{vol } HNO_3 \text{ required} = (10.0\ \text{mmol})\left(\frac{1.00\ \text{mL}}{0.250\ \text{mmol}}\right) = 40.0\ \text{mL}$$

40.0 mL of 0.250 M HNO_3 are required to reach the equivalence point.

(a)	$CH_3NH_2(aq)$	+	$H_2O(l)$	⇌	$CH_3NH_3^+(aq)$	+	$OH^-(aq)$
initial (M)	0.100				0		~0
change (M)	−x				+x		+x
equil (M)	0.100 − x				x		x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 3.7 \times 10^{-4} = \frac{x^2}{0.100 - x}$$

$x^2 + (3.7 \times 10^{-4})x - (3.7 \times 10^{-5}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(3.7 \times 10^{-4}) \pm \sqrt{(3.7 \times 10^{-4})^2 - (4)(-3.7 \times 10^{-5})}}{2(1)} = \frac{-3.7 \times 10^{-4} \pm 0.0122}{2}$$

x = 0.0059 and −0.0063

Of the two solutions for x, only the positive value of x has physical meaning because x is the $[OH^-]$.

$[OH^-] = x = 0.0059\ \text{M}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-3}} = 1.7 \times 10^{-12}\ \text{M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(1.7 \times 10^{-12}) = 11.77$$

(b) 20.0 mL of HNO_3 is halfway to the equivalence point.

$$\text{For } CH_3NH_3^+,\ K_a = \frac{K_w}{K_b \text{ for } CH_3NH_2} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-4}} = 2.7 \times 10^{-11}$$

$$\text{pH} = pK_a = -\log(2.7 \times 10^{-11}) = 10.57$$

(c) At the equivalence point only the salt $CH_3NH_3NO_3$ is in solution.

mmol $CH_3NH_3NO_3$ = (0.100 mmol/mL)(100.0 mL) = 10.0 mmol

$$[CH_3NH_3^+] = \frac{10.0\ \text{mmol}}{(100.0\ \text{mL} + 40.0\ \text{mL})} = 0.0714\ \text{M}$$

	$CH_3NH_3^+(aq)$	+	$H_2O(l)$	⇌	$H_3O^+(aq)$	+	$CH_3NH_2(aq)$
initial (M)	0.0714		~0		0		
change (M)	−x				+x		+x
equil (M)	0.0714 − x				x		x

$$K_a = \frac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]} = 2.7 \text{ x } 10^{-11} = \frac{x^2}{0.0714 \text{ _ } x} \approx \frac{x^2}{0.0714}$$

Solve for x. $x = [H_3O^+] = 1.4 \text{ x } 10^{-6}$ M

$pH = -\log[H_3O^+] = -\log(1.4 \text{ x } 10^{-6}) = 5.85$

(d) mmol CH_3NH_2 = (0.100 mmol/mL)(100.0 mL) = 10.0 mmol

mmol HNO_3 = (0.250 mmol/mL)(60.0 mL) = 15.0 mmol

Neutralization reaction:	$CH_3NH_2(aq)$ +	$H_3O^+(aq)$ ⏐	$CH_3NH_3^+(aq)$ +	$H_2O(l)$
before reaction (mmol)	10.0	15.0	0	
change (mmol)	−10.0	−10.0	+10.0	
after reaction (mmol)	0	5.0	10.0	

After the equivalence point the pH of the solution is determined by the $[H_3O^+]$.

$$[H_3O^+] = \frac{5.0 \text{ mmol}}{(100.0 \text{ mL} + 60.0 \text{ mL})} = 3.1 \text{ x } 10^{-2} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(3.1 \text{ x } 10^{-2}) = 1.51$

16.84 For H_2A^+, $K_{a1} = 4.6 \text{ x } 10^{-3}$ and $K_{a2} = 2.0 \text{ x } 10^{-10}$

(a) (10.0 mL)(0.100 mmol/mL) = 1.00 mmol NaOH added = 1.00 mmol HA produced.

(50.0 mL)(0.100 mmol/mL) = 5.00 mmol H_2A^+

5.00 mmol H_2A^+ − 1.00 mmol NaOH = 4.00 mmol H_2A^+ after neutralization

$$[H_2A^+] = \frac{4.00 \text{ mmol}}{(50.0 \text{ mL} + 10.0 \text{ mL})} = 6.67 \text{ x } 10^{-2} \text{ M}$$

$$[HA] = \frac{1.00 \text{ mmol}}{(50.0 \text{ mL} + 10.0 \text{ mL})} = 1.67 \text{ x } 10^{-2} \text{ M}$$

$$pH = pK_{a1} + \log\frac{[HA]}{[H_2A^+]} = -\log(4.6 \text{ x } 10^{-3}) + \log\left(\frac{1.67 \text{ x } 10^{-2}}{6.67 \text{ x } 10^{-2}}\right) = 1.74$$

(b) Halfway to the first equivalence point, $pH = pK_{a1} = 2.34$

(c) At the first equivalence point, $pH = \frac{pK_{a1} + pK_{a2}}{2} = 6.02$

(d) Halfway between the first and second equivalence points, $pH = pK_{a2} = 9.70$

(e) At the second equivalence point only the basic salt, NaA, is in solution.

$$K_b = \frac{K_w}{K_a \text{ for HA}} = \frac{K_w}{K_a 2} = \frac{1.0 \text{ x } 10^{-14}}{2.0 \text{ x } 10^{-10}} = 5.0 \text{ x } 10^{-5}$$

mmol A^- = (50.0 mL)(0.100 mmol/mL) = 5.00 mmol

$$[A^-] = \frac{5.0 \text{ mmol}}{(50.0 \text{ mL} + 100.0 \text{ mL})} = 3.3 \text{ x } 10^{-2} \text{ M}$$

	$A^-(aq)$ +	$H_2O(l)$ Ω	$HA(aq)$ +	$OH^-(aq)$
initial (M)	0.033		0	~0
change (M)	−x		+x	+x
equil (M)	0.033 − x		x	x

$$K_b = \frac{[HA][OH^-]}{[A^-]} = 5.0 \text{ x } 10^{-5} = \frac{(x)(x)}{0.033 \text{ _ } x} \approx \frac{x^2}{0.033}$$

Solve for x.

$x = [OH^-] = \sqrt{(5.0 \times 10^{-5})(0.033)} = 1.3 \times 10^{-3}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-3}} = 7.7 \times 10^{-12}$ M

$pH = -\log[H_3O^+] = -\log(7.7 \times 10^{-12}) = 11.11$

16.85 For H_2CO_3, $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$

(a) (25.0 mL)(0.0200 mmol/mL) = 0.500 mmol H_2CO_3

(10.0 mL)(0.0250 mmol/mL) = 0.250 mmol KOH added

0.500 mmol H_2CO_3 – 0.250 mmol KOH = 0.250 mmol HCO_3^- produced

This is halfway to the first equivalence point where $pH = pK_{a1} = -\log(4.3 \times 10^{-7}) = 6.37$

(b) At the first equivalence point, $pH = \frac{pK_{a1} + pK_{a2}}{2} = 8.31$

(c) Halfway between the first and second equivalence points, $pH = pK_{a2} = 10.25$

(d) At the second equivalence point only the basic salt, K_2CO_3, is in solution.

$K_b = \frac{K_w}{K_a \text{ for } HCO_3^-} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.8 \times 10^{-4}$

mmol CO_3^{2-} = mmol H_2CO_3 = 0.500 mmol

$[CO_3^{2-}] = \frac{0.500 \text{ mmol}}{(25.0 \text{ mL} + 40.0 \text{ mL})} = 0.00769$ M

	$CO_3^{2-}(aq)$	+ $H_2O(l)$	⇌	$HCO_3^-(aq)$	+ $OH^-(aq)$
initial (M)	0.00769			0	~0
change (M)	–x			+x	+x
equil (M)	0.00769 – x			x	x

$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 1.8 \times 10^{-4} = \frac{(x)(x)}{0.00769 - x}$

Use the quadratic formula to solve for x.

$x = \frac{-(1.8 \times 10^{-4}) \pm \sqrt{(1.8 \times 10^{-4})^2 - (4)(1)(-1.4 \times 10^{-6})}}{2(1)} = \frac{(-1.8 \times 10^{-4}) \pm (2.37 \times 10^{-3})}{2}$

$x = -1.27 \times 10^{-3}$ and 1.09×10^{-3}

Of the two solutions for x, only the positive value of x has physical meaning because x is the $[OH^-]$.

$[OH^-] = x = 1.09 \times 10^{-3}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.09 \times 10^{-3}} = 9.2 \times 10^{-12}$ M

$pH = -\log[H_3O^+] = -\log(9.2 \times 10^{-12}) = 11.04$

(e) excess KOH

(50.0 mL – 40.0 mL)(0.025 mmol/mL) = 0.250 mmol KOH = 0.250 mmol OH^-

$[OH^-] = \frac{0.250 \text{ mmol}}{(25.0 \text{ mL} + 50.0 \text{ mL})} = 3.33 \times 10^{-3}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.33 \times 10^{-3}} = 3.0 \times 10^{-12}$ M

pH = $-\log[H_3O^+] = -\log(3.0 \times 10^{-12}) = 11.52$

16.86 When equal volumes of acid and base react, all concentrations are cut in half.

(a) At the equivalence point only the salt $NaNO_2$ is in solution.

$[NO_2^-] = 0.050$ M

For NO_2^-, $K_b = \frac{K_w}{K_a \text{ for } HNO_2} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$

	$NO_2^-(aq)$	+ $H_2O(l)$	⇌	$HNO_2(aq)$	+	$OH^-(aq)$
Initial (M)	0.050			0		~0
change (M)	−x			+x		+x
equil (M)	0.050 − x			x		x

$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = 2.2 \times 10^{-11} = \frac{(x)(x)}{0.050 - x} \approx \frac{x^2}{0.050}$

Solve for x. $x = [OH^-] = 1.1 \times 10^{-6}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-6}} = 9.1 \times 10^{-9}$ M

pH = $-\log[H_3O^+] = -\log(9.1 \times 10^{-9}) = 8.04$

Phenol red would be a suitable indicator. (see Figure 15.4)

(b) The pH is 7.00 at the equivalence point for the titration of a strong acid (HI) with a strong base (NaOH).

Bromthymol blue or phenol red would be suitable indicators. (Any indicator that changes color in the pH range 4 − 10 is satisfactory for a strong acid − strong base titration.)

(c) At the equivalence point only the salt CH_3NH_3Cl is in solution.

$[CH_3NH_3^+] = 0.050$ M

For $CH_3NH_3^+$, $K_a = \frac{K_w}{K_b \text{ for } CH_3NH_2} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-4}} = 2.7 \times 10^{-11}$

	$CH_3NH_3^+(aq)$	+ $H_2O(l)$	⇌	$H_3O^+(aq)$	+	$CH_3NH_2(aq)$
initial (M)	0.050			~0		0
change (M)	−x			+x		+x
equil (M)	0.050 − x			x		x

$K_a = \frac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]} = 2.7 \times 10^{-11} = \frac{(x)(x)}{0.050 - x} \approx \frac{x^2}{0.050}$

Solve for x. $x = [H_3O^+] = 1.2 \times 10^{-6}$ M

pH = $-\log[H_3O^+] = -\log(1.2 \times 10^{-6}) = 5.92$

Chlorphenol red would be a suitable indicator.

16.87 When equal volumes of acid and base react, all concentrations are cut in half.

(a) At the equivalence point only the salt $C_5H_{11}NHNO_3$ is in solution.

$[C_5H_{11}NH^+] = 0.10$ M

For $C_5H_{11}NH^+$, $K_a = \frac{K_w}{K_b \text{ for } C_5H_{11}N} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-3}} = 7.7 \times 10^{-12}$

	$C_5H_{11}NH^+(aq)$ + $H_2O(l)$ Ω	$H_3O^+(aq)$ +	$C_5H_{11}N(aq)$
initial (M)	0.10	~0	0
change (M)	−x	+x	+x
equil (M)	0.10 − x	x	x

$K_a = \frac{[H_3O^+][C_5H_{11}N]}{[C_5H_{11}NH^+]} = 7.7 \times 10^{-12} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$

Solve for x. $x = [H_3O^+] = 8.8 \times 10^{-7}$ M

$pH = -\log[H_3O^+] = -\log(8.8 \times 10^{-7}) = 6.06$

Alizarin would be a suitable indicator (see Figure 15.4)

(b) At the equivalence point only the salt Na_2SO_3 is in solution.

$[SO_3^{2-}] = 0.10$ M

For SO_3^{2-}, $K_b = \frac{K_w}{K_a \text{ for } HSO_3^-} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-8}} = 1.6 \times 10^{-7}$

	$SO_3^{2-}(aq)$ + $H_2O(l)$ Ω	$HSO_3^-(aq)$ +	$OH^-(aq)$
Initial (M)	0.10	0	~0
change (M)	−x	+x	+x
equil (M)	0.10 − x	x	x

$K_b = \frac{[HSO_3^-][OH^-]}{[SO_3^{2-}]} = 1.6 \times 10^{-7} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$

Solve for x. $x = [OH^-] = 1.26 \times 10^{-4}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.26 \times 10^{-4}} = 7.9 \times 10^{-11}$ M

$pH = -\log[H_3O^+] = -\log(7.9 \times 10^{-11}) = 10.10$

Thymolphthalein would be a suitable indicator.

(c) The pH is 7.00 at the equivalence point for the titration of a strong acid (HBr) with a strong base ($Ba(OH)_2$).

Alizarin, bromthymol blue, or phenol red would be suitable indicators. (Any indicator that changes color in the pH range 4 - 10 is satisfactory for a strong acid - strong base titration.)

Solubility Equilibria

16.88 (a) $Ag_2CO_3(s)$ Ω $2\,Ag^+(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ag^+]^2[CO_3^{2-}]$

(b) $PbCrO_4(s)$ Ω $Pb^{2+}(aq) + CrO_4^{2-}(aq)$ $K_{sp} = [Pb^{2+}][CrO_4^{2-}]$

(c) $Al(OH)_3(s)$ Ω $Al^{3+}(aq) + 3\,OH^-(aq)$ $K_{sp} = [Al^{3+}][OH^-]^3$

(d) $Hg_2Cl_2(s)$ Ω $Hg_2^{2+}(aq) + 2\,Cl^-(aq)$ $K_{sp} = [Hg_2^{2+}][Cl^-]^2$

16.89 (a) $K_{sp} = [Ca^{2+}][OH^-]^2$ (b) $K_{sp} = [Ag^+]^3[PO_4^{3-}]$

(c) $K_{sp} = [Ba^{2+}][CO_3^{2-}]$ (d) $K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

16.90 (a) $K_{sp} = [Pb^{2+}][I^-]^2 = (5.0 \times 10^{-3})(1.3 \times 10^{-3})^2 = 8.4 \times 10^{-9}$

(b) $[I^{-}] = \sqrt{\frac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\frac{(8.4 \times 10^{-9}}{(2.5 \times 10^{-4})}} = 5.8 \times 10^{-3}$ M

(c) $[Pb^{2+}] = \frac{K_{sp}}{[I^{-}]^2} = \frac{(8.4 \times 10^{-9})}{(2.5 \times 10^{-4})^2} = 0.13$ M

16.91 (a) $K_{sp} = [Ca^{2+}]^3[PO_4^{2-}]^2 = (2.9 \times 10^{-7})^3(2.9 \times 10^{-7})^2 = 2.1 \times 10^{-33}$

(b) $[Ca^{2+}] = \sqrt[3]{\frac{K_{sp}}{[PO_4^{2-}]^2}} = \sqrt[3]{\frac{2.1 \times 10^{-33}}{(0.010)^2}} = 2.8 \times 10^{-10}$ M

(c) $[PO_4^{2-}] = \sqrt{\frac{K_{sp}}{[Ca^{2+}]^3}} = \sqrt{\frac{2.1 \times 10^{-33}}{(0.010)^3}} = 4.6 \times 10^{-14}$ M

16.92 $Ag_2CO_3(s) \rightleftharpoons 2\ Ag^{+}(aq) + CO_3^{2-}(aq)$

equil (M) $2x \quad x$

$[Ag^{+}] = 2x = 2.56 \times 10^{-4}$ M; $[CO_3^{2-}] = x = (2.56 \times 10^{-4}\ M)/2 = 1.28 \times 10^{-4}$ M

$K_{sp} = [Ag^{+}]^2[CO_3^{2-}] = (2.56 \times 10^{-4})^2(1.28 \times 10^{-4}) = 8.39 \times 10^{-12}$

16.93 (a) $[Cd^{2+}] = [CO_3^{2-}] = 2.5 \times 10^{-6}$ M

$K_{sp} = [Cd^{2+}][CO_3^{2-}] = (2.5 \times 10^{-6})^2 = 6.2 \times 10^{-12}$

(b) $[Ca^{2+}] = 1.06 \times 10^{-2}$ M

$[OH^{-}] = 2[Ca^{2+}] = 2(1.06 \times 10^{-2}\ M) = 2.12 \times 10^{-2}$ M

$K_{sp} = [Ca^{2+}][OH^{-}]^2 = (1.06 \times 10^{-2})(2.12 \times 10^{-2})^2 = 4.76 \times 10^{-6}$

(c) $PbBr_2$, 367.01 amu

$[Pb^{2+}]$ = molarity of $PbBr_2 = \frac{\left(4.34\ g \times \frac{1\ mol}{367.01\ g}\right)}{1\ L} = 1.18 \times 10^{-2}$ M

$[Br^{-}] = 2[Pb^{2+}] = 2(1.18 \times 10^{-2}\ M) = 2.36 \times 10^{-2}$ M

$K_{sp} = [Pb^{2+}][Br^{-}]^2 = (1.18 \times 10^{-2})(2.36 \times 10^{-2})^2 = 6.57 \times 10^{-6}$

(d) $BaCrO_4$, 253.32 amu

$[Ba^{2+}] = [CrO_4^{2-}]$ = molarity of $BaCrO_4 = \frac{\left(2.8 \times 10^{-3}\ g \times \frac{1\ mol}{253.32\ g}\right)}{1\ L} = 1.1 \times 10^{-5}$ M

$K_{sp} = [Ba^{2+}][CrO_4^{2-}] = (1.1 \times 10^{-5})^2 = 1.2 \times 10^{-10}$

16.94 (a) $BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$

equil (M) $x \quad x$

$K_{sp} = [Ba^{2+}][CrO_4^{2-}] = 1.2 \times 10^{-10} = (x)(x)$

molar solubility = $x = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5}$ M

(b) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^{-}(aq)$

equil (M) $x \quad 2x$

$K_{sp} = [Mg^{2+}][OH^{-}]^2 = 5.6 \times 10^{-12} = x(2x)^2 = 4x^3$

molar solubility = $x = \sqrt[3]{\frac{5.6 \times 10^{-12}}{4}} = 1.1 \times 10^{s4}$ M

(c) $Ag_2SO_3(s) \Omega 2\ Ag^+(aq) + SO_3^{2s}(aq)$

equil (M) $2x \quad x$

$K_{sp} = [Ag^+]^2[SO_3^{2s}] = 1.5 \times 10^{s14} = (2x)^2x = 4x^3$

molar solubility = $x = \sqrt[3]{\frac{1.5 \times 10^{-14}}{4}} = 1.6 \times 10^{s5}$ M

16.95 (a) $Ag_2CO_3(s) \Omega 2\ Ag^+(aq) + CO_3^{2s}(aq)$

equil (M) $2x \quad x$

$K_{sp} = [Ag^+]^2[CO_3^{2s}] = 8.4 \times 10^{s12} = (2x)^2(x) = 4x^3$

molar solubility = $x = \sqrt[3]{\frac{8.4 \times 10^{-12}}{4}} = 1.3 \times 10^{s4}$ M

Ag_2CO_3, 275.75 amu

solubility = $(1.3 \times 10^{s4}$ mol/L)(275.75 g/mol) = 0.036 g/L

(b) $CuBr(s) \Omega Cu^+(aq) + Br^s(aq)$

equil (M) $x \quad x$

$K_{sp} = [Cu^+][Br^s] = 6.3 \times 10^{s9} = (x)(x)$

molar solubility = $x = \sqrt{6.3 \times 10^{-9}} = 7.9 \times 10^{s5}$ M

CuBr, 143.45 amu

solubility = $(7.9 \times 10^{s5}$ mol/L)(143.45 g/mol) = 0.011 g/L

(c) $Cu_3(PO_4)_2(s) \Omega 3\ Cu^{2+}(aq) + 2\ PO_4^{3s}(aq)$

equil (M) $3x \quad 2x$

$K_{sp} = [Cu^{2+}]^3[PO_4^{3s}]^2 = 1.4 \times 10^{s37} = (3x)^3(2x)^2 = 108x^5$

molar solubility = $x = \sqrt[5]{\frac{1.4 \times 10^{-37}}{108}} = 1.7 \times 10^{s8}$

$Cu_3(PO_4)_2$, 380.58 amu

solubility = $(1.7 \times 10^{s8}$ mol/L)(380.58 g/mol) = 6.5×10^{s6} g/L

Factors That Affect Solubility

16.96 $Ag_2CO_3(s) \Omega 2\ Ag^+(aq) + CO_3^{2s}(aq)$

(a) $AgNO_3$, source of Ag^+; equilibrium shifts left

(b) HNO_3, source of H_3O^+, removes CO_3^{2s}; equilibrium shifts right

(c) Na_2CO_3, source of CO_3^{2s}; equilibrium shifts left

(d) NH_3, forms $Ag(NH_3)_2^+$; removes Ag^+; equilibrium shifts right

16.97 $BaF_2(s) \Omega Ba^{2+}(aq) + 2\ F^s(aq)$

(a) H^+ from HCl reacts with F^s forming the weak acid HF. The equilibrium shifts to the right increasing the solubility of BaF_2.

(b) KF, source of F^s; equilibrium shifts left, solubility of BaF_2 decreases.

(c) No change in solubility.

(d) $Ba(NO_3)_2$, source of Ba^{2+}; equilibrium shifts left, solubility of BaF_2 decreases.

16.98 (a) $PbCrO_4(s) \Omega Pb^{2+}(aq) + CrO_4^{2s}(aq)$

equil (M) x x

$K_{sp} = [Pb^{2+}][CrO_4^{2s}] = 2.8 \times 10^{s13} = (x)(x)$

molar solubility = $x = \sqrt{2.8 \times 10^{-13}} = 5.3 \times 10^{s7}$ M

(b) $PbCrO_4(s) \Omega Pb^{2+}(aq) + CrO_4^{2s}(aq)$

initial(M) 0 1.0×10^{s3}

equil (M) x $1.0 \times 10^{s3} + x$

$K_{sp} = [Pb^{2+}][CrO_4^{2s}] = 1.2 \times 10^{s10} = (x)(1.0 \times 10^{s3} + x) \; . \; (x)(1.0 \times 10^{s3})$

molar solubility = $x = \dfrac{2.8 \times 10^{-13}}{1 \times 10^{-3}} = 2.8 \times 10^{s10}$ M

16.99 (a) $SrF_2(s) \Omega Sr^{2+}(aq) + 2\,F^s(aq)$

initial (M) 0.010 0

equil (M) 0.010 + x 2x

$K_{sp} = [Sr^{2+}][F^s]^2 = 4.3 \times 10^{s9} = (0.010 + x)(2x)^2 \; . \; (0.010)(2x)^2 = 0.040\,x^2$

molar solubility = $x = \sqrt{\dfrac{4.3 \times 10^{-9}}{0.040}} = 3.3 \times 10^{s4}$ M

(b) $SrF_2(s) \Omega Sr^{2+}(aq) + 2\,F^s(aq)$

initial (M) 0 0.010

equil (M) x 0.010 + 2x

$K_{sp} = [Sr^{2+}][F^s]^2 = 4.3 \times 10^{s9} = (x)(0.010 + 2x)^2 \; . \; (x)(0.010)^2 = x(0.00010)$

molar solubility = $x = \dfrac{4.3 \times 10^{-9}}{0.00010} = 4.3 \times 10^{s5}$ M

16.100 (b), (c), and (d) are more soluble in acidic solution.

(a) $AgBr(s) \Omega Ag^{+}(aq) + Br^s(aq)$

(b) $CaCO_3(s) + H_3O^{+}(aq) \Omega Ca^{2+}(aq) + HCO_3^{s}(aq) + H_2O(l)$

(c) $Ni(OH)_2(s) + 2\,H_3O^{+}(aq) \Omega Ni^{2+}(aq) + 4\,H_2O(l)$

(d) $Ca_3(PO_4)_2(s) + 2\,H_3O^{+}(aq) \Omega 3\,Ca^{2+}(aq) + 2\,HPO_4^{2s}(aq) + 2\,H_2O(l)$

16.101 (a), (b), and (d) are more soluble in acidic solution.

(a) $MnS(s) + 2\,H_3O^{+}(aq) \Omega Mn^{2+}(aq) + H_2S(aq) + 2\,H_2O(l)$

(b) $Fe(OH)_3(s) + 3\,H_3O^{+}(aq) \Omega Fe^{3+}(aq) + 6\,H_2O(l)$

(c) $AgCl(s) \Omega Ag^{+}(aq) + Cl^s(aq)$

(d) $BaCO_3(s) + H_3O^{+}(aq) \Omega Ba^{2+}(aq) + HCO_3^{s}(aq) + H_2O(l)$

16.102 On mixing equal volumes of two solutions, the concentrations of both solutions are cut in half.

	$Ag^{+}(aq)$	+	$2\,CN^s(aq)$	Ω	$Ag(CN)_2^s(aq)$
before reaction (M)	0.0010		0.10		0
assume 100% reaction	S0.0010		S2(0.0010)		0.0010

after reaction (M)	0	0.098	0.0010
assume small back rxn	+x	+2x	Sx
equil (M)	x	0.098 + 2x	0.0010 S x

$$K_f = 3.0 \times 10^{20} = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{(0.0010 \_ x)}{x(0.098 + 2x)^2} \approx \frac{0.0010}{x(0.098)^2}$$

Solve for x. $x = [Ag^+] = 3.5 \times 10^{S22}$ M

16.103

	$Cr^{3+}(aq)$	+ $4\ OH^S(aq)$ Ω	$Cr(OH)_4{}^S(aq)$
before reaction (M)	0.0050	1.0	0
assume 100% reaction	S0.0050	S(4)(0.0050)	+0.0050
after reaction(M)	0	0.98	0.0050
assume small back rxn	+x	+4x	Sx
equil (M)	x	0.98 + 4x	0.0050 S x

$$K_f = \frac{[Cr(OH)_4^-]}{[Cr^{3+}][OH^-]^4} = 8 \times 10^{29} = \frac{(0.0050 \_ x)}{(x)(0.98 + 4x)^4} \approx \frac{(0.0050)}{(x)(0.98)^4}$$

Solve for x. $x = [Cr^{3+}] = 6.8 \times 10^{S33}$ M = 7×10^{S33} M

$$\text{fraction uncomplexed } Cr^{3+} = \frac{[Cr^{3+}]}{[Cr(OH)_4^-]} = \frac{7 \times 10^{-33}\ M}{0.0050\ M} = 1.4 \times 10^{S30} = 1 \times 10^{S30}$$

16.104 (a) $AgI(s)$ Ω $Ag^+(aq) + I^S(aq)$ $K_{sp} = 8.5 \times 10^{S17}$

$Ag^+(aq) + 2\ CN^S(aq)$ | $Ag(CN)_2{}^S(aq)$ $K_f = 3.0 \times 10^{20}$

dissolution rxn $AgI(s) + 2\ CN^S(aq)$ Ω $Ag(CN)_2{}^S(aq) + I^S(aq)$

$K = (K_{sp})(K_f) = (8.5 \times 10^{S17})(3.0 \times 10^{20}) = 2.6 \times 10^4$

(b) $Al(OH)_3(s)$ Ω $Al^{3+}(aq) + 3\ OH^S(aq)$ $K_{sp} = 1.9 \times 10^{S33}$

$Al^{3+}(aq) + 4\ OH^S(aq)$ | $Al(OH)_4{}^S(aq)$ $K_f = 3 \times 10^{33}$

dissolution rxn $Al(OH)_3(s) + OH^S(aq)$ Ω $Al(OH)_4{}^S(aq)$

$K = (K_{sp})(K_f) = (1.9 \times 10^{S33})(3 \times 10^{33}) = 6$

(c) $Zn(OH)_2(s)$ Ω $Zn^{2+}(aq) + 2\ OH^S(aq)$ $K_{sp} = 4.1 \times 10^{S17}$

$Zn^{2+}(aq) + 4\ NH_3(aq)$ | $Zn(NH_3)_4{}^{2+}(aq)$ $K_f = 7.8 \times 10^8$

dissolution rxn $Zn(OH)_2(s) + 4\ NH_3(aq)$ Ω $Zn(NH_3)_4{}^{2+} + 2\ OH^S(aq)$

$K = (K_{sp})(K_f) = (4.1 \times 10^{S17})(7.8 \times 10^8) = 3.2 \times 10^{S8}$

16.105 (a) $Zn(OH)_2(s)$ Ω $Zn^{2+}(aq) + 2\ OH^S(aq)$ $K_{sp} = 4.1 \times 10^{S17}$

$Zn^{2+}(aq) + 4\ OH^S(aq)$ | $Zn(OH)_4{}^{2S}(aq)$ $K_f = 3 \times 10^{15}$

dissolution rxn $Zn(OH)_2(s) + 2\ OH^S(aq)$ Ω $Zn(OH)_4{}^{2S}(aq)$

$K = (K_{sp})(K_f) = (4.1 \times 10^{S17})(3 \times 10^{15}) = 0.1$

(b) $Cu(OH)_2(s)$ Ω $Cu^{2+}(aq) + 2\ OH^S(aq)$ $K_{sp} = 1.6 \times 10^{S19}$

$Cu^{2+}(aq) + 4\ NH_3(aq)$ | $Cu(NH_3)_4{}^{2+}(aq)$ $K_f = 5.6 \times 10^{11}$

dissolution rxn $Cu(OH)_2(s) + 4\ NH_3(aq)$ Ω $Cu(NH_3)_4{}^{2+} + 2\ OH^S(aq)$

$K = (K_{sp})(K_f) = (1.6 \times 10^{-19})(5.6 \times 10^{11}) = 9.0 \times 10^{-8}$

(c) $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ $\quad K_{sp} = 5.4 \times 10^{-13}$

$Ag^+(aq) + 2\ NH_3(aq) \rightarrow Ag(NH_3)_2^+(aq)$ $\quad K_f = 1.7 \times 10^7$

dissolution rxn $AgBr(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Br^-(aq)$

$K = (K_{sp})(K_f) = (5.4 \times 10^{-13})(1.7 \times 10^7) = 9.2 \times 10^{-6}$

16.106 (a) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

equil (M)	x	x

$K_{sp} = [Ag^+][I^-] = 8.5 \times 10^{-17} = (x)(x)$

molar solubility = $x = \sqrt{8.5 \times 10^{-17}} = 9.2 \times 10^{-9}$ M

(b) $AgI(s) + 2\ CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + I^-(aq)$

initial (M)	0.10	0	0
change (M)	−2x	+x	+x
equil (M)	0.10 − 2x	x	x

$K = (K_{sp})(K_f) = (8.5 \times 10^{-17})(3.0 \times 10^{20}) = 2.6 \times 10^4$

$$K = 2.6 \times 10^4 = \frac{[Ag(CN)_2^-][I^-]}{[CN^-]^2} = \frac{x^2}{(0.10 - 2x)^2}$$

Take the square root of both sides and solve for x.

molar solubility = x = 0.050 M

16.107 $Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$

initial (M)	0.50	0
change (M)	−x	+x
equil (M)	0.50 − x	x

$K = (K_{sp})(K_f) = (6.7 \times 10^{-31})(8 \times 10^{29}) = 0.54$

$$K = 0.54 = \frac{[Cr(OH)_4^-]}{[OH^-]} = \frac{x}{0.50 - x}$$

$0.27 - 0.54x = x$

$0.27 = 1.54x$

$$\text{molar solubility} = x = \frac{0.27}{1.54} = 0.2 \text{ M}$$

Precipitation; Qualitative Analysis

16.108 For $BaSO_4$, $K_{sp} = 1.1 \times 10^{-10}$

Total volume = 300 mL + 100 mL = 400 mL

$$[Ba^{2+}] = \frac{(4.0 \times 10^{-3}\ M)(100\ mL)}{(400\ mL)} = 1.0 \times 10^{-3}\ M$$

$$[SO_4^{2-}] = \frac{(6.0 \times 10^{-4}\ M)(300\ mL)}{(400\ mL)} = 4.5 \times 10^{-4}\ M$$

$IP = [Ba^{2+}]_t[SO_4^{2-}]_t = (1.0 \times 10^{-3})(4.5 \times 10^{-4}) = 4.5 \times 10^{-7}$

$IP > K_{sp}$; $BaSO_4(s)$ will precipitate.

16.109 On mixing equal volumes of two solutions, the concentrations of both solutions are cut in half.

For $PbCl_2$, $K_{sp} = 1.2 \times 10^{s5} = [Pb^{2+}][Cl^s]^2$

$IP = (0.0050)(0.0050)^2 = 1.2 \times 10^{s7}$

$IP < K_{sp}$; no precipitate will form.

$$[Cl^s] = \sqrt{\frac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\frac{1.2 \times 10^{-5}}{5.0 \times 10^{-3}}} = 0.049 \text{ M}$$

A $[Cl^s]$ just greater than 0.049 M will result in precipitation.

16.110 $BaSO_4$, $K_{sp} = 1.1 \times 10^{s10}$; $Fe(OH)_3$, $K_{sp} = 2.6 \times 10^{s39}$

Total volume = 80 mL + 20 mL = 100 mL

$$[Ba^{2+}] = \frac{(1.0 \times 10^{-5} \text{ M})(80 \text{ mL})}{(100 \text{ mL})} = 8.0 \times 10^{s6} \text{ M}$$

$[OH^s] = 2[Ba^{2+}] = 2(8.0 \times 10^{s6}) = 1.6 \times 10^{s5}$ M

$$[Fe^{3+}] = \frac{2(1.0 \times 10^{-5} \text{ M})(20 \text{ mL})}{(100 \text{ mL})} = 4.0 \times 10^{s6} \text{ M}$$

$$[SO_4^{2s}] = \frac{3(1.0 \times 10^{-5} \text{ M})(20 \text{ mL})}{(100 \text{ mL})} = 6.0 \times 10^{s6} \text{ M}$$

For $BaSO_4$, $IP = [Ba^{2+}]_t[SO_4^{2s}]_t = (8.0 \times 10^{s6})(6.0 \times 10^{s6}) = 4.8 \times 10^{s11}$

$IP < K_{sp}$; $BaSO_4$ will not precipitate.

For $Fe(OH)_3$, $IP = [Fe^{3+}]_t[OH^s]_t^3 = (4.0 \times 10^{s6})(1.6 \times 10^{s5})^3 = 1.6 \times 10^{s20}$

$IP > K_{sp}$; $Fe(OH)_3(s)$ will precipitate.

16.111 (a) $$[CO_3^{2s}] = \frac{(2.0 \times 10^{-3} \text{ M})(0.10 \text{ mL})}{(250 \text{ mL})} = 8.0 \times 10^{s7} \text{ M}$$

$K_{sp} = 5.0 \times 10^{s9} = [Ca^{2+}][CO_3^{2s}]$

$IP = [Ca^{2+}][CO_3^{2s}] = (8.0 \times 10^{s4})(8.0 \times 10^{s7}) = 6.4 \times 10^{s10}$

$IP < K_{sp}$; no precipitate will form.

(b) Na_2CO_3, 106 amu; 10 mg = 0.010 g

$$[CO_3^{2s}] = \frac{\left(0.010 \text{ g} \times \frac{1 \text{ mol}}{106 \text{ g}}\right)}{0.250 \text{ L}} = 3.8 \times 10^{s4} \text{ M}$$

$IP = [Ca^{2+}][CO_3^{2s}] = (8.0 \times 10^{s4})(3.8 \times 10^{s4}) = 3.0 \times 10^{s7}$

$IP > K_{sp}$; $CaCO_3(s)$ will precipitate.

16.112 pH = 10.80; $[H_3O^+] = 10^{spH} = 10^{s10.80} = 1.6 \times 10^{s11}$ M

$$[OH^s] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-11}} = 6.2 \times 10^{s4} \text{ M}$$

For $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{s12}$

$IP = [Mg^{2+}]_t[OH^s]_t^2 = (2.5 \times 10^{s4})(6.2 \times 10^{s4})^2 = 9.6 \times 10^{s11}$

$IP > K_{sp}$; $Mg(OH)_2(s)$ will precipitate

16.113 $Mg(OH)_2$, $K_{sp} = 5.6 \times 10^{-12}$; $Al(OH)_3$, $K_{sp} = 1.9 \times 10^{-33}$

pH = 8; $[H_3O^+] = 10^{-pH} = 10^{-8} = 1 \times 10^{-8}$ M

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1 \times 10^{-8}} = 1 \times 10^{-6} \text{ M}$$

For $Mg(OH)_2$, $IP = [Mg^{2+}][OH^-]^2 = (0.01)(1 \times 10^{-6})^2 = 1 \times 10^{-14}$

$IP < K_{sp}$; no $Mg(OH)_2$ will precipitate.

For $Al(OH)_3$, $IP = [Al^{3+}][OH^-]^3 = (0.01)(1 \times 10^{-6})^3 = 1 \times 10^{-20}$

$IP > K_{sp}$; $Al(OH)_3$ will precipitate.

16.114 $K_{spa} = \dfrac{[M^{2+}][H_2S]}{[H_3O^+]^2}$; FeS, $K_{spa} = 6 \times 10^{2}$; SnS, $K_{spa} = 1 \times 10^{-5}$

Fe^{2+} and Sn^{2+} can be separated by bubbling H_2S through an acidic solution containing the two cations because their K_{spa} values are so different.

For FeS and SnS, $Q_c = \dfrac{(0.01)(0.10)}{(0.3)^2} = 1.1 \times 10^{-2}$

For FeS, $Q_c < K_{spa}$, and no FeS will precipitate.

For SnS, $Q_c > K_{spa}$, and SnS will precipitate.

16.115 CoS, $K_{spa} = \dfrac{[Co^{2+}][H_2S]}{[H_3O^+]^2} = 3$

(i) In 0.5 M HCl, $[H_3O^+] = 0.5$ M

$$Q_c = \frac{[Co^{2+}]_t[H_2S]_t}{[H_3O^+]_t^2} = \frac{(0.10)(0.10)}{(0.5)^2} = 0.04;$$ $Q_c < K_{spa}$; CoS will not precipitate

(ii) pH = 8; $[H_3O^+] = 10^{-pH} = 10^{-8} = 1 \times 10^{-8}$ M

$$Q_c = \frac{[Co^{2+}]_t[H_2S]_t}{[H_3O^+]_t^2} = \frac{(0.10)(0.10)}{(1 \times 10^{-8})^2} = 1 \times 10^{14};$$ $Q_c > K_{spa}$; CoS(s) will precipitate

16.116 (a) add Cl^- to precipitate AgCl
(b) add CO_3^{2-} to precipitate $CaCO_3$
(c) add H_2S to precipitate MnS
(d) add NH_3 and NH_4Cl to precipitate $Cr(OH)_3$
(Need buffer to control $[OH^-]$; excess OH^- produces the soluble $Cr(OH)_4^-$.)

16.117 (a) add Cl^- to precipitate Hg_2Cl_2
(b) add $(NH_4)_2HPO_4$ to precipitate $MgNH_4PO_4$
(c) add HCl and H_2S to precipitate HgS
(d) add Cl^- to precipitate $PbCl_2$

General Problems

16.118 Prepare aqueous solutions of the three salts. Add a solution of $(NH_4)_2HPO_4$. If a white precipitate forms, the solution contains Mg^{2+}. Perform flame test on the other two solutions. A yellow flame test indicates Na^+. A violet flame test indicates K^+.

16.119 (a), solution contains HCN and CN^s
(c), solution can contain HCN and CN^s
(e), solution can contain HCN and CN^s

16.120 (a), solution contains H_2CO_3 and HCO_3^s
(b), solution contains HCO_3^s and CO_3^{2s}
(d), solution contains HCO_3^s and CO_3^{2s}

16.121

(a) The pH for the weak acid is higher.
(b) Initially, the pH rises more quickly for the weak acid, but then the curve becomes more level in the region halfway to the equivalence point.
(c) The pH is higher at the equivalence point for the weak acid.
(d) Both curves are identical beyond the equivalence point because the pH is determined by the excess $[OH^s]$.
(e) If the acid concentrations are the same, the volume of base needed to reach the equilavence point is the same.

16.122 (a)

(b) mol NaOH required =

$$\left(\frac{0.010\ \text{mol HA}}{\text{L}}\right)(0.0500\ \text{L})\left(\frac{1\ \text{mol NaOH}}{1\ \text{mol HA}}\right) = 0.000\,50\ \text{mol}$$

$$\text{vol NaOH required} = (0.000\ 50\ \text{mol})\left(\frac{1\ \text{L}}{0.010\ \text{mol}}\right) = 0.050\ \text{L} = 50\ \text{mL}$$

(c) A basic salt is present at the equivalence point; pH > 7.00

(d) Halfway to the equivalence point, the pH = pK_a = 4.00

16.123 (a) $AgBr(s) \Omega Ag^{+}(aq) + Br^{S}(aq)$

(i) HBr is a source of Br^{S} (reaction product). The solubility of AgBr is decreased.

(ii) unaffected

(iii) $AgNO_3$ is a source of Ag^{+} (reaction product). The solubility of AgBr is decreased.

(iv) NH_3 forms a complex with Ag^{+}, removing it from solution. The solubility of AgBr is increased.

(b) $BaCO_3(s) \Omega Ba^{2+}(aq) + CO_3^{2S}(aq)$

(i) HNO_3 reacts with CO_3^{2S}, removing it from the solution. The solubility of $BaCO_3$ is increased.

(ii) $Ba(NO_3)_2$ is a source of Ba^{2+} (reaction product). The solubility of $BaCO_3$ is decreased.

(iii) Na_2CO_3 is a source of CO_3^{2S} (reaction product). The solubility of $BaCO_3$ is decreased.

(iv) CH_3CO_2H reacts with CO_3^{2S}, removing it from the solution. The solubility of $BaCO_3$ is increased.

16.124 For NH_4^{+}, $K_a = \dfrac{K_w}{K_b \text{ for } NH_3} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{S10}$

$pK_a = S\log K_a = S\log(5.6 \times 10^{S10}) = 9.25$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^{+}]}; \qquad 9.40 = 9.25 + \log\frac{[NH_3]}{[NH_4^{+}]}$$

$$\log\frac{[NH_3]}{[NH_4^{+}]} = 9.40\ \text{S}\ 9.25 = 0.15; \qquad \frac{[NH_3]}{[NH_4^{+}]} = 10^{0.15} = 1.41$$

Because the volume is the same for both NH_3 and NH_4^+, $\frac{\text{mol } NH_3}{\text{mol } NH_4^+} = 1.41$.

mol NH_3 = (0.20 mol/L)(0.250 L) = 0.050 mol NH_3

$$\text{mol } NH_4^+ = \frac{\text{mol } NH_3}{1.41} = \frac{0.050}{1.41} = 0.035 \text{ mol } NH_4^+$$

$$\text{vol } NH_4^+ = (0.035 \text{ mol})\left(\frac{1 \text{ L}}{3.0 \text{ mol}}\right) = 0.012 \text{ L} = 12 \text{ mL}$$

12 mL of 3.0 M NH_4Cl must be added to 250 mL of 0.20 M NH_3 to obtain a buffer solution having a pH = 9.40.

16.125 $H_2PO_4^-(aq) + H_2O(l) \Omega H_3O^+(aq) + HPO_4^{2-}(aq)$

(a) Na_2HPO_4, source of HPO_4^{2-}, equilibrium shifts left, pH increases.
(b) Addition of the strong acid, HBr, decreases the pH.
(c) Addition of the strong base, KOH, increases the pH.
(d) There is no change in the pH with the addition of the neutral salt KI.
(e) H_3PO_4, source of $H_2PO_4^-$, equilibrium shifts right, pH decreases.
(f) Na_3PO_4, source of PO_4^{3-}, decreases $[H_3O^+]$ by forming HPO_4^{2-}, pH increases.

16.126 pH = 10.35; $[H_3O^+] = 10^{-pH} = 10^{-10.35} = 4.5 \times 10^{-11}$ M

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-11}} = 2.2 \times 10^{-4} \text{ M}$$

$$[Mg^{2+}] = \frac{[OH^-]}{2} = \frac{2.2 \times 10^{-4}}{2} = 1.1 \times 10^{-4} \text{ M}$$

$K_{sp} = [Mg^{2+}][OH^-]^2 = (1.1 \times 10^{-4})(2.2 \times 10^{-4})^2 = 5.3 \times 10^{-12}$

16.127 mmol Hg_2^{2+} = (0.010 mmol/mL)(1.0 mL) = 0.010 mmol
mmol Cl^- = (6 mmol/mL)(0.05 mL) = 0.3 mmol
Assume complete reaction.

	$Hg_2^{2+}(aq)$	+ 2 $Cl^-(aq)$	$\vert$ $Hg_2Cl_2(s)$
before reaction (mmol)	0.010	0.3	
change (mmol)	−0.010	−2(0.010)	
after reaction (mmol)	0	0.28	

$$[Cl^-] = \frac{0.28 \text{ mmol}}{1.05 \text{ mL}} = 0.27 \text{ M}$$

Allow Hg_2Cl_2 to establish a new equilibrium.

	$Hg_2Cl_2(s)$ Ω	$Hg_2^{2+}(aq)$ +	2 $Cl^-(aq)$
initial (M)		0	0.27
equil (M)		x	0.27 + 2x

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.4 \times 10^{-18} = x(0.27 + 2x)^2 \approx x(0.27)^2$

$$x = [Hg_2^{2+}] = \frac{1.4 \times 10^{-18}}{(0.27)^2} = 2 \times 10^{-17} \text{ mol/L}$$

Hg_2^{2+}, 401.18 amu
Hg_2^{2+} concentration = $(2 \times 10^{-17}$ mol/L)(401.18 g/mol) = 8×10^{-15} g/L

16.128 NaOH, 40.0 amu; $20\ g \times \frac{1\ mol}{40.0\ g} = 0.50\ mol\ NaOH$

$(0.500\ L)(1.5\ mol/L) = 0.75\ mol\ NH_4Cl$

	$NH_4^+(aq)$	+	$OH^-(aq)$	$\rightarrow$	$NH_3(aq)$	+	$H_2O(l)$
before reaction (mol)	0.75		0.50		0		
change (mol)	−0.50		−0.50		+0.50		
after reaction (mol)	0.25		0		0.50		

This reaction produces a buffer solution.

$[NH_4^+] = 0.25\ mol/0.500\ L = 0.50\ M; \quad [NH_3] = 0.50\ mol/0.500\ L = 1.0\ M$

$$pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + \log\frac{[NH_3]}{[NH_4^+]}$$

For NH_4^+, $K_a = \frac{K_w}{K_b\ for\ NH_3} = \frac{1.0\ x\ 10^{-14}}{1.8\ x\ 10^{-5}} = 5.6\ x\ 10^{-10}$; $pK_a = -\log K_a = 9.25$

$$pH = 9.25 + \log\left(\frac{1.0}{0.5}\right) = 9.55$$

16.129 (a) AgCl, $K_{sp} = [Ag^+][Cl^-] = 1.8\ x\ 10^{-10}$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8\ x\ 10^{-10}}{0.030} = 6.0\ x\ 10^{-9}\ M$$

(b) Hg_2Cl_2, $K_{sp} = [Hg_2^{2+}][Cl^-]^2 = 1.4\ x\ 10^{-18}$

$$[Cl^-] = \sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}} = \sqrt{\frac{1.4\ x\ 10^{-18}}{0.030}} = 6.8\ x\ 10^{-9}\ M$$

(c) $PbCl_2$, $K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.2\ x\ 10^{-5}$

$$[Cl^-] = \sqrt{\frac{K_{sp}}{[Pb^{2+}]}} = \sqrt{\frac{1.2\ x\ 10^{-5}}{0.030}} = 0.020\ M$$

AgCl(s) will begin to precipitate when the $[Cl^-]$ just exceeds $6.0\ x\ 10^{-9}$ M. At this Cl^- concentration, IP < K_{sp} for $PbCl_2$ so all of the Pb^{2+} will remain in solution.

16.130 For NH_4^+, $K_a = \frac{K_w}{K_b\ for\ NH_3} = \frac{1.0\ x\ 10^{-14}}{1.8\ x\ 10^{-5}} = 5.6\ x\ 10^{-10}$; $pK_a = -\log K_a = 9.25$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = 9.25 + \log\frac{(0.50)}{(0.30)} = 9.47$$

$[H_3O^+] = 10^{-pH} = 10^{-9.47} = 3.4\ x\ 10^{-10}\ M$

For MnS, $K_{spa} = \frac{[Mn^{2+}][H_2S]}{[H_3O^+]^2} = 3\ x\ 10^{10}$

$$\text{molar solubility} = [Mn^{2+}] = \frac{K_{spa}[H_3O^+]^2}{[H_2S]} = \frac{(3\ x\ 10^{10})(3.4\ x\ 10^{-10})^2}{(0.10)} = 3.5\ x\ 10^{-8}\ M$$

MnS, 87.00 amu; solubility = $(3.5\ x\ 10^{-8}\ mol/L)(87.00\ g/mol) = 3\ x\ 10^{-6}\ g/L$

16.131 pH = 9.00; $[H_3O^+] = 10^{-pH} = 10^{-9.00} = 1.0\ x\ 10^{-9}\ M$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-9}} = 1.0 \times 10^{-5}\ M$$

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$$

equil (M) x 1.0×10^{-5} (fixed by buffer)

$K_{sp} = [Mg^{2+}][OH^-]^2 = 5.6 \times 10^{-12} = x(1.0 \times 10^{-5})^2$

$$\text{molar solubility} = x = \frac{5.6 \times 10^{-12}}{(1.0 \times 10^{-5})^2} = 0.056\ M$$

16.132 60.0 mL = 0.0600 L

$$\text{mol } H_3PO_4 = 0.0600\ L \times \frac{1.00\ mol\ H_3PO_4}{1.00\ L} = 0.0600\ mol\ H_3PO_4$$

$$\text{mol LiOH} = 1.00\ L \times \frac{0.100\ mol\ LiOH}{1.00\ L} = 0.100\ mol\ LiOH$$

	$H_3PO_4(aq)$ +	$OH^-(aq)$	$H_2PO_4^-(aq)$ +	$H_2O(l)$
before reaction (mol)	0.0600	0.100	0	
change (mol)	−0.0600	−0.0600	+0.0600	
after reaction (mol)	0	0.040	0.0600	

	$H_2PO_4^-(aq)$ +	$OH^-(aq)$	$HPO_4^{2-}(aq)$ +	$H_2O(l)$
before reaction (mol)	0.0600	0.040	0	
change (mol)	−0.040	−0.040	+0.040	
after reaction (mol)	0.020	0	0.040	

The resulting solution is a buffer because it contains the conjugate acid-base pair, $H_2PO_4^-$ and HPO_4^{2-}, at acceptable buffer concentrations.

For $H_2PO_4^-$, $K_{a2} = 6.2 \times 10^{-8}$ and $pK_{a2} = -\log K_{a2} = -\log(6.2 \times 10^{-8}) = 7.21$

$$pH = pK_{a2} + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.21 + \log\frac{(0.040\ mol/1.06\ L)}{(0.020\ mol/1.06\ L)}$$

$$pH = 7.21 + \log\frac{(0.040)}{(0.020)} = 7.21 + 0.30 = 7.51$$

16.133 (a) The mixture of 0.100 mol H_3PO_4 and 0.150 mol NaOH is a buffer and contains mainly $H_2PO_4^-$ and HPO_4^{2-} from the reactions:

	$H_3PO_4(aq)$ +	$OH^-(aq)$	$H_2PO_4^-(aq)$ +	$H_2O(l)$
before (mol)	0.100	0.150	0	
change (mol)	−0.100	−0.100	+0.100	
after (mol)	0	0.050	0.100	

	$H_2PO_4^-(aq)$ +	$OH^-(aq)$	$HPO_4^{2-}(aq)$ +	$H_2O(l)$
before (mol)	0.100	0.050	0	
change (mol)	−0.050	−0.050	+0.050	
after (mol)	0.050	0	0.050	

If water were used to dilute the solution instead of HCl, the pH would be equal to pK_{a2} because $[H_2PO_4^{-}] = [HPO_4^{2-}] = 0.050 \text{ mol}/1.00 \text{ L} = 0.050 \text{ M}$

$H_2PO_4^{-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$

$pK_{a2} = -\log K_{2a} = -\log(6.2 \times 10^{-8}) = 7.21$

$$pH = pK_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]} = pK_{a2} + \log(1) = pK_{a2} = 7.21$$

The pH is lower (6.73) because the added HCl converts some HPO_4^{2-} to $H_2PO_4^{-}$.

	$HPO_4^{2-}(aq)$	+ $H_3O^{+}(aq)$	$\rightleftharpoons$ $H_2PO_4^{-}(aq)$	+ $H_2O(l)$
before (M)	0.050	x	0.050	
change (M)	−x	−x	+x	
after (M)	0.050 − x	0	0.050 + x	

$[HPO_4^{2-}] + [H_2PO_4^{-}] = (0.050 - x) + (0.050 + x) = 0.100 \text{ M}$

$$pH = pK_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^{-}]}$$

$[HPO_4^{2-}] = 0.100 - [H_2PO_4^{-}]$

$$6.73 = 7.21 + \log \frac{(0.100 - [H_2PO_4^{-}])}{[H_2PO_4^{-}]}$$

$$6.73 - 7.21 = -0.48 = \log \frac{(0.100 - [H_2PO_4^{-}])}{[H_2PO_4^{-}]}$$

$$10^{-0.48} = 0.331 = \frac{(0.100 - [H_2PO_4^{-}])}{[H_2PO_4^{-}]}$$

$(0.331)[H_2PO_4^{-}] = 0.100 - [H_2PO_4^{-}]$

$(1.331)[H_2PO_4^{-}] = 0.100$

$[H_2PO_4^{-}] = 0.100/1.331 = 0.075 \text{ M}$

$[HPO_4^{2-}] = 0.100 - [H_2PO_4^{-}] = 0.100 - 0.075 = 0.025 \text{ M}$

$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + H_2PO_4^{-}(aq) \qquad K_{a1} = 7.5 \times 10^{-3}$

$$K_{a1} = \frac{[H_3O^{+}][H_2PO_4^{-}]}{[H_3PO_4]}$$

$$[H_3PO_4] = \frac{[H_3O^{+}][H_2PO_4^{-}]}{K_{a1}}$$

$[H_3O^{+}] = 10^{-pH} = 10^{-6.73} = 1.86 \times 10^{-7} \text{ M}$

$$[H_3PO_4] = \frac{(1.86 \times 10^{-7})(0.075)}{7.5 \times 10^{-3}} = 1.9 \times 10^{-6} \text{ M}$$

(b) If distilled water were used and not HCl, the mole amounts of both $H_2PO_4^{-}$ and HPO_4^{2-} would be 0.050 mol. The HCl converted some HPO_4^{2-} to $H_2PO_4^{-}$.

	$HPO_4^{2-}(aq)$	+ $H_3O^{+}(aq)$	$\rightleftharpoons$ $H_2PO_4^{-}(aq)$	+ $H_2O(l)$
before (mol)	0.050	x	0.050	
change (mol)	−x	−x	+x	
after (mol)	0.050 − x	0	0.050 + x	

From part (a), $[HPO_4^{2S}] = 0.025$ M
mol HPO_4^{2S} = (0.025 mol/L)(1.00 L) = 0.025 mol = 0.050 S x
x = mol H_3O^+ = mol HCl inadvertently added = 0.050 S 0.025 = 0.025 mol HCl

16.134 For CH_3CO_2H, $K_a = 1.8 \times 10^{S5}$ and $pK_a = S\log K_a = S\log(1.8 \times 10^{S5}) = 4.74$
The mixture will be a buffer solution containing the conjugate acid-base pair, CH_3CO_2H and $CH_3CO_2^S$, having a pH near the pK_a of CH_3CO_2H.

$$pH = pK_a + \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$4.85 = 4.74 + \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}; \quad 4.85 \text{ S } 4.74 = \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$0.11 = \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}; \quad \frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = 10^{0.11} = 1.3$$

In the Henderson-Hasselbalch equation, moles can be used in place of concentrations because both components are in the same volume so the volume terms cancel.
20.0 mL = 0.0200 L

Let X equal the volume of 0.10 M CH_3CO_2H and Y equal the volume of 0.15 M $CH_3CO_2^S$. Therefore, X + Y = 0.0200 L and

$$\frac{Y \text{ x } [CH_3CO_2^-]}{X \text{ x } [CH_3CO_2H]} = \frac{Y\,(0.15 \text{ mol/L})}{X\,(0.10 \text{ mol/L})} = 1.3$$

X = 0.0200 S Y

$$\frac{Y\,(0.15 \text{ mol/L})}{(0.020 \text{ _ } Y)(0.10 \text{ mol/L})} = 1.3$$

$$\frac{0.15Y}{0.0020 \text{ _ } 0.10Y} = 1.3$$

0.15Y = 1.3(0.0020 S 0.10Y)
0.15Y = 0.0026 S 0.13Y
0.15Y + 0.13Y = 0.0026
0.28Y = 0.0026
Y = 0.0026/0.28 = 0.0093 L
X = 0.0200 S Y = 0.0200 S 0.0093 = 0.0107 L
X = 0.0107 L = 10.7 mL and Y = 0.0093 L = 9.3 mL
You need to mix together 10.7 mL of 0.10 M CH_3CO_2H and 9.3 mL of 0.15 M $NaCH_3CO_2$ to prepare 20.0 mL of a solution with a pH of 4.85.

16.135 $[H_3O^+] = 10^{SpH} = 10^{S2.37} = 0.004\,27$ M

$$H_3Cit(aq) + H_2O(l) \;\Omega\; H_3O^+(aq) + H_2Cit^S(aq)$$

$$K_{a1} = 7.1 \times 10^{S4} = \frac{[H_3O^+][H_2Cit^-]}{[H_3Cit]}$$

$(7.1 \times 10^{S4})[H_3Cit] = (0.004\,27)[H_2Cit^S]$
$[H_3Cit] = (0.004\,27)[H_2Cit^S]/(7.1 \times 10^{S4}) = (6.01)[H_2Cit^S]$

$H_2Cit^{s}(aq) + H_2O(l) \Omega H_3O^{+}(aq) + HCit^{2s}(aq)$

$K_{a2} = 1.7 \times 10^{s5} = \dfrac{[H_3O^{+}][HCit^{2-}]}{[H_2Cit^{-}]}$

$(1.7 \times 10^{s5})[H_2Cit^{s}] = (0.004\ 27)[HCit^{2s}]$

$[HCit^{2s}] = (1.7 \times 10^{s5})[H_2Cit^{s}]/(0.004\ 27) = (0.003\ 98)[H_2Cit^{s}]$

$[H_3Cit] + [H_2Cit^{s}] + [HCit^{2s}] + [Cit^{3s}] = 0.350$ M

Now assume $[Cit^{3s}] . 0$, so $[H_3Cit] + [H_2Cit^{s}] + [HCit^{2s}] = 0.350$ M and then by substitution:

$(6.01)[H_2Cit^{s}] + [H_2Cit^{s}] + (0.003\ 98)[H_2Cit^{s}] = 0.350$ M

$(7.01)[H_2Cit^{s}] = 0.350$ M

$[H_2Cit^{s}] = 0.350\ M/7.01 = 0.050$ M

$[H_3Cit] = (6.01)[H_2Cit^{s}] = (6.01)(0.050\ M) = 0.30$ M

$[HCit^{2s}] = (0.003\ 98)[H_2Cit^{s}] = (0.003\ 98)(0.050\ M) = 2.0 \times 10^{s4}$ M

$HCit^{2s}(aq) + H_2O(l) \Omega H_3O^{+}(aq) + Cit^{3s}(aq)$

$K_{a3} = 4.1 \times 10^{s7} = \dfrac{[H_3O^{+}][Cit^{3-}]}{[HCit^{2-}]}$

$[Cit^{3s}] = \dfrac{(K_{a3})[HCit^{2-}]}{[H_3O^{+}]} = \dfrac{(4.1 \times 10^{-7})(2.0 \times 10^{-4})}{(0.004\ 27)} = 1.9 \times 10^{s8}$ M

16.136 (a) HCl is a strong acid. HCN is a weak acid with $K_a = 4.9 \times 10^{s10}$. Before the titration, the $[H_3O^{+}] = 0.100$ M. The HCN contributes an insignificant amount of additional H_3O^{+}, so the pH = Slog$[H_3O^{+}]$ = Slog(0.100) = 1.00

(b) 100.0 mL = 0.1000 L

$\text{mol } H_3O^{+} = 0.1000\ L \times \dfrac{0.100\ \text{mol HCl}}{1.00\ L} = 0.0100\ \text{mol } H_3O^{+}$

add 75.0 mL of 0.100 M NaOH; 75.0 mL = 0.0750 L

$\text{mol } OH^{s} = 0.0750\ L \times \dfrac{0.100\ \text{mol NaOH}}{1.00\ L} = 0.00750\ \text{mol } OH^{s}$

	$H_3O^{+}(aq) + OH^{s}(aq)$	$\mid 2\ H_2O(l)$
before reaction (mol)	0.0100 0.0075	
change (mol)	S0.0075 S0.0075	
after reaction (mol)	0.0025 0	

$[H_3O^{+}] = \dfrac{0.0025\ \text{mol } H_3O^{+}}{0.1000\ L + 0.0750\ L} = 0.0143$ M

pH = Slog$[H_3O^{+}]$ = Slog(0.0143) = 1.84

(c) 100.0 mL of 0.100 M NaOH will completely neutralize all of the H_3O^{+} from 100.0 mL of 0.100 M HCl. Only NaCl and HCN remain in the solution. NaCl is a neutral salt and does not affect the pH of the solution. [HCN] changes because of dilution. Because the solution volume is doubled, [HCN] is cut in half.

[HCN] = 0.100 M/2 = 0.0500 M

	$HCN(aq)$ + $H_2O(l)$ Ω	$H_3O^+(aq)$ +	$CN^-(aq)$
initial (M)	0.0500	~0	0
change (M)	Sx	+x	+x
equil (M)	0.0500 S x	x	x

$$K_a = \frac{[H_3O^+][CN^-]}{HCN} = 4.9 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$$[H_3O^+] = x = \sqrt{(0.0500)(4.9 \times 10^{-10})} = 4.95 \times 10^{-6}\ M$$

$pH = -\log[H_3O^+] = -\log(4.95 \times 10^{-6}) = 5.31$

(d) Add an additional 25.0 mL of 0.100 M NaOH.

25.0 mL = 0.0250 L

$$\text{additional mol } OH^- = 0.0250\ L \times \frac{0.100\ mol\ NaOH}{1.00\ L} = 0.00250\ mol\ OH^-$$

$$\text{mol HCN} = 0.200\ L \times \frac{0.0500\ mol\ HCN}{1.00\ L} = 0.0100\ mol\ HCN$$

	$HCN(aq)$ +	$OH^-(aq)$ ⏐	$CN^-(aq)$ +	$H_2O(l)$
before reaction (mol)	0.0100	0.00250	0	
change (mol)	S0.00250	S0.00250	+0.00250	
after reaction (mol)	0.0075	0	0.00250	

The resulting solution is a buffer because it contains the conjugate acid-base pair, HCN and CN^-, at acceptable buffer concentrations.

For HCN, $K_a = 4.9 \times 10^{-10}$ and $pK_a = -\log K_a = -\log(4.9 \times 10^{-10}) = 9.31$

$$pH = pK_a + \log\frac{[CN^-]}{[HCN]} = 9.31 + \log\frac{(0.00250\ mol / 0.2250\ L)}{(0.0075\ mol / 0.2250\ L)}$$

$$pH = 9.31 + \log\frac{(0.00250)}{(0.0075)} = 9.31 - 0.48 = 8.83$$

16.137 (a)

	$Cd(OH)_2(s)$ Ω	$Cd^{2+}(aq)$ +	$2\ OH^-(aq)$
initial (M)		0	~0
equil (M)		x	2x

$$K_{sp} = [Cd^{2+}][OH^-]^2 = 5.3 \times 10^{-15} = (x)(2x)^2 = 4x^3$$

$$\text{molar solubility} = x = \sqrt[3]{\frac{5.3 \times 10^{-15}}{4}} = 1.1 \times 10^{-5}\ M$$

$$[OH^-] = 2x = 2(1.1 \times 10^{-5}\ M) = 2.2 \times 10^{-5}\ M$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{2.2 \times 10^{-5}} = 4.5 \times 10^{-10}\ M$$

$pH = -\log[H_3O^+] = -\log(4.5 \times 10^{-10}) = 9.35$

(b) 90.0 mL = 0.0900 L

mol HNO_3 = (0.100 mol/L)(0.0900 L) = 0.009 00 mol HNO_3

The addition of HNO_3 dissolves some $Cd(OH)_2(s)$.

$$Cd(OH)_2(s) + 2\ HNO_3(aq) \mid Cd^{2+}(aq) + 2\ H_2O(l)$$

before (mol) 0.100 0.009 00 1.1 x 10^{s5}
change (mol) S0.0045 S2(0.0045) 1.1 x 10^{s5} + 0.0045
after (mol) 0.0955 0 ~0.0045
total volume = 100.0 mL + 90.0 mL = 190.0 mL = 0.1900 L
$[Cd^{2+}]$ = 0.0045 mol/0.1900 L = 0.024 M
K_{sp} = 5.3 x 10^{s15} = $[Cd^{2+}][OH^s]^2$ = (0.024)$[OH^s]^2$

$$[OH^s] = \sqrt{\frac{5.3 \times 10^{-15}}{0.024}} = 4.7 \times 10^{s7} \text{ M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{4.7 \times 10^{-7}} = 2.1 \times 10^{s8} \text{ M}$$

pH = Slog$[H_3O^+]$ = Slog(2.1 x 10^{s8}) = 7.68

(c) volume HNO_3 = 0.0100 mol $Cd(OH)_2$ x $\frac{2 \text{ mol } HNO_3}{1 \text{ mol } Cd(OH)_2}$ x $\frac{1.00 \text{ L}}{0.100 \text{ mol}}$ x $\frac{1000 \text{ mL}}{1.00 \text{ L}}$ = 200 mL

16.138 (a) $Zn(OH)_2(s) \Omega Zn^{2+}(aq) + 2\ OH^s(aq)$
initial (M) 0 ~0
equil (M) x 2x
$K_{sp} = [Zn^{2+}][OH^s]^2 = 4.1 \times 10^{s17} = (x)(2x)^2 = 4x^3$

$$\text{molar solubility} = x = \sqrt[3]{\frac{4.1 \times 10^{-17}}{4}} = 2.2 \times 10^{s6} \text{ M}$$

(b) $[OH^s] = 2x = 2(2.2 \times 10^{s6} \text{ M}) = 4.4 \times 10^{s6}$ M

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-6}} = 2.3 \times 10^{s9} \text{ M}$$

pH = Slog$[H_3O^+]$ = Slog(2.3 x 10^{s9}) = 8.64

(c) $Zn(OH)_2(s) \Omega Zn^{2+}(aq) + 2\ OH^s(aq)$ $K_{sp} = 4.1 \times 10^{s17}$
$\underline{Zn^{2+}(aq) + 4\ OH^s(aq) \Omega Zn(OH)_4^{2s}(aq)}$ $K_f = 3 \times 10^{15}$
$Zn(OH)_2(s) + 2\ OH^s(aq) \Omega Zn(OH)_4^{2s}(aq)$ $K = K_{sp} \cong K_f = 0.123$
initial (M) 0.10 0
change (M) S2x +x
equil (M) 0.10 S 2x x

$$K = \frac{[Zn(OH)_4^{2-}]}{[OH^-]^2} = 0.123 = \frac{x}{(0.10 - 2x)^2}$$

$0.492x^2$ S 1.0492x + 0.00123 = 0
Use the quadratic formula to solve for x.

$$x = \frac{-(-1.0492) \pm \sqrt{(-1.0492)^2 - (4)(0.492)(0.00123)}}{2(0.492)} = \frac{1.0492 \pm 1.0480}{0.984}$$

x = 2.1 and 1.2 x 10^{s3}
Of the two solutions for x, only 1.2 x 10^{s3} has physical meaning because the other solution leads to a negative $[OH^s]$.
molar solubility of $Zn(OH)_4^{2s}$ in 0.10 M NaOH = x = 1.2 x 10^{s3} M

16.139 (a) $Fe(OH)_3(s) \Omega Fe^{3+}(aq) + 3\ OH^{-}(aq)$ $K_{sp} = 2.6 \times 10^{-39}$

$H_3Cit(aq) + H_2O(l) \Omega H_3O^{+}(aq) + H_2Cit^{-}(aq)$ $K_{a1} = 7.1 \times 10^{-4}$

$H_2Cit^{-}(aq) + H_2O(l) \Omega H_3O^{+}(aq) + HCit^{2-}(aq)$ $K_{a2} = 1.7 \times 10^{-5}$

$HCit^{2-}(aq) + H_2O(l) \Omega H_3O^{+}(aq) + Cit^{3-}(aq)$ $K_{a3} = 4.1 \times 10^{-7}$

$Fe^{3+}(aq) + Cit^{3-}(aq) \Omega Fe(Cit)(aq)$ $K_f = 6.3 \times 10^{11}$

$3\ [H_3O^{+}(aq) + OH^{-}(aq) \Omega 2\ H_2O(l)]$ $(1/K_w)^3 = 1.0 \times 10^{42}$

$Fe(OH)_3(s) + H_3Cit(aq) \Omega Fe(Cit)(aq) + 3\ H_2O(l)$

$K = K_{sp}\, K_{a1}\, K_{a2}\, K_{a3} K_f (1/K_w)^3 = 8.1$

(b)

	$Fe(OH)_3(s)$ +	$H_3Cit(aq)$ Ω	$Fe(Cit)(aq)$ +	$3\ H_2O(l)$
initial (M)		0.500	0	
change (M)		−x	+x	
equil (M)		0.500 − x	x	

$$K = \frac{[Fe(Cit)]}{[H_3Cit]} = 8.1 = \frac{x}{0.500 - x}$$

$8.1(0.500 - x) = x$

$4.05 - 8.1x = x$

$4.05 = 9.1x$

x = molar solubility = 4.05/9.1 = 0.45 M

Multi-Concept Problems

16.140 (a) $HA^{-}(aq) + H_2O(l) \Omega H_3O^{+}(aq) + A^{2-}(aq)$ $K_{a2} = 10^{-10}$

$HA^{-}(aq) + H_2O(l) \Omega H_2A(aq) + OH^{-}(aq)$ $K_b = \dfrac{K_w}{K_a 1} = 10^{-10}$

$2\ HA^{-}(aq) \Omega H_2A(aq) + A^{2-}(aq)$ $K = \dfrac{K_a 2}{K_a 1} = 10^{-6}$

$2\ H_2O(l) \Omega H_3O^{+}(aq) + OH^{-}(aq)$ $K_w = 1.0 \times 10^{-14}$

The principal reaction of the four is the one with the largest K, and that is the third reaction.

(b) $K_{a1} = \dfrac{[H_3O^{+}][HA^{-}]}{[H_2A]}$ and $K_{a2} = \dfrac{[H_3O^{+}][A^{2-}]}{[HA^{-}]}$

$[H_3O^{+}] = \dfrac{K_a 1\ [H_2A]}{[HA^{-}]}$ and $[H_3O^{+}] = \dfrac{K_a 2\ [HA^{-}]}{[A^{2-}]}$

$\dfrac{K_a 1\ [H_2A]}{[HA^{-}]} \times \dfrac{K_a 2\ [HA^{-}]}{[A^{2-}]} = [H_3O^{+}]^2$; $\dfrac{K_a 1 K_a 2\ [H_2A]}{[A^{2-}]} = [H_3O^{+}]^2$

Because the principal reaction is $2\ HA^{-}(aq) \Omega H_2A(aq) + A^{2-}(aq)$, $[H_2A] = [A^{2-}]$.

$K_{a1}\, K_{a2} = [H_3O^{+}]^2$

$\log K_{a1} + \log K_{a2} = 2 \log [H_3O^{+}]$

$$\frac{\log K_a1 \; + \; \log K_a2}{2} = \log[H_3O^+]; \quad \frac{-\log K_a1 \; + \; (-\log K_a2)}{2} = -\log[H_3O^+]$$

$$\frac{pK_a1 \; + \; pK_a2}{2} = pH$$

(c)

	$2\,HA^-(aq)$	$\rightleftharpoons$	$H_2A(aq)$	+	$A^{2-}(aq)$
initial (M)	1.0		0		0
change (M)	−2x		+x		+x
equil (M)	1.0 − 2x		x		x

$$K = \frac{[H_2A][A^{2-}]}{[HA^-]^2} = 1 \times 10^{-6} = \frac{x^2}{(1.0 - 2x)^2}$$

Take the square root of both sides and solve for x.

$x = [A^{2-}] = 1 \times 10^{-3}$ M

mol A^{2-} = $(1 \times 10^{-3}$ mol/L)(0.0500 L) = 5×10^{-5} mol A^{2-}

number of A^{2-} ions = $(5 \times 10^{-5}$ mol $A^{2-})(6.022 \times 10^{23}$ ions/mol) = 3×10^{19} A^{2-} ions

16.141 (a) (i)

	$en(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$enH^+(aq)$	+	$OH^-(aq)$
initial (M)	0.100				0		~0
change (M)	−x				+x		+x
equil (M)	0.100 − x				x		x

$$K_b = \frac{[enH^+][OH^-]}{[en]} = 5.2 \times 10^{-4} = \frac{(x)(x)}{0.100 - x}$$

$x^2 + (5.2 \times 10^{-4})x - (5.2 \times 10^{-5}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(5.2 \times 10^{-4}) \pm \sqrt{(5.2 \times 10^{-4})^2 - 4(1)(-5.2 \times 10^{-5})}}{2(1)} = \frac{-5.2 \times 10^{-4} \pm 0.01443}{2}$$

x = −0.0075 and 0.0070

Of the two solutions for x, only the positive value of x has physical meaning because x is the $[OH^-]$.

$[OH^-] = x = 0.0070$ M

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0070} = 1.43 \times 10^{-12} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(1.43 \times 10^{-12}) = 11.84$

(ii) (30.0 mL)(0.100 mmol/mL) = 3.00 mmol en

(15.0 mL)(0.100 mmol/mL) = 1.50 mmol HCl

Halfway to the first equivalence point, $[OH^-] = K_{b1}$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.92 \times 10^{-11} \text{ M}$$

$pH = -\log[H_3O^+] = -\log(1.92 \times 10^{-11}) = 10.72$

(iii) At the first equivalence point pH = $\frac{pK_a1 + pK_a2}{2}$ = 9.14

(iv) Halfway between the first and second equivalence points, $[OH^-] = K_{b2} = 3.7 \times 10^{-7}$ M

$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-7}} = 2.70 \times 10^{-8}$ M

$pH = -\log[H_3O^+] = -\log(2.70 \times 10^{-8}) = 7.57$

(v) At the second equivalence point only the acidic enH_2Cl_2 is in solution.

For enH_2^{2+}, $K_a = \frac{K_w}{K_b \text{ for } enH^+} = \frac{K_w}{K_b2} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-7}} = 2.70 \times 10^{-8}$

$[enH_2^{2+}] = \frac{3.00 \text{ mmol}}{(30.0 \text{ mL} + 60.0 \text{ mL})} = 0.0333$ M

	$enH_2^{2+}(aq)$ + $H_2O(l)$	Ω	$H_3O^+(aq)$ +	$enH^+(aq)$
initial (M)	0.0333		~0	0
change (M)	−x		+x	+x
equil (M)	0.0333 − x		x	x

$K_a = \frac{[H_3O^+][enH^+]}{[enH_2^{2+}]} = 2.70 \times 10^{-8} = \frac{(x)(x)}{0.0333 - x} \approx \frac{x^2}{0.0333}$

Solve for x. $x = [H_3O^+] = \sqrt{(2.70 \times 10^{-8})(0.0333)} = 3.00 \times 10^{-5}$ M

$pH = -\log[H_3O^+] = -\log(3.00 \times 10^{-5}) = 4.52$

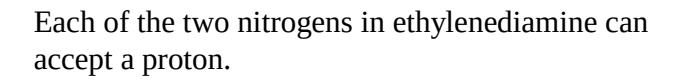
(vi) excess HCl

(75.0 mL − 60.0 mL)(0.100 mmol/mL) = 1.50 mmol HCl = 1.50 mmol H_3O^+

$[H_3O^+] = \frac{1.50 \text{ mmol}}{(30.0 \text{ mL} + 75.0 \text{ mL})} = 0.0143$ M

$pH = -\log[H_3O^+] = -\log(0.0143) = 1.84$

(b)



(c) Each nitrogen is sp^3 hybridized.

16.142 (a) The first equivalence point is reached when all the H_3O^+ from the HCl and the H_3O^+ form the first ionization of H_3PO_4 is consumed.

At the first equivalence point pH = $\frac{pK_{a1} + pK_{a2}}{2}$ = 4.66

$[H_3O^+] = 10^{-pH} = 10^{(-4.66)} = 2.2 \times 10^{-5}$ M

(88.0 mL)(0.100 mmol/mL) = 8.80 mmol NaOH are used to get to the first equivalence point

(b) mmol (HCl + H_3PO_4) = mmol NaOH = 8.8 mmol

mmol H_3PO_4 = (126.4 mL − 88.0 mL)(0.100 mmol/mL) = 3.84 mmol

mmol HCl = (8.8 − 3.84) = 4.96 mmol

$[HCl] = \frac{4.96 \text{ mmol}}{40.0 \text{ mL}} = 0.124$ M; $[H_3PO_4] = \frac{3.84 \text{ mmol}}{40.0 \text{ mL}} = 0.0960$ M

(c) 100% of the HCl is neutralized at the first equivalence point.

(d)

	$H_3PO_4(aq)$	+	$H_2O(l)$	Ω	$H_3O^+(aq)$	+	$H_2PO_4^-(aq)$
initial (M)	0.0960				0.124		0
change (M)	−x				+x		+x
equil (M)	0.0960 − x				0.124 + x		x

$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3} = \frac{(0.124 + x)(x)}{0.0960 - x}$

$x^2 + 0.132x - (7.2 \times 10^{-4}) = 0$

Use the quadratic formula to solve for x.

$x = \frac{-(0.132) \pm \sqrt{(0.132)^2 - 4(1)(-7.2 \times 10^{-4})}}{2(1)} = \frac{-0.132 \pm 0.142}{2}$

x = −0.137 and 0.005

Of the two solutions for x, only the positive value of x has physical meaning because the other solution would give a negative $[H_3O^+]$.

$[H_3O^+] = 0.124 + x = 0.124 + 0.005 = 0.129$ M

$pH = -\log[H_3O^+] = -\log(0.129) = 0.89$

(e)

(f) Bromcresol green or methyl orange are suitable indicators for the first equivalence point. Thymolphthalein is a suitable indicator for the second equivalence point.

16.143 (a) $PV = nRT$; $25^oC = 298$ K

$$n_{HCl} = \frac{PV}{RT} = \frac{\left(732 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)(1.000 \text{ L})}{\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298 \text{ K})} = 0.0394 \text{ mol HCl}$$

Na_2CO_3, 105.99 amu

$$\text{mol } Na_2CO_3 = 6.954 \text{ g } Na_2CO_3 \times \frac{1 \text{ mol } Na_2CO_3}{105.99 \text{ g } Na_2CO_3} = 0.0656 \text{ mol } Na_2CO_3$$

	$CO_3^{2-}(aq)$	+ $H_3O^+(aq)$	$HCO_3^-(aq)$	+ $H_2O(l)$
before reaction (mol)	0.0656	0.0394	0	
change (mol)	−0.0394	−0.0394	+0.0394	
after reaction (mol)	0.0656 − 0.0394	0	0.0394	

mol CO_3^{2-} = 0.0656 − 0.0394 = 0.0262 mol and mol HCO_3^- = 0.0394 mol
Therefore, we have an HCO_3^-/CO_3^{2-} buffer solution.

$$pH = pK_{a2} + \log \frac{[CO_3^{2-}]}{[HCO_3^-]} = -\log(5.6 \times 10^{-11}) + \log \frac{0.0262 \text{ mol/V}}{0.0394 \text{ mol/V}}$$

pH = 10.25 − 1.77 = 10.08

(b) mol Na^+ = 2(0.0656 mol) = 0.1312 mol
mol CO_3^{2-} = 0.0262 mol
mol HCO_3^- = 0.0394 mol
<u>mol Cl^- = 0.0394 mol</u>
total ion moles = 0.2362 mol

$$\Delta T_f = K_f \text{ A } m, \qquad \Delta T_f = \left(1.86 \frac{^oC \bullet kg}{mol}\right)\left(\frac{0.2362 \text{ mol}}{0.2500 \text{ kg}}\right) = 1.76^oC$$

Solution freezing point = $0^oC - \Delta T_f = -1.76^oC$

(c) H_2O, 18.02 amu

$$\text{mol } H_2O = 250.0 \text{ g} \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 13.87 \text{ mol } H_2O$$

$$X_{solv} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol ions}} = \frac{13.87 \text{ mol}}{13.87 \text{ mol} + 0.2362 \text{ mol}} = 0.9833$$

$P_{soln} = P_{solv} \cong X_{solv} = (23.76 \text{ mm Hg})(0.9833) = 23.36 \text{ mm Hg}$

16.144 $25^oC = 298$ K

$$\Pi = 2MRT; \quad M = \frac{\Pi}{2RT} = \frac{\left(74.4 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)}{(2)\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298 \text{ K})} = 0.00200 \text{ M}$$

$[M^+] = [X^s] = 0.00200$ M

$K_{sp} = [M^+][X^s] = (0.00200)^2 = 4.00 \times 10^{s6}$

16.145 (a) $HCO_3^s(aq) + OH^s(aq) \mid CO_3^{2s}(aq) + H_2O(l)$

(b) mol HCO_3^s = (0.560 mol/L)(0.0500 L) = 0.0280 mol HCO_3^s

mol OH^s = (0.400 mol/L)(0.0500 L) = 0.0200 mol OH^s

	$HCO_3^s(aq)$	+ $OH^s(aq)$	$\mid$ $CO_3^{2s}(aq)$	+ $H_2O(l)$
before reaction (mol)	0.0280	0.0200	0	
change (mol)	S0.0200	S0.0200	+0.0200	
after reaction (mol)	0.0280 S 0.0200	0	0.0200	

mol HCO_3^s = 0.0280 S 0.0200 = 0.0080 mol

$$[HCO_3^s] = \frac{0.0080 \text{ mol}}{0.1000 \text{ L}} = 0.080 \text{ M} \qquad [CO_3^{2s}] = \frac{0.0200 \text{ mol}}{0.1000 \text{ L}} = 0.200 \text{ M}$$

	$HCO_3^s(aq)$ + $H_2O(l)$	Ω	$H_3O^+(aq)$ +	$CO_3^{2s}(aq)$
initial (M)	0.080		~0	0.200
change (M)	Sx		+x	+x
equil (M)	0.080 S x		x	0.200 + x

$$K_a = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11} = \frac{x(0.200 + x)}{0.080 - x} \approx \frac{x(0.200)}{0.080}$$

Solve for x. $x = [H_3O^+] = 2.24 \times 10^{s11}$ M

pH = S$\log[H_3O^+]$ = S$\log(2.24 \times 10^{s11})$ = 10.65

Because this solution contains both a weak acid (HCO_3^s) and its conjugate base, the solution is a buffer.

(c) $HCO_3^s(aq) + OH^s(aq) \mid CO_3^{2s}(aq) + H_2O(l)$

$\Delta H^o_{rxn} = [\Delta H^o_f(CO_3^{2s}) + \Delta H^o_f(H_2O)]$ S $[\Delta H^o_f(HCO_3^s) + \Delta H^o_f(OH^s)]$

$\Delta H^o_{rxn} = [(1 \text{ mol})(\text{S}677.1 \text{ kJ/mol}) + (1 \text{ mol})(\text{S}285.8 \text{ kJ/mol})]$

S $[(1 \text{ mol})(\text{S}692.0 \text{ kJ/mol}) + (1 \text{ mol})(\text{S}230 \text{ kJ/mol})]$

ΔH^o_{rxn} = S 40.9 kJ

0.0200 moles each of HCO_3^s and OH^s reacted.

heat produced = q = (0.0200 mol)(40.9 kJ/mol) = 0.818 kJ = 818 J

(d) q = m x specific heat x ΔT

$$\Delta T = \frac{q}{m \times \text{specific heat}} = \frac{818\ J}{(100.0\ g)[4.18\ J/(g \bullet {}^{o}C)]} = 2.0^{o}C$$

Final temperature = $25^{o}C + 2.0^{o}C = 27^{o}C$

16.146 (a) species present initially:

NH_4^+	CO_3^{2S}	H_2O
acid	base	acid or base

$2H_2O(l)$ Ω $H_3O^+(aq) + OH^S(aq)$

$NH_4^+(aq) + H_2O(l)$ Ω $NH_3(aq) + H_3O^+(aq)$

$CO_3^{2S}(aq) + H_2O(l)$ Ω $HCO_3^S(aq) + OH^S(aq)$

NH_3, $K_b = 1.8 \times 10^{S5}$

NH_4^+, $K_a = 5.6 \times 10^{S10}$

CO_3^{2S}, $K_b = 1.8 \times 10^{S4}$

HCO_3^S, $K_a = 5.6 \times 10^{S11}$

In the mixture, proton transfer takes place from the stronger acid to the stronger base, so the principal reaction is $NH_4^+(aq) + CO_3^{2S}(aq)$ Ω $HCO_3^S(aq) + NH_3(aq)$

(b)

	$NH_4^+(aq) + OH^S(aq)$ Ω $NH_3(aq) + H_2O(l)$	$K_1 = 1/K_b(NH_3)$
	$CO_3^{2S}(aq) + H_2O(l)$ Ω $HCO_3^S(aq) + OH^S(aq)$	$K_2 = K_b(CO_3^{2S})$
	$NH_4^+(aq) + CO_3^{2S}(aq)$ Ω $HCO_3^S(aq) + NH_3(aq)$	$K = K_1 \cong K_2$

	NH_4^+	CO_3^{2S}	HCO_3^S	NH_3
initial (M)	0.16	0.080	0	0.16
change (M)	Sx	Sx	+x	+x
equil (M)	0.16 S x	0.080 S x	x	0.16 + x

$$K = \frac{[HCO_3^-][NH_3]}{[NH_4^+][CO_3^{2-}]} = \frac{1.8 \times 10^{-4}}{1.8 \times 10^{-5}} = 10 = \frac{x(0.16 + x)}{(0.16 - x)(0.080 - x)}$$

$9x^2$ S $2.56x + 0.128 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-2.56) \pm \sqrt{(-2.56)^2 - (4)(9)(0.128)}}{2(9)} = \frac{2.56 \pm 1.395}{18}$$

x = 0.220 and 0.0647

Of the two solutions for x, only 0.00647 has physical meaning because 0.220 leads to negative concentrations.

$[NH_4^+] = 0.16$ S x = 0.16 S 0.0647 = 0.0953 M = 0.095 M

$[NH_3] = 0.16 + x = 0.16 + 0.0647 = 0.225$ M = 0.22 M

$[CO_3^{2S}] = 0.080$ S x = 0.080 S 0.0647 = 0.0153 M = 0.015 M

$[HCO_3^S] = x = 0.0647$ M = 0.065 M

The solution is a buffer containing two different sets of conjugate acid-base pairs. Either pair can be used to calculate the pH.

For NH_4^+, $K_a = 5.6 \times 10^{S10}$ and $pK_a = 9.25$

$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]} = 9.25 + \log \frac{(0.225)}{(0.0953)} = 9.62$

$[H_3O^+] = 10^{-pH} = 10^{-9.62} = 2.4 \times 10^{-10}$ M

$[OH^-] = \frac{1.0 \times 10^{-14}}{2.4 \times 10^{-10}} = 4.2 \times 10^{-5}$ M

$[H_2CO_3] = \frac{[HCO_3^-][H_3O^+]}{K_a} = \frac{(0.647)(2.4 \times 10^{-10})}{(4.3 \times 10^{-7})} = 3.6 \times 10^{-4}$ M

(c) For MCO_3, IP = $[M^{2+}][CO_3^{2-}] = (0.010)(0.0153) = 1.5 \times 10^{-4}$

$K_{sp}(CaCO_3) = 5.0 \times 10^{-9}$, $10^3 K_{sp} = 5.0 \times 10^{-6}$

$K_{sp}(BaCO_3) = 2.6 \times 10^{-9}$, $10^3 K_{sp} = 2.6 \times 10^{-6}$

$K_{sp}(MgCO_3) = 6.8 \times 10^{-6}$, $10^3 K_{sp} = 6.8 \times 10^{-3}$

IP > $10^3 K_{sp}$ for $CaCO_3$ and $BaCO_3$, but IP < $10^3 K_{sp}$ for $MgCO_3$ so the $[CO_3^{2-}]$ is large enough to give observable precipitation of $CaCO_3$ and $BaCO_3$, but not $MgCO_3$.

(d) For $M(OH)_2$, IP = $[M^{2+}][OH^-]^2 = (0.010)(4.17 \times 10^{-5})^2 = 1.7 \times 10^{-11}$

$K_{sp}(Ca(OH)_2) = 4.7 \times 10^{-6}$, $10^3 K_{sp} = 4.7 \times 10^{-3}$

$K_{sp}(Ba(OH)_2) = 5.0 \times 10^{-3}$, $10^3 K_{sp} = 5.0$

$K_{sp}(Mg(OH)_2) = 5.6 \times 10^{-12}$, $10^3 K_{sp} = 5.6 \times 10^{-9}$

IP < $10^3 K_{sp}$ for all three $M(OH)_2$. None precipitate.

(e)

	$CO_3^{2-}(aq)$	+	$H_2O(l)$	Ω	$HCO_3^-(aq)$	+	$OH^-(aq)$
initial (M)	0.08				0		~0
change (M)	−x				+x		+x
equil (M)	0.08 − x				x		x

$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = 1.8 \times 10^{-4} = \frac{x^2}{(0.08 - x)}$

$x^2 + (1.8 \times 10^{-4})x - (1.44 \times 10^{-5}) = 0$

Use the quadratic formula to solve for x.

$x = \frac{-(1.8 \times 10^{-4}) \pm \sqrt{(1.8 \times 10^{-4})^2 - (4)(1)(-1.44 \times 10^{-5})}}{2(1)} = \frac{-(1.8 \times 10^{-4}) \pm 7.59 \times 10^{-3}}{2}$

x = 0.0037 and −0.0039

Of the two solutions for x, only 0.0037 has physical meaning because −0.0039 leads to negative concentrations.

$[OH^-] = x = 3.7 \times 10^{-3}$ M

For MCO_3, IP = $[M^{2+}][CO_3^{2-}] = (0.010)(0.08) = 8.0 \times 10^{-4}$

For $M(OH)_2$, IP = $[M^{2+}][OH^-]^2 = (0.010)(3.7 \times 10^{-3})^2 = 1.4 \times 10^{-7}$

Comparing IP=s here and $10^3 K_{sp}$=s in (c) and (d) above, Ca^{2+} and Ba^{2+} cannot be separated from Mg^{2+} using 0.08 M Na_2CO_3. Na_2CO_3 is more basic than $(NH_4)_2CO_3$ and $Mg(OH)_2$ would precipitate along with $CaCO_3$ and $BaCO_3$.

16.147 (a) H_2SO_4, 98.09 amu

Assume 1.00 L = 1000 mL of solution.

mass of solution = (1000 mL)(1.836 g/mL) = 1836 g

mass H_2SO_4 = (0.980)(1836 g) = 1799 g H_2SO_4

mol H_2SO_4 = 1799 g H_2SO_4 x $\frac{1\ mol\ H_2SO_4}{98.09\ g\ H_2SO_4}$ = 18.3 mol H_2SO_4

[H_2SO_4] = 18.3 mol/ 1.00 L = 18.3 M

(b) Na_2CO_3, 105.99 amu; 1 kg = 1000 g = 2.2046 lb

$H_2SO_4(aq) + Na_2CO_3(s) \mid Na_2SO_4(aq) + H_2O(l) + CO_2(g)$

mass H_2SO_4 = (0.980)(36 tons) x $\frac{2000\ lb}{1\ ton}$ x $\frac{1000\ g}{2.2046\ lb}$ = 3.20×10^7 g H_2SO_4

mol H_2SO_4 = 3.20×10^7 g H_2SO_4 x $\frac{1\ mol\ H_2SO_4}{98.09\ g\ H_2SO_4}$ = 3.26×10^5 mol H_2SO_4

mass Na_2CO_3 = 3.26×10^5 mol H_2SO_4 x $\frac{1\ mol\ Na_2CO_3}{1\ mol\ H_2SO_4}$ x $\frac{105.99\ g\ Na_2CO_3}{1\ mol\ Na_2CO_3}$ x $\frac{1\ kg}{1000\ g}$ = 3.5×10^4 kg Na_2CO_3

(c) mol CO_2 = 3.26×10^5 mol H_2SO_4 x $\frac{1\ mol\ CO_2}{1\ mol\ H_2SO_4}$ = 3.26×10^5 mol CO_2

$18^oC = 18 + 273 = 291$ K

PV = nRT

$$V = \frac{nRT}{P} = \frac{(3.26 \times 10^5\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(291\ K)}{\left(745\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)} = 7.9 \times 10^6\ L$$

16.148 $Pb(CH_3CO_2)_2$, 325.29 amu; PbS, 239.27 amu

(a) mass PbS = (2 mL)(1 g/mL)(0.003) x $\frac{1\ mol\ Pb(CH_3CO_2)_2}{325.29\ g\ Pb(CH_3CO_2)_2}$ x $\frac{1\ mol\ PbS}{1\ mol\ Pb(CH_3CO_2)_2}$ x $\frac{239.27\ g\ PbS}{1\ mol\ PbS}$ x (30/100) = 0.0013 g

= 1.3 mg PbS per dye application

(b) $[H_3O^+] = 10^{-pH} = 10^{-5.50} = 3.16 \times 10^{-6}$ M

	$PbS(s) + 2\ H_3O^+(aq)$	Ω	$Pb^{2+}(aq) + H_2S(aq) + 2\ H_2O(l)$
initial (M)	3.16×10^{-6}		0 0
change (M)	−2x		+x +x
equil (M)	$3.16 \times 10^{-6} - 2x$		x x

$$K_{spa} = \frac{[Pb^{2+}][H_2S]}{[H_3O^+]^2} = \frac{x^2}{(3.16 \times 10^{-6} - 2x)^2} \approx \frac{x^2}{(3.16 \times 10^{-6})^2} = 3 \times 10^{-7}$$

$x^2 = (3.16 \times 10^{-6})^2(3 \times 10^{-7}) = 3.0 \times 10^{-18}$

$x = 1.7 \times 10^{-9}$ M = [Pb^{2+}] for a saturated solution.

mass of PbS dissolved per washing =

(3 gal)(3.7854 L/1 gal)(1.7 x 10^{s9} mol/L) x $\frac{239.27\ g\ PbS}{1\ mol\ PbS}$ = 4.7 x 10^{s6} g PbS/washing

Number of washings required to remove 50% of the PbS from one application =

$$\frac{(0.0013\ g\ PbS)(50/100)}{(4.7\ x\ 10^{-6}\ g\ PbS/washing)} = 1.4\ x\ 10^{2}$$

washings

(c) The number of washings does not look reasonable. It seems too high considering that frequent dye application is recommended. If the PbS is located mainly on the surface of the hair, as is believed to be the case, solid particles of PbS can be lost by abrasion during shampooing.

17 Thermodynamics: Entropy, Free Energy, and Equilibrium

17.1 (a) spontaneous; (b), (c), and (d) nonspontaneous

17.2 (a) $H_2O(g) \rightarrow H_2O(l)$
A liquid is more ordered than a gas. Therefore, ΔS is negative.
(b) $I_2(g) \rightarrow 2\ I(g)$
ΔS is positive because the reaction increases the number of gaseous particles from 1 mol to 2 mol.
(c) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
ΔS is positive because the reaction increases the number of gaseous molecules.
(d) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
A solid is more ordered than +1 and -1 charged ions in an aqueous solution. Therefore, ΔS is negative.

17.3 (a) $A_2 + AB_3 \rightarrow 3\ AB$
(b) ΔS is positive because the reaction increases the number of gaseous molecules.

17.4 (a) disordered N_2O
(b) silica glass (amorphous solid, more disorder)
(c) 1 mole N_2 at STP (larger volume, more disorder)
(d) 1 mole N_2 at 273 K and 0.25 atm (larger volume, more disorder)

17.5 $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$\Delta S^o = [S^o(CaO) + S^o(CO_2)] - S^o(CaCO_3)$
$\Delta S^o = [(1\ mol)(39.7\ J/(K \cdot mol)) + (1\ mol)(213.6\ J/(K \cdot mol))]$
$- (1\ mol)(92.9\ J/(K \cdot mol)) = +160.4\ J/K$

17.6 From Problem 17.5, $\Delta S_{sys} = \Delta S^o = 160.4\ J/K$
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
$\Delta H^o = [\Delta H^o_f(CaO) + \Delta H^o_f(CO_2)] - \Delta H^o_f(CaCO_3)$
$\Delta H^o = [(1\ mol)(-635.1\ kJ/mol) + (1\ mol)(-393.5\ kJ/mol)]$
$- (1\ mol)(-1206.9\ kJ/mol) = +178.3\ kJ$

$$\Delta S_{surr} = \frac{-\Delta H^o}{T} = \frac{-178{,}300\ J}{298\ K} = -598\ J/K$$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 160.4\ J/K + (-598\ J/K) = -438\ J/K$
Because ΔS_{total} is negative, the reaction is not spontaneous under standard-state conditions at 25°C.

17.7 (a) $\Delta G = \Delta H - T\Delta S = 57.1\ kJ - (298\ K)(0.1758\ kJ/K) = +4.7\ kJ$
Because $\Delta G > 0$, the reaction is nonspontaneous at 25°C (298 K)

(b) Set $\Delta G = 0$ and solve for T.

$0 = \Delta H - T\Delta S; \quad T = \frac{\Delta H}{\Delta S} = \frac{57.1 \text{ kJ}}{0.1758 \text{ kJ/K}} = 325 \text{ K} = 52^{o}\text{C}$

17.8 (a) $\Delta G = \Delta H - T\Delta S = 58.5 \text{ kJ/mol} - (598 \text{ K})[0.0929 \text{ kJ/(K} \cdot \text{mol)}] = +2.9 \text{ kJ/mol}$
Because $\Delta G > 0$, Hg does not boil at 325°C and 1 atm.
(b) The boiling point (phase change) is associated with an equilibrium. Set $\Delta G = 0$ and solve for T, the boiling point.

$0 = \Delta H_{vap} - T\Delta S_{vap}; \quad T_{bp} = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{58.5 \text{ kJ/mol}}{0.0929 \text{ kJ/(K} \bullet \text{ mol)}} = 630 \text{ K} = 357^{o}\text{C}$

17.9 $\Delta H < 0$ (reaction involves bond making - exothermic)
$\Delta S < 0$ (the reaction becomes more ordered in going from reactants (2 atoms) to products (1 molecule)
$\Delta G < 0$ (the reaction is spontaneous)

17.10 From Problems 17.5 and 17.6: $\Delta H^{o} = 178.3$ kJ and $\Delta S^{o} = 160.4$ J/K = 0.1604 kJ/K
(a) $\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = 178.3 \text{ kJ} - (298 \text{ K})(0.1604 \text{ kJ/K}) = +130.5 \text{ kJ}$
(b) Because $\Delta G > 0$, the reaction is nonspontaneous at 25°C (298 K).
(c) Set $\Delta G = 0$ and solve for T, the temperature above which the reaction becomes spontaneous.

$0 = \Delta H - T\Delta S; \quad T = \frac{\Delta H}{\Delta S} = \frac{178.3 \text{ kJ}}{0.1604 \text{ kJ/K}} = 1112 \text{ K} = 839^{o}\text{C}$

17.11 $2\ AB_2 \rightarrow A_2 + 2\ B_2$
(a) ΔS^{o} is positive because the reaction increases the number of molecules.
(b) ΔH^{o} is positive because the reaction is endothermic.
$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$
For the reaction to be spontaneous, ΔG^{o} must be negative. This will only occur at high temperature where $T\Delta S^{o}$ is greater than ΔH^{o}.

17.12 (a) $CaC_2(s) + 2\ H_2O(l) \rightarrow C_2H_2(g) + Ca(OH)_2(s)$
$\Delta G^{o} = [\Delta G^{o}_f(C_2H_2) + \Delta G^{o}_f(Ca(OH)_2)] - [\Delta G^{o}_f(CaC_2) + 2\ \Delta G^{o}_f(H_2O)]$
$\Delta G^{o} = [(1 \text{ mol})(209.2 \text{ kJ/mol}) + (1 \text{ mol})(-898.6 \text{ kJ/mol})]$
$- [(1 \text{ mol})(-64.8 \text{ kJ/mol}) + (2 \text{ mol})(-237.2 \text{ kJ/mol})] = -150.2 \text{ kJ}$
This reaction can be used for the synthesis of C_2H_2 because $\Delta G < 0$.
(b) It is not possible to synthesize acetylene from solid graphite and gaseous H_2 at 25°C and 1 atm because $\Delta G^{o}_f(C_2H_2) > 0$.

17.13 $C(s) + 2\ H_2(g) \rightarrow C_2H_4(g)$

$Q_p = \frac{P_{C_2H_4}}{(P_{H_2})^2} = \frac{(0.10)}{(100)^2} = 1.0 \times 10^{-5}$

$\Delta G = \Delta G^{o} + RT \ln Q_p$

$\Delta G = 68.1 \text{ kJ/mol} + [8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](298 \text{ K})\ln(1.0 \times 10^{-5}) = +39.6 \text{ kJ/mol}$
Because $\Delta G > 0$, the reaction is spontaneous in the reverse direction.

17.14 $\Delta G = \Delta G^o + RT \ln Q$ and $\Delta G^o = 15$ kJ

For $A_2(g) + B_2(g) = 2\,AB(g)$, $Q_p = \dfrac{(P_{AB})^2}{(P_{A_2})(P_{B_2})}$

Let the number of molecules be proportional to the partial pressure.
(1) $Q_p = 1.0$ (2) $Q_p = 0.0667$ (3) $Q_p = 18$
(a) Reaction (3) has the largest ΔG because Q_p is the largest. Reaction (2) has the smallest ΔG because Q_p is the smallest.
(b) $\Delta G = \Delta G^o = 15$ kJ because $Q_p = 1$ and ln (1) = 0.

17.15 From Problem 17.10, $\Delta G^o = +130.5$ kJ
$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-130.5 \text{ kJ/mol}}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = -52.7$$

$K_p = e^{-52.7} = 1 \times 10^{-23}$

17.16 $H_2O(l) \rightleftharpoons H_2O(g)$
$K_p = P_{H_2O}$; K_p is equal to the vapor pressure for H_2O.
$\Delta G^o = \Delta G^o_f(H_2O(g)) - \Delta G^o_f(H_2O(l))$
$\Delta G^o = (1 \text{ mol})(-228.6 \text{ kJ/mol}) - (1 \text{ mol})(-237.2 \text{ kJ/mol}) = +8.6 \text{ kJ}$
$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-8.6 \text{ kJ/mol}}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = -3.5$$

$K_p = P_{H_2O} = e^{-3.5} = 0.03$ atm

17.17 $\Delta G^o = -RT \ln K = -[8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](298 \text{ K}) \ln (1.0 \times 10^{-14}) = 80 \text{ kJ/mol}$

17.18 Photosynthetic cells in plants use the sun's energy to make glucose, which is then used by animals as their primary source of energy. The energy an animal obtains from glucose is then used to build and organize complex molecules, resulting in a decrease in entropy for the animal. At the same time, however, the entropy of the surroundings increases as the animal releases small, simple waste products such as CO_2 and H_2O. Furthermore, heat is released by the animal, further increasing the entropy of the surroundings. Thus, an organism pays for its decrease in entropy by increasing the entropy of the rest of the universe.

17.19 You would expect to see violations of the second law if you watched a movie run backwards. Consider an action-adventure movie with a lot of explosions. An explosion is a spontaneous process that increases the entropy of the universe. You would see an explosion go backwards if you run the the movie backwards but this is impossible because it would decrease the entropy of the universe.

Understanding Key Concepts

17.20 (a)

(b) $\Delta H = 0$ (no heat is gained or lost in the mixing of ideal gases)
$\Delta S > 0$ (the mixture of the two gases is more disordered)
$\Delta G < 0$ (the mixing of the two gases is spontaneous)
(c) For an isolated system, $\Delta S_{surr} = 0$ and $\Delta S_{sys} = \Delta S_{Total} > 0$ for the spontaneous process.
(d) $\Delta G > 0$ and the process is nonspontaneous.

17.21 $\Delta H > 0$ (heat is absorbed during sublimation)
$\Delta S > 0$ (gas is more disordered than solid)
$\Delta G < 0$ (the reaction is spontaneous)

17.22 $\Delta H < 0$ (heat is lost during condensation)
$\Delta S < 0$ (liquid is more ordered than vapor)
$\Delta G < 0$ (the reaction is spontaneous)

17.23 $\Delta H = 0$ (system is an ideal gas at constant temperature)
$\Delta S < 0$ (there is more order in the smaller volume)
$\Delta G > 0$ (compression of a gas is not spontaneous)

17.24 (a) $2\ A_2 + B_2 \rightarrow 2\ A_2B$
(b) $\Delta H < 0$ (because ΔS is negative, ΔH must also be negative in order for ΔG to be negative)
$\Delta S < 0$ (the reaction becomes more ordered in going from reactants (3 molecules) to products (2 molecules))
$\Delta G < 0$ (the reaction is spontaneous)

17.25 (a) For <u>initial state 1</u>, $Q_p < K_p$
(more reactant (A_2) than product (A) compared to the equilibrium state)
For <u>initial state 2</u>, $Q_p > K_p$
(more product (A) than reactant (A_2) compared to the equilibrium state)

(b) $\Delta H > 0$ (reaction involves bond breaking - endothermic)
$\Delta S > 0$ (equilibrium state is more disordered than initial state 1)
$\Delta G < 0$ (reaction spontaneously proceeds toward equilibrium)

(c) $\Delta H < 0$ (reaction involves bond making - exothermic)
$\Delta S < 0$ (equilibrium state is more ordered than initial state 2)

$\Delta G < 0$ (reaction spontaneously proceeds toward equilibrium)

(d) State 1 lies to the left of the minimum in Figure 17.10. State 2 lies to the right of the minimum.

17.26 (a) $\Delta H^o > 0$ (reaction involves bond breaking - endothermic)
$\Delta S^o > 0$ (2 A's are more disordered than A_2)
(b) ΔS^o is for the complete conversion of 1 mole of A_2 in its standard state to 2 moles of A in its standard state.
(c) There is not enough information to say anything about the sign of ΔG^o. ΔG^o decreases (becomes less positive or more negative) as the temperature increases.
(d) K_p increases as the temperature increases. As the temperature increases there will be more A and less A_2.
(e) $\Delta G = 0$ at equilibrium.

17.27 (a) Because the free energy decreases as pure reactants form products and also decreases as pure products form reactants, the free energy curve must go through a minimum somewhere between pure reactants and pure products. At the minimum point, $\Delta G = 0$ and the system is at equilibrium.
(b) The minimum in the plot is on the left side of the graph because $\Delta G^o > 0$ and the equilibrium composition is rich in reactants.

17.28 $\Delta G^o = -RT \ln K$ where $K = \frac{[X]}{[A]}$ or $\frac{[Y]}{[A]}$ or $\frac{[Z]}{[A]}$
Let the number of molecules be proportional to the concentration.
(1) K = 1, ln K = 0, and $\Delta G^o = 0$.
(2) K > 1, ln K is positive, and ΔG^o is negative.
(3) K < 1, ln K is negative, and ΔG^o is positive.

17.29 The equilibrium mixture is richer in reactant A at the higher temperature. This means the reaction is exothermic ($\Delta H < 0$). At 25°C, $\Delta G^o < 0$ because K > 1 and at 45°C, $\Delta G^o > 0$ because K < 1. Using the relationship. $\Delta G^o = \Delta H^o - T\Delta S^o$, with $\Delta H^o < 0$, ΔG^o will become positive at the higher temperature only if ΔS^o is negative.

Additional Problems
Spontaneous Processes

17.30 A spontaneous process is one that proceeds on its own without any external influence.
For example: $H_2O(s) \rightarrow H_2O(l)$ at 25°C
A nonspontaneous process takes place only in the presence of some continuous external influence.
For example: $2\ NaCl(s) \rightarrow 2\ Na(s) + Cl_2(g)$

17.31 Spontaneous does not mean instantaneous. Even though the decomposition can occur (is spontaneous), the rate of decomposition is determined by the kinetics of the reaction.

17.32 (a) and (d) nonspontaneous; (b) and (c) spontaneous

17.33 (a) and (c) spontaneous; (b) and (d) nonspontaneous.

17.34 (b) and (d) spontaneous (because of the large positive K_p's)

17.35 (a) and (d) nonspontaneous (because of the small K's).

Entropy

17.36 Molecular randomness or disorder is called entropy. For the following reaction, the entropy (disorder) increases: $H_2O(s) \rightarrow H_2O(l)$ at 25^oC.

17.37 Exothermic reactions can become nonspontaneous at high temperatures if ΔS is negative. Endothermic reactions can become spontaneous at high temperatures if ΔS is positive.

17.38 (a) + (solid → gas) (b) - (liquid → solid)
(c) - (aqueous ions → solid) (d) + ($CO_2(aq) \rightarrow CO_2(g)$)

17.39 (a) + (increase in moles of gas)
(b) - (decrease in moles of gas and formation of liquid)
(c) + (aqueous ions to gas)
(d) - (decrease in moles of gas)

17.40 (a) - (liquid → solid)
(b) - (decrease in number of O_2 molecules)
(c) + (gas is more disordered in larger volume)
(d) - (aqueous ions → solid)

17.41 (a) + (solid dissolved in water) (b) + (increase in moles of gas)
(c) + (mixed gases are more disordered) (d) + (liquid to gas)

17.42 $S = k \ln W$, $k = 1.38 \times 10^{-23}$ J/K
(a) $S = (1.38 \times 10^{-23} \text{ J/K}) \ln (4^{12}) = 2.30 \times 10^{-22}$ J/K
(b) $S = (1.38 \times 10^{-23} \text{ J/K}) \ln (4^{120}) = 2.30 \times 10^{-21}$ J/K
(c) $S = (1.38 \times 10^{-23} \text{ J/K}) \ln (4^{6.02 \times 10^{23}}) = 11.5$ J/K
If all C–D bonds point in the same direction, S = 0.

17.43 $S = k \ln W$, $k = 1.38 \times 10^{-23}$ J/K
(a) $W = 1$; $S = k \ln (1) = 0$
(b) $W = 3^2 = 9$; $S = k \ln (3^2) = 3.03 \times 10^{-23}$ J/K
(c) $W = 1$; $S = k \ln (1) = 0$
(d) $W = 3^3 = 27$; $S = k \ln (3^3) = 4.55 \times 10^{-23}$ J/K
(e) $W = 1$; $S = k \ln (1) = 0$
(f) $W = 3^{6.02 \times 10^{23}}$; $S = k \ln (3^{6.02 \times 10^{23}}) = 9.13$ J/K

$\Delta S = R \ln\left(\frac{V_f}{V_i}\right) = (8.314 \text{ J/K})\ln 3 = 9.13 \text{ J/K}$ The results are the same.

17.44 (a) H_2 at 25°C in 50 L (larger volume)
(b) O_2 at 25°C, 1 atm (larger volume)
(c) H_2 at 100°C, 1 atm (larger volume and higher T)
(d) CO_2 at 100°C, 0.1 atm (larger volume and higher T)

17.45 (a) ice at 0°C, because of the higher temperature.
(b) N_2 at STP, because it has the larger volume.
(c) N_2 at 0°C and 50 L, because it has the larger volume.
(d) water vapor at 150°C and 1 atm, because it has a larger volume and higher temperature.

Standard Molar Entropies and Standard Entropies of Reaction

17.46 The standard molar entropy of a substance is the entropy of 1 mol of the pure substance at 1 atm pressure and 25°C.
$\Delta S^o = S^o(\text{products}) - S^o(\text{reactants})$

17.47 (a) Units of $S^o = \frac{J}{K \bullet mol}$ (b) Units of ΔS^o = J/K
Standard molar entropies are called absolute entropies because they are measured with respect to an absolute reference point, the entropy of the substance at 0 K.
$S^o = 0 \frac{J}{K \bullet mol}$ at T = 0 K.

17.48 (a) $C_2H_6(g)$; more atoms/molecule
(b) $CO_2(g)$; more atoms/molecule
(c) $I_2(g)$; gas is more disordered than the solid
(d) $CH_3OH(g)$; gas is more disordered than the liquid.

17.49 (a) $NO_2(g)$; more atoms/molecule
(b) $CH_3CO_2H(l)$; more atoms/molecule
(c) $Br_2(l)$; liquid is more disordered than the solid
(d) $SO_3(g)$; gas is more disordered than the solid

17.50 (a) $2\ H_2O_2(l) \rightarrow 2\ H_2O(l) + O_2(g)$
$\Delta S^o = [2\ S^o(H_2O(l)) + S^o(O_2)] - 2\ S^o(H_2O_2)$
$\Delta S^o = [(2 \text{ mol})(69.9 \text{ J/(K} \cdot \text{mol)}) + (1 \text{ mol})(205.0 \text{ J/(K} \cdot \text{mol)})]$
$- (2 \text{ mol})(110 \text{ J/(K} \cdot \text{mol)}) = +125 \text{ J/K}$ (+, because moles of gas increase)

(b) $2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl(s)$
$\Delta S^o = 2\ S^o(NaCl) - [2\ S^o(Na) + S^o(Cl_2)]$
$\Delta S^o = (2 \text{ mol})(72.1 \text{ J/(K} \cdot \text{mol)}) - [(2 \text{ mol})(51.2 \text{ J/(K} \cdot \text{mol)}) + (1 \text{ mol})(223.0 \text{ J/(K} \cdot \text{mol)})]$
$\Delta S^o = -181.2 \text{ J/K}$ (-, because moles of gas decrease)

(c) $2\ O_3(g) \rightarrow 3\ O_2(g)$
$\Delta S^o = 3\ S^o(O_2) - 2\ S^o(O_3)$
$\Delta S^o = (3\ mol)(205.0\ J/(K \cdot mol)) - (2\ mol)(238.8\ J/(K \cdot mol))$
$\Delta S^o = +137.4\ J/K$ (+, because moles of gas increase)
(d) $4\ Al(s) + 3\ O_2(g) \rightarrow 2\ Al_2O_3(s)$
$\Delta S^o = 2\ S^o(Al_2O_3) - [4\ S^o(Al) + 3\ S^o(O_2)]$
$\Delta S^o = (2\ mol)(50.9\ J/(K \cdot mol)) - [(4\ mol)(28.3\ J/(K \cdot mol)) + (3\ mol)(205.0\ J/(K \cdot mol))]$
$\Delta S^o = -626.4\ J/K$ (-, because moles of gas decrease)

17.51 (a) $2\ S(s) + 3\ O_2(g) \rightarrow 2\ SO_3(g)$
$\Delta S^o = 2\ S^o(SO_3) - [2\ S^o(S) + 3\ S^o(O_2)]$
$\Delta S^o = (2\ mol)(256.6\ J/(K \cdot mol)) - [(2\ mol)(31.8\ J/(K \cdot mol)) + (3\ mol)(205.0\ J/(K \cdot mol))]$
$\Delta S^o = -165.4\ J/K$ (-, because moles of gas decrease)
(b) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
$\Delta S^o = S^o(H_2SO_4) - [S^o(SO_3) + S^o(H_2O)]$
$\Delta S^o = (1\ mol)(20\ J/(K \cdot mol)) - [(1\ mol)(256.6\ J/(K \cdot mol)) + (1\ mol)(69.9\ J/(K \cdot mol))]$
$\Delta S^o = -306\ J/K$ (-, because of the conversion of a gas and water to an aqueous solution)
(c) $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$
$\Delta S^o = [S^o(Ag^+) + S^o(Cl^-)] - S^o(AgCl)]$
$\Delta S^o = [(1\ mol)(72.7\ J/(K \cdot mol)) + (1\ mol)(56.5\ J/(K \cdot mol))] - (1\ mol)(96.2\ J/(K \cdot mol))]$
$\Delta S^o = +33.0\ J/K$ (+, because a solid is converted to ions in aqueous solution)
(d) $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(g)$
$\Delta S^o = [S^o(N_2O) + 2\ S^o(H_2O)] - S^o(NH_4NO_3)$
$\Delta S^o = [(1\ mol)(219.7\ J/(K \cdot mol)) + (2\ mol)(188.7\ J/(K \cdot mol))] - (1\ mol)(151.1\ J/(K \cdot mol))$
$\Delta S^o = +446.0\ J/K$ (+, because moles of gas increase)

Entropy and the Second Law of Thermodynamics

17.52 In any spontaneous process, the total entropy of a system and its surroundings always increases.

17.53 For a spontaneous process, $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$. For an isolated system, $\Delta S_{surr} = 0$, and so $\Delta S_{sys} > 0$ is the criterion for spontaneous change. An example of a spontaneous process in an isolated system is the mixing of two gases.

17.54 $\Delta S_{surr} = \dfrac{-\Delta H}{T}$; the temperature (T) is always positive.
(a) For an exothermic reaction, ΔH is negative and ΔS_{surr} is positive.
(b) For an endothermic reaction, ΔH is positive and ΔS_{surr} is negative.

17.55 $\Delta S_{surr} \propto \dfrac{1}{T}$
Consider the surroundings as an infinitely large constant-temperature bath to which heat can be added without changing its temperature. If the surroundings have a low temperature, they have only a small amount of disorder, in which case addition of a given

quantity of heat results in a substantial increase in the amount of disorder (a relatively large value of ΔS_{surr}). If the surroundings have a high temperature, they already have a large amount of disorder, and addition of the same quantity of heat produces only a marginal increase in the amount of disorder (a relatively small value of ΔS_{surr}). Thus, we expect ΔS_{surr} to vary inversely with temperature.

17.56 $N_2(g) + 2\ O_2(g) \rightarrow N_2O_4(g)$

$\Delta H^o = \Delta H^o_f(N_2O_4) = 9.16$ kJ

$\Delta S_{sys} = \Delta S^o = S^o(N_2O_4) - [S^o(N_2) + 2\ S^o(O_2)]$

$\Delta S_{sys} = (1\text{ mol})(304.2\text{ J/(K}\cdot\text{ mol)})$

$- [(1\text{ mol})(191.5\text{ J/(K} \cdot \text{ mol)}) + (2\text{ mol})(205.0\text{ J/(K} \cdot \text{ mol)})] = -297.3$ J/K

$$\Delta S_{surr} = \frac{-\Delta H^o}{T} = \frac{-9.16\text{ kJ}}{298\text{ K}} = -0.0307\text{ kJ/K} = -30.7\text{ J/K}$$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -297.3$ J/K + (-30.7 J/K) = -328.0 J/K

Because $\Delta S_{total} < 0$, the reaction is nonspontaneous.

17.57 $Cu_2S(s) + O_2(g) \rightarrow 2\ Cu(s) + SO_2(g)$

$\Delta H^o = \Delta H^o_f(SO_2) - \Delta H^o_f(Cu_2S)$

$\Delta H^o = (1\text{ mol})(-296.8\text{ kJ/mol}) - (1\text{ mol})(-79.5\text{ kJ/mol}) = -217.3$ kJ

$\Delta S_{sys} = \Delta S^o = [2\ S^o(Cu) + S^o(SO_2)] - [S^o(Cu_2S) + S^o(O_2)]$

$\Delta S_{sys} = [(2\text{ mol})(33.1\text{ J/(K} \cdot \text{ mol)}) + (1\text{ mol})(248.1\text{ J/(K} \cdot \text{ mol)})]$

$- [(1\text{ mol})(120.9\text{ J/(K} \cdot \text{ mol)}) + (1\text{ mol})(205.0\text{ J/(K} \cdot \text{ mol)})] = -11.6$ J/K

$$\Delta S_{surr} = -\Delta H^o \text{ over } T = \frac{-(-217{,}300\text{ J})}{298.15\text{ K}} = +728.8\text{ J/K}$$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -11.6$ J/K + 728.8 J/K = +717.2 J/K

Because ΔS_{total} is positive, the reaction is spontaneous under standard-state conditions at 25°C.

17.58 (a) $$\Delta S_{surr} = \frac{-\Delta H_{vap}}{T} = \frac{-30{,}700\text{ J/mol}}{343\text{ K}} = -89.5\text{ J/(K} \cdot \text{ mol)}$$

$\Delta S_{total} = \Delta S_{vap} + \Delta S_{surr} = 87.0\text{ J/(K} \cdot \text{ mol)} + (-89.5\text{ J/(K} \cdot \text{ mol)}) = -2.5\text{ J/(K} \cdot \text{ mol)}$

(b) $$\Delta S_{surr} = \frac{-\Delta H_{vap}}{T} = \frac{-30{,}700\text{ J/mol}}{353\text{ K}} = -87.0\text{ J/(K} \cdot \text{ mol)}$$

$\Delta S_{total} = \Delta S_{vap} + \Delta S_{surr} = 87.0\text{ J/(K} \cdot \text{ mol)} + (-87.0\text{ J/(K} \cdot \text{ mol)}) = 0$

(c) $$\Delta S_{surr} = \frac{-\Delta H_{vap}}{T} = \frac{-30{,}700\text{ J/mol}}{363\text{ K}} = -84.6\text{ J/(K} \cdot \text{ mol)}$$

$\Delta S_{total} = \Delta S_{vap} + \Delta S_{surr} = 87.0\text{ J/(K} \cdot \text{ mol)} + (-84.6\text{ J/(K} \cdot \text{ mol)}) = +2.4\text{ J/(K} \cdot \text{ mol)}$

Benzene does not boil at 70°C (343 K) because ΔS_{total} is negative.

The normal boiling point for benzene is 80°C (353 K), where $\Delta S_{total} = 0$.

17.59 (a) $\Delta S_{surr} = \dfrac{-\Delta H_{fusion}}{T} = \dfrac{-30{,}200\ J/mol}{1050\ K} = -28.8\ J/(K \cdot mol)$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 28.1\ J/(K \cdot mol) + (-28.8\ J/(K \cdot mol)) = -0.7\ J/(K \cdot mol)$

(b) $\Delta S_{surr} = \dfrac{-\Delta H_{fusion}}{T} = \dfrac{-30{,}200\ J/mol}{1075\ K} = -28.1\ J/(K \cdot mol)$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 28.1\ J/(K \cdot mol) + (-28.1\ J/(K \cdot mol)) = 0$

(c) $\Delta S_{surr} = \dfrac{-\Delta H_{fusion}}{T} = \dfrac{-30{,}200\ J/mol}{1100\ K} = -27.5\ J/(K \cdot mol)$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 28.1\ J/(K \cdot mol) + (-27.5\ J/(K \cdot mol)) = +0.6\ J/(K \cdot mol)$
NaCl melts at 1100 K because $\Delta S_{total} > 0$.
The melting point of NaCl is 1075 K, where $\Delta S_{total} = 0$.

Free Energy

17.60

ΔH	ΔS	ΔG = ΔH - TΔS	Reaction Spontaneity
-	+	-	Spontaneous at all temperatures
-	-	- or +	Spontaneous at low temperatures where $\lvert \Delta H \rvert > \lvert T\Delta S \rvert$
			Nonspontaneous at high temperatures where $\lvert \Delta H \rvert < \lvert T\Delta S \rvert$
+	-	+	Nonspontaneous at all temperatures
+	+	- or +	Spontaneous at high temperatures where $T\Delta S > \Delta H$
			Nonspontaneous at low temperature where $T\Delta S < \Delta H$

17.61 When ΔH and ΔS are both positive or both negative, the temperature determines the direction of spontaneous reaction. See Problem 17.60 for an explanation.

17.62 (a) 0°C (temperature is below mp); $\Delta H > 0$, $\Delta S > 0$, $\Delta G > 0$
(b) 15°C (temperature is above mp); $\Delta H > 0$, $\Delta S > 0$, $\Delta G < 0$

17.63 (a) $\Delta H = 0$

$\Delta S = R \ln \dfrac{V_{final}}{V_{initial}} = (8.314\ J/K) \ln 2 = 5.76\ J/K$

$\Delta G = \Delta H - T\Delta S$
Because $\Delta H = 0$, $\Delta G = -T\Delta S = -(298\ K)(5.76\ J/K) = -1717\ J = -1.72\ kJ$

(b) For a process in an isolated system, $\Delta S_{surr} = 0$. Therefore, $\Delta S_{total} = \Delta S_{sys} > 0$, and the process is spontaneous.

17.64 $\Delta H_{vap} = 30.7$ kJ/mol
$\Delta S_{vap} = 87.0$ J/(K · mol) = 87.0×10^{-3} kJ/(K · mol)
$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$
(a) $\Delta G_{vap} = 30.7$ kJ/mol - (343 K)(87.0×10^{-3} kJ/(K · mol)) = +0.9 kJ/mol
At 70°C (343 K), benzene does not boil because ΔG_{vap} is positive.
(b) $\Delta G_{vap} = 30.7$ kJ/mol - (353 K)(87.0×10^{-3} kJ/(K · mol)) = 0
80°C (353 K) is the boiling point for benzene because $\Delta G_{vap} = 0$
(c) $\Delta G_{vap} = 30.7$ kJ/mol - (363 K)(87.0×10^{-3} kJ/(K · mol)) = -0.9 kJ/mol
At 90°C (363 K), benzene boils because ΔG_{vap} is negative.

17.65 $\Delta H_{fusion} = 30.2$ kJ/mol; $\Delta S_{fusion} = 28.1 \times 10^{-3}$ kJ/(K · mol)
$\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion}$
(a) $\Delta G_{fusion} = 30.2$ kJ/mol - (1050 K)(28.1×10^{-3} kJ/(K · mol)) = +0.7 kJ/mol
At 1050 K, NaCl does not melt because ΔG_{fusion} is positive.
(b) $\Delta G_{fusion} = 30.2$ kJ/mol - (1075 K)(28.1×10^{-3} kJ/(K · mol)) = 0
1075 K is the melting point for NaCl because $\Delta G_{fusion} = 0$.
(c) $\Delta G_{fusion} = 30.2$ kJ/mol - (1100 K)(28.1×10^{-3} kJ/(K · mol)) = -0.7 kJ/mol
At 1100 K, NaCl does melt because ΔG_{fusion} is negative.

17.66 At the melting point (phase change), $\Delta G_{fusion} = 0$
$\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion}$
$0 = \Delta H_{fusion} - T\Delta S_{fusion}$; $T = \dfrac{\Delta H_{fusion}}{\Delta S_{fusion}} = \dfrac{17.3 \text{ kJ/mol}}{43.8 \times 10^{-3} \text{ kJ/(K • mol)}} = 395 \text{ K} = 122^{\circ}\text{C}$

17.67 128°C = 401 K
At the melting point (phase change), $\Delta G_{fusion} = 0$
$\Delta G_{fusion} = \Delta H_{fusion} - T\Delta S_{fusion}$
$0 = \Delta H_{fusion} - T\Delta S_{fusion}$
$\Delta H_{fusion} = T\Delta S_{fusion} = (401 \text{ K})[47.7 \times 10^{-3} \text{ kJ/(K · mol)}] = 19.1$ kJ/mol

Standard Free-Energy Changes and Standard Free Energies of Formation

17.68 (a) ΔG^{o} is the change in free energy that occurs when reactants in their standard states are converted to products in their standard states.
(b) ΔG^{o}_{f} is the free-energy change for formation of one mole of a substance in its standard state from the most stable form of the constituent elements in their standard states.

17.69 The standard state of a substance (solid, liquid, or gas) is the most stable form of a pure substance at 25°C and 1 atm pressure. For solutes, the condition is 1 M at 25°C.

17.70 (a) $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$

$\Delta H^o = 2\ \Delta H^o_f(NO_2) = (2\ mol)(33.2\ kJ/mol) = 66.4\ kJ$

$\Delta S^o = 2\ S^o(NO_2) - [S^o(N_2) + 2\ S^o(O_2)]$

$\Delta S^o = (2\ mol)(240.0\ J/(K \cdot mol)) - [(1\ mol)(191.5\ J/(K \cdot mol)) + (2\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -121.5\ J/K = -121.5 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = 66.4\ kJ - (298\ K)(-121.5 \times 10^{-3}\ kJ/K) = +102.6\ kJ$

Because ΔG^o is positive, the reaction is nonspontaneous under standard-state conditions at 25°C.

(b) $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$

$\Delta H^o = 2\ \Delta H^o_f(KCl) - 2\ \Delta H^o_f(KClO_3)$

$\Delta H^o = (2\ mol)(-436.7\ kJ/mol) - (2\ mol)(-397.7\ kJ/mol) = -78.0\ kJ$

$\Delta S^o = [2\ S^o(KCl) + 3\ S^o(O_2)] - 2\ S^o(KClO_3)$

$\Delta S^o = [(2\ mol)(82.6\ J/(K \cdot mol)) + (3\ mol)(205.0\ J/(K \cdot mol))] - (2\ mol)(143\ J/(K \cdot mol))$

$\Delta S^o = 494.2\ J/(K \cdot mol) = 494.2 \times 10^{-3}\ kJ/(K \cdot mol)$

$\Delta G^o = \Delta H^o - T\Delta S^o = -78.0\ kJ - (298\ K)(494.2 \times 10^{-3}\ kJ/(K \cdot mol)) = -225.3\ kJ$

Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.

(c) $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3CO_2H(l) + H_2O(l)$

$\Delta H^o = [\Delta H^o_f(CH_3CO_2H) + \Delta H^o_f(H_2O)] - \Delta H^o_f(CH_3CH_2OH)$

$\Delta H^o = [(1\ mol)(-484.5\ kJ/mol) + (1\ mol)(-285.8\ kJ/mol)] - (1\ mol)(-277.7\ kJ/mol) = -492.6\ kJ$

$\Delta S^o = [S^o(CH_3CO_2H) + S^o(H_2O)] - [S^o(CH_3CH_2OH) + S^o(O_2)]$

$\Delta S^o = [(1\ mol)(160\ J/(K \cdot mol)) + (1\ mol)(69.9\ J/(K \cdot mol))]$
$- [(1\ mol)(161\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -136.1\ J/(K \cdot mol) = -136.1 \times 10^{-3}\ kJ/(K \cdot mol)$

$\Delta G^o = \Delta H^o - T\Delta S^o = -492.6\ kJ - (298\ K)(-136.1 \times 10^{-3}\ kJ/(K \cdot mol)) = -452.0\ kJ$

Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.

17.71 (a) $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$

$\Delta H^o = 2\ \Delta H^o_f(SO_3) - 2\ \Delta H^o_f\ SO_2)$

$\Delta H^o = (2\ mol)(-395.7\ kJ/mol) - (2\ mol)(-296.8\ kJ/mol) = -197.8\ kJ$

$\Delta S^o = 2\ S^o(SO_3) - [2\ S^o(SO_2) + S^o(O_2)]$

$\Delta S^o = (2\ mol)(256.6\ J/(K \cdot mol)) - [(2\ mol)(248.1\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -188.0\ J/K = -188.0 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -197.8\ kJ - (298\ K)(-188.0 \times 10^{-3}\ kJ/K) = -141.8\ kJ$

Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.

(b) $N_2(g) + 2\ H_2(g) \rightarrow N_2H_4(l)$

$\Delta H^o = \Delta H^o_f(N_2H_4)$

$\Delta H^o = (1\ mol)(50.6\ kJ/mol) = 50.6\ kJ$

$\Delta S^o = S^o(N_2H_4) - [S^o(N_2) + 2\ S^o(H_2)]$

$\Delta S^o = (1\ mol)(121.2\ J/(K \cdot mol)) - [(1\ mol)(191.5\ J/(K \cdot mol)) + (2\ mol)(130.6\ J/(K \cdot mol))]$

$\Delta S^o = -331.5\ J/K = -331.5 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = 50.6\ kJ - (298\ K)(-331.5 \times 10^{-3}\ kJ/K) = +149.4\ kJ$

Because ΔG^o is positive, the reaction is nonspontaneous under standard-state conditions at 25°C.

(c) $CH_3OH(l) + O_2(g) \rightarrow HCO_2H(l) + H_2O(l)$

$\Delta H^o = [\Delta H^o_f(HCO_2H) + \Delta H^o_f(H_2O)] - \Delta H^o_f(CH_3OH)$

$\Delta H^o = [(1\ mol)(-424.7\ kJ/mol) + (1\ mol)(-285.8\ kJ/mol)] - (1\ mol)(-238.7\ kJ/mol) = -471.8\ kJ$

$\Delta S^o = [S^o(HCO_2H) + S^o(H_2O)] - [S^o(CH_3OH) + S^o(O_2)]$

$\Delta S^o = [(1\ mol)(129.0\ J/(K \cdot mol)) + (1\ mol)(69.9\ J/(K \cdot mol))]$
$- [(1\ mol)(127\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$
$\Delta S^o = -133.1\ J/K = -133.1 \times 10^{-3}\ kJ/K$
$\Delta G^o = \Delta H^o - T\Delta S^o = -471.8\ kJ - (298\ K)(-133.1 \times 10^{-3}\ kJ/K) = -432.1\ kJ$
Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.

17.72 (a) $N_2(g) + 2\ O_2(g) \rightarrow 2\ NO_2(g)$
$\Delta G^o = 2\ \Delta G^o_f(NO_2) = (2\ mol)(51.3\ kJ/mol) = +102.6\ kJ$
(b) $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$
$\Delta G^o = 2\ \Delta G^o_f(KCl) - 2\ \Delta G^o_f(KClO_3)$
$\Delta G^o = (2\ mol)(-409.2\ kJ/mol) - (2\ mol)(-296.3\ kJ/mol) = -225.8\ kJ$
(c) $CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3CO_2H(l) + H_2O(l)$
$\Delta G^o = [\Delta G^o_f(CH_3CO_2H) + \Delta G^o_f(H_2O)] - \Delta G^o_f(CH_3CH_2OH)$
$\Delta G^o = [(1\ mol)(-390\ kJ/mol) + (1\ mol)(-237.2\ kJ/mol)] - (1\ mol)(-174.9\ kJ/mol) = -452\ kJ$

17.73 (a) $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$
$\Delta G^o = 2\ \Delta G^o_f(SO_3) - 2\ \Delta G^o_f(SO_2)$
$\Delta G^o = (2\ mol)(-371.1\ kJ/mol) - (2\ mol)(-300.2\ kJ/mol) = -141.8\ kJ$
(b) $N_2(g) + 2\ H_2(g) \rightarrow N_2H_4(l)$
$\Delta G^o = \Delta G^o_f(N_2H_4) = (1\ mol)(149.2\ kJ/mol) = 149.2\ kJ$
(c) $CH_3OH(l) + O_2(g) \rightarrow HCO_2H(l) + H_2O(l)$
$\Delta G^o = [\Delta G^o_f(HCO_2H) + \Delta G^o_f(H_2O)] - \Delta G^o_f(CH_3OH)$
$\Delta G^o = [(1\ mol)(-361.4\ kJ/mol) + (1\ mol)(-237.2\ kJ/mol)] - (1\ mol)(-166.4\ kJ/mol)$
$\Delta G^o = -432.2\ kJ$

17.74 A compound is thermodynamically stable with respect to its constituent elements at 25°C if ΔG^o_f is negative.

	ΔG^o_f (kJ/mol)	Stable
(a) $BaCO_3(s)$	-1138	yes
(b) $HBr(g)$	-53.4	yes
(c) $N_2O(g)$	+104.2	no
(d) $C_2H_4(g)$	+68.1	no

17.75 A compound is thermodynamically stable with respect to its constituent elements at 25°C if ΔG^o_f is negative.

	ΔG^o_f (kJ/mol)	Stable
(a) $C_6H_6(l)$	+124.5	no
(b) $NO(g)$	+86.6	no
(c) $PH_3(g)$	+13	no
(d) $FeO(s)$	-255	yes

17.76 $CH_2{=}CH_2(g) + H_2O(l) \rightarrow CH_3CH_2OH(l)$
$\Delta H^o = \Delta H^o_f(CH_2CH_2OH) - [\Delta H^o_f(CH_2{=}CH_2) + \Delta H^o_f(H_2O)]$

ΔH^o = (1 mol)(-277.7 kJ/mol) - [(1 mol)(52.3 kJ/mol) + (1 mol)(-285.8 kJ/mol)]
ΔH^o = - 44.2 kJ
$\Delta S^o = S^o(CH_3CH_2OH) - [S^o(CH_2{=}CH_2) + S^o(H_2O)]$
ΔS^o = (1 mol)(161 J/(K · mol)) - [(1 mol)(219.5 J/(K · mol)) + (1 mol)(69.9 J/(K · mol))]
ΔS^o = -128 J/(K · mol) = -128 x 10^{-3} kJ/(K · mol)
$\Delta G^o = \Delta H^o - T\Delta S^o$ = - 44.2 kJ - (298 K)(-128 x 10^{-3} kJ/K) = -6.1 kJ
Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.
The reaction becomes nonspontaneous at high temperatures because ΔS^o is negative.
To find the crossover temperature, set $\Delta G = 0$ and solve for T.

$$T = \frac{\Delta H^o}{\Delta S^o} = \frac{-44{,}200\ J}{-128\ J/K} = 345\ K = 72^oC$$

The reaction becomes nonspontaneous at 72°C.

17.77 $2\ H_2S(g) + SO_2(g) \rightarrow 3\ S(s) + 2\ H_2O(g)$
$\Delta H^o = 2\ \Delta H^o_f(H_2O) - [2\ \Delta H^o_f(H_2S) + \Delta H^o_f(SO_2)]$
ΔH^o = (2 mol)(-241.8 kJ/mol) - [(2 mol)(-20.6 kJ/mol) + (1 mol)(-296.8 kJ/mol) = -145.6 kJ
$\Delta S^o = [3\ S^o(S) + 2\ S^o(H_2O)] - [2\ S^o(H_2S) + S^o(SO_2)]$
ΔS^o = [(3 mol)(31.8 J/(K · mol)) + (2 mol)(188.7 J/(K · mol))]
- [(2 mol)(205.7 J/(K · mol)) + (1 mol)(248.1 J/(K · mol))]
ΔS^o = -186.7 J/K = -186.7 x 10^{-3} kJ/K
$\Delta G^o = \Delta H^o - T\Delta S^o$ = -145.6 kJ - (298 K)(-186.7 x 10^{-3} kJ/K) = -90.0 kJ
Because ΔG^o is negative, the reaction is spontaneous under standard-state conditions at 25°C.
The reaction becomes nonspontaneous at high temperatures because ΔS^o is negative.
To find the crossover temperature set $\Delta G = 0$ and solve for T.

$$T = \frac{\Delta H^o}{\Delta S^o} = \frac{-145{,}600\ J}{-186.7\ J/K} = 780\ K = 507^oC$$

The reaction becomes nonspontaneous at 507°C.

17.78 $3\ C_2H_2(g) \rightarrow C_6H_6(l)$
$\Delta G^o = \Delta G^o_f(C_6H_6) - 3\ \Delta G^o_f(C_2H_2)$
ΔG^o = (1 mol)(124.5 kJ/mol) - (3 mol)(209.2 kJ/mol) = -503.1 kJ
Because ΔG^o is negative, the reaction is possible. Look for a catalyst.
Because ΔG^o_f for benzene is positive (+124.5 kJ/mol), the synthesis of benzene from graphite and gaseous H_2 at 25°C and 1 atm pressure is not possible.

17.79 $CH_2ClCH_2Cl(l) \rightarrow CH_2{=}CHCl(g) + HCl(g)$
$\Delta G^o = [\Delta G^o_f(CH_2{=}CHCl) + \Delta G^o_f(HCl)] - \Delta G^o_f(CH_2ClCH_2Cl)$
ΔG^o = [(1 mol)(51.9 kJ/mol) + (1 mol)(-95.3 kJ/mol)] - (1 mol)(-79.6 kJ/mol) = +36.2 kJ
Because ΔG^o is positive, the reaction is nonspontaneous under standard-state conditions at 25°C.

$CH_2ClCH_2Cl(l) \rightarrow CH_2{=}CHCl(g) + HCl(g)$
Sum: $\underline{NaOH(aq) + HCl(g) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)}$
$CH_2ClCH_2Cl(l) + NaOH(aq) \rightarrow CH_2{=}CHCl(g) + Na^+(aq) + Cl^-(aq) + H_2O(l)$
$\Delta G^o = [\Delta G^o_f(CH_2{=}CHCl) + \Delta G^o_f(Na^+) + \Delta G^o_f(Cl^-) + \Delta G^o_f(H_2O)]$

$$- [\Delta G^o_f(CH_2ClCH_2Cl) + \Delta G^o_f(NaOH)]$$

ΔG^o = [(1 mol)(51.9 kJ/mol) + (1 mol)(-261.9 kJ/mol)
+ (1 mol)(-131.3 kJ/mol) + (1 mol)(-237.2 kJ/mol)]
- [(1 mol)(-79.6 kJ/mol) + (1 mol)(-419.2 kJ/mol)] = -79.7 kJ

Using NaOH(aq), ΔG^o = -79.7 kJ and the reaction is spontaneous. (More generally, base removes HCl, driving the reaction to the right.)

The synthesis of a compound from its constituent elements is thermodynamically feasible at 25°C and 1 atm pressure if ΔG^o_f is negative.

Because $\Delta G^o_f(CH_2=CHCl)$ = +51.9 kJ, the synthesis of vinyl chloride from its elements is not possible at 25°C and 1 atm pressure.

Free Energy, Composition, and Chemical Equilibrium

17.80 $\Delta G = \Delta G^o + RT \ln Q$

17.81 $\Delta G = \Delta G^o + RT \ln Q$

(a) If Q < 1, then RT ln Q is negative and $\Delta G < \Delta G^o$.

(b) If Q = 1, then RT ln Q = 0 and $\Delta G = \Delta G^o$.

(c) If Q > 1, then RT ln Q is positive and $\Delta G > \Delta G^o$.

As Q increases the thermodynamic driving force decreases.

17.82 $\Delta G = \Delta G^o + RT \ln\left[\dfrac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})}\right]$

(a) ΔG = (-141.8 kJ/mol) + [8.314 x 10^{-3} kJ/(K · mol)](298 K)$\ln\left[\dfrac{(1.0)^2}{(100)^2(100)}\right]$ = -176.0 kJ/mol

(b) ΔG = (-141.8 kJ/mol) + [8.314 x 10^{-3} kJ/(K · mol)](298 K)$\ln\left[\dfrac{(10)^2}{(2.0)^2(1.0)}\right]$ = -133.8 kJ/mol

(c) Q = 1, ln Q = 0, $\Delta G = \Delta G^o$ = -141.8 kJ/mol

17.83 $\Delta G = \Delta G^o + RT \ln\left[\dfrac{[NH_2CONH_2]}{(P_{NH_3})^2(P_{CO_2})}\right]$

(a) ΔG = -13.6 kJ/mol + [8.314 x 10^{-3} kJ/(K · mol)](298 K)$\ln\left[\dfrac{1.0}{(10)^2(10)}\right]$ = -30.7 kJ/mol

Because ΔG is negative, the reaction is spontaneous.

(b) ΔG = -13.6 kJ/mol + [8.314 x 10^{-3} kJ/(K · mol)](298 K)$\ln\left[\dfrac{1.0}{(0.10)^2(0.10)}\right]$ = +3.5 kJ/mol

Because ΔG is positive, the reaction is nonspontaneous.

17.84 $\Delta G^o = -RT \ln K$

(a) If K > 1, ΔG^o is negative. (b) If K = 1, ΔG^o = 0.

(c) If $K < 1$, ΔG^o is positive.

17.85 $K = e^{\frac{-\Delta G^o}{RT}}$ (a) If ΔG^o is positive, K is small. (b) If ΔG^o is negative, K is large.

17.86 $\Delta G^o = -RT \ln K_p = -141.8$ kJ

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-141.8 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = 57.23$$

$K_p = e^{57.23} = 7.1 \times 10^{24}$

17.87 $\Delta G^o = - RT \ln K = -13.6$ kJ

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(-13.6 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = 5.49$$

$K = e^{5.49} = 2.4 \times 10^2$

17.88 $C_2H_5OH(l) \rightleftharpoons C_2H_5OH(g)$

$\Delta G^o = \Delta G^o_f(C_2H_5OH(g)) - \Delta G^o_f(C_2H_5OH(l))$

$\Delta G^o = (1 \text{ mol})(-168.6 \text{ kJ/mol}) - (1 \text{ mol})(-174.9 \text{ kJ/mol}) = +6.3$ kJ

$\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(6.3 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = -2.54$$

$K = e^{-2.54} = 0.079$; $K = K_p = P_{C_2H_5OH} = 0.079$ atm

17.89 $\Delta G^o = -RT \ln K_a$

$\Delta G^o = -[8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{ mol)}](298 \text{ K}) \ln(3.0 \times 10^{-4}) = +20.1$ kJ/mol

17.90 $2\ CH_2{=}CH_2(g) + O_2(g) \rightarrow 2\ C_2H_4O(g)$

$\Delta G^o = 2\ \Delta G^o_f(C_2H_4O) - 2\ \Delta G^o_f(CH_2{=}CH_2)$

$\Delta G^o = (2 \text{ mol})(-13.1 \text{ kJ/mol}) - (2 \text{ mol})(68.1 \text{ kJ/mol}) = -162.4$ kJ

$\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(-162.4 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = 65.55$$

$K = K_p = e^{65.55} = 2.9 \times 10^{28}$

17.91 $CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$

$\Delta G^o = \Delta G^o_f(CH_3OH) - \Delta G^o_f(CO)$

$\Delta G^o = (1 \text{ mol})(-161.9 \text{ kJ/mol}) - (1 \text{ mol})(-137.2 \text{ kJ/mol}) = -24.7$ kJ

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-24.7 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](298 \text{ K})} = 9.97$$

$K_p = e^{9.97} = 2.1 \times 10^4$

$\Delta G = \Delta G^o + RT \ln Q$

$$\Delta G = -24.7 \text{ kJ/mol} + [8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{ mol)}](298 \text{ K}) \ln\left[\frac{20}{(20)(20)^2}\right] = -39.5 \text{ kJ/mol}$$

General Problems

17.92 The kinetic parameters [(a), (b), and (h)] are affected by a catalyst. The thermodynamic and equilibrium parameters [(c), (d), (e), (f), and (g)] are not affected by a catalyst.

17.93 (a), (c), and (d) are nonspontaneous; (b) is spontaneous.

17.94 (a) Spontaneous does not mean fast, just possible.
(b) For a spontaneous reaction $\Delta S_{total} > 0$. ΔS_{sys} can be positive or negative.
(c) An endothermic reaction can be spontaneous if $\Delta S_{sys} > 0$.
(d) This statement is true because the sign of ΔG changes when the direction of a reaction is reversed.

17.95

Point Total	Possible Ways	Number of Ways
2	(1+1)	1
3	(2+1)(1+2)	2
4	(1+3)(2+2)(3+1)	3
5	(1+4)(2+3)(3+2)(4+1)	4
6	(1+5)(2+4)(3+3)(4+2)(5+1)	5
7	(1+6)(2+5)(3+4)(4+3)(5+2)(6+1)	6
8	(2+6)(3+5)(4+4)(5+3)(6+2)	5
9	(3+6)(4+5)(5+4)(6+3)	4
10	(4+6)(5+5)(6+4)	3
11	(6+5)(5+6)	2
12	(6+6)	1

Because a point total of 7 can be rolled in the most ways, it is the most probable point total.

17.96

17.97 (a) $Q = 1$, $\ln Q = 0$, $\Delta G = \Delta G^o = +79.9$ kJ
Because ΔG is positive, the reaction is spontaneous in the reverse direction.
(b) $\Delta G = \Delta G^o + RT \ln Q$; $Q = [H_3O^+][OH^-] = (1.0 \times 10^{-7})^2 = 1.0 \times 10^{-14}$
$\Delta G = 79.9 \text{ kJ/mol} + [8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](298 \text{ K}) \ln(1.0 \times 10^{-14}) = 0$
Because $\Delta G = 0$, the reaction is at equilibrium.
(c) $\Delta G = \Delta G^o + RT \ln Q$

$Q = [H_3O^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-10}) = 1.0 \times 10^{-17}$
$\Delta G = 79.9 \text{ kJ/mol} + [8.314 \times 10^{-3} \text{ kJ/(K} \cdot \text{mol)}](298 \text{ K}) \ln(1.0 \times 10^{-17}) = -17.1 \text{ kJ/mol}$
Because ΔG is negative, the reaction is spontaneous in the forward direction.
The results are consistent with Le Châtelier's principle. When the $[H_3O^+]$ and $[OH^-]$ are larger than the equilibrium concentrations (a), the reverse reaction takes place. When the product of $[H_3O^+]$ and the $[OH^-]$ is less than the equilibrium value, the forward reaction is spontaneous.
$\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-79.9 \text{ kJ/mol}}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{mol)}](298 \text{ K})} = -32.25$$

$K = K_a = e^{-32.25} = 9.9 \times 10^{-15}$

17.98 At the normal boiling point, $\Delta G = 0$.

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}; \qquad T = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{38{,}600 \text{ J}}{110 \text{ J/K}} = 351 \text{ K} = 78^oC$$

17.99 At the normal boiling point, $\Delta G_{vap} = 0$. $61^oC = 334$ K

$$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}; \qquad \Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{29{,}240 \text{ J}}{334 \text{ K}} = 87.5 \text{ J/K}$$

17.100 $\Delta G = \Delta H - T\Delta S$
(a) ΔH must be positive (endothermic) and greater than $T\Delta S$ in order for ΔG to be positive (nonspontaneous reaction).
(b) Set $\Delta G = 0$ and solve for ΔH.
$\Delta G = 0 = \Delta H - T\Delta S = \Delta H - (323 \text{ K})(104 \text{ J/K}) = \Delta H - (33592 \text{ J}) = \Delta H - (33.6 \text{ kJ})$
$\Delta H = 33.6$ kJ
ΔH must be greater than 33.6 kJ.

17.101 $NH_4NO_3(s) \rightarrow N_2O(g) + 2\ H_2O(g)$
(a) $\Delta G^o = [\Delta G^o_f(N_2O) + 2\ \Delta G^o_f(H_2O)] - \Delta G^o_f(NH_4NO_3)$
$\Delta G^o = [(1 \text{ mol})(104.2 \text{ kJ/mol}) + (2 \text{ mol})(-228.6 \text{ kJ/mol})] - (1 \text{ mol})(-184.0 \text{ kJ/mol})$
$\Delta G^o = -169.0$ kJ
Because ΔG^o is negative, the reaction is spontaneous.
(b) Because the reaction increases the number of moles of gas, ΔS^o is positive.
$\Delta G^o = \Delta H^o - T\Delta S^o$
As the temperature is raised, ΔG^o becomes more negative.
(c) $\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(-169.0 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{mol)}](298 \text{ K})} = 68.21$$

$K = K_p = e^{68.21} = 4.2 \times 10^{29}$
(d) $Q = (P_{N_2O})(P_{H_2O})^2 = (30)(30)^2 = (30)^3$
$\Delta G = \Delta G^o + RT \ln Q$
$\Delta G = -169.0 \text{ kJ/mol} + [8.314 \times 10^{-3} \text{kJ/(K} \cdot \text{mol)}](298 \text{ K}) \ln[(30)^3] = -143.7 \text{ kJ/mol}$

17.102 (a) $2\ Mg(s) + O_2(g) \rightarrow 2\ MgO(s)$

$\Delta H^o = 2\ \Delta H^o_f(MgO) = (2\ mol)(-601.7\ kJ/mol) = -1203.4\ kJ$

$\Delta S^o = 2\ S^o(MgO) - [2\ S^o(Mg) + S^o(O_2)]$

$\Delta S^o = (2\ mol)(26.9\ J/(K \cdot mol)) - [(2\ mol)(32.7\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -216.6\ J/K = -216.6 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -1203.4\ kJ - (298\ K)(-216.6 \times 10^{-3}\ kJ/K) = -1138.8\ kJ$

Because ΔG^o is negative, the reaction is spontaneous at 25°C. ΔG^o becomes less negative as the temperature is raised.

(b) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

$\Delta H^o = [\Delta H^o_f(MgO) + \Delta H^o_f(CO_2)] - \Delta H^o_f(MgCO_3)$

$\Delta H^o = [(1\ mol)(-601.1\ kJ/mol) + (1\ mol)(-393.5\ kJ/mol)] - (1\ mol)(-1096\ kJ/mol) = +101\ kJ$

$\Delta S^o = [S^o(MgO) + S^o(CO_2)] - S^o(MgCO_3)$

$\Delta S^o = [(1\ mol)(26.9\ J/(K \cdot mol)) + (1\ mol)(213.6\ J/(K \cdot mol))] - (1\ mol)(65.7\ J/(K \cdot mol))$

$\Delta S^o = 174.8\ J/K = 174.8 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = 101\ kJ - (298\ K)(174.8 \times 10^{-3}\ kJ/K) = +49\ kJ$

Because ΔG^o is positive, the reaction is not spontaneous at 25°C. ΔG^o becomes less positive as the temperature is raised.

(c) $Fe_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Fe(s)$

$\Delta H^o = \Delta H^o_f(Al_2O_3) - \Delta H^o_f(Fe_2O_3)$

$\Delta H^o = (1\ mol)(-1676\ kJ/mol) - (1\ mol)(-824.2\ kJ/mol) = -852\ kJ$

$\Delta S^o = [S^o(Al_2O_3) + 2\ S^o(Fe)] - [S^o(Fe_2O_3) + 2\ S^o(Al)]$

$\Delta S^o = [(1\ mol)(50.9\ J/(K \cdot mol)) + (2\ mol)(27.3\ J/(K \cdot mol))]$
$- [(1\ mol)(87.4\ J/(K \cdot mol)) + (2\ mol)(28.3\ J/(K \cdot mol))]$

$\Delta S^o = -38.5\ J/K = -38.5 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -852\ kJ - (298\ K)(-38.5 \times 10^{-3}\ kJ/K) = -840\ kJ$

Because ΔG^o is negative, the reaction is spontaneous at 25°C. ΔG^o becomes less negative as the temperature is raised.

(d) $2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

$\Delta H^o = [\Delta H^o_f(Na_2CO_3) + \Delta H^o_f(CO_2) + \Delta H^o_f(H_2O)] - 2\ \Delta H^o_f(NaHCO_3)$

$\Delta H^o = [(1\ mol)(-1130.7\ kJ/mol) + (1\ mol)(-393.5\ kJ/mol)$
$+ (1\ mol)(-241.8\ kJ/mol)] - (2\ mol)(-950.8\ kJ/mol) = +135.6\ kJ$

$\Delta S^o = [S^o(Na_2CO_3) + S^o(CO_2) + S^o(H_2O)] - 2\ S^o(NaHCO_3)$

$\Delta S^o = [(1\ mol)(135.0\ J/(K \cdot mol)) + (1\ mol)(213.6\ J/(K \cdot mol))$
$+ (1\ mol)(188.7\ J/(K \cdot mol))] - (2\ mol)(102\ J/(K \cdot mol))$

$\Delta S^o = +333\ J/K = +333 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = +135.6\ kJ - (298\ K)(+333 \times 10^{-3}\ kJ/K) = +36.4\ kJ$

Because ΔG^o is positive, the reaction is not spontaneous at 25°C. ΔG^o becomes less positive as the temperature is raised.

17.103 (a)

	$\Delta H_{vap}/T_{bp}$
ammonia	120 J/K
benzene	87 J/K
carbon tetrachloride	85 J/K

chloroform	87 J/K
mercury	90 J/K

(b) All processes are the conversion of a liquid to a gas at the boiling point. They should should all have similar ΔS values. $\Delta H_{vap}/T_{bp}$ is equal to ΔS_{vap}.
(c) NH_3 deviates from Trouton's rule because of hydrogen bonding. Because $NH_3(l)$ is more ordered than the other liquids, ΔS_{vap} is larger.

17.104 (a) $6\ C(s) + 3\ H_2(g) \rightarrow C_6H_6(l)$

$\Delta S^o_f = S^o(C_6H_6) - [6\ S^o(C) + 3\ S^o(H_2)]$

$\Delta S^o_f = (1\ mol)(172.8\ J/(K \cdot mol)) - [(6\ mol)(5.7\ J/(K \cdot mol)) + (3\ mol)(130.6\ J/(K \cdot mol))]$

$\Delta S^o_f = -253\ J/K = -253\ J/(K \cdot mol)$

$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f$

$$\Delta S^o_f = \frac{\Delta H^o_f - \Delta G^o_f}{T} = \frac{49.0\ kJ/mol - 124.5\ kJ/mol}{298\ K} = -0.253\ kJ/(K \cdot mol)$$

$\Delta S^o_f = -253\ J/(K \cdot mol)$

Both calculations lead to the same value of ΔS^o_f.

(b) $Ca(s) + S(s) + 2\ O_2(g) \rightarrow CaSO_4(s)$

$\Delta S^o_f = S^o(CaSO_4) - [S^o(Ca) + S^o(S) + 2\ S^o(O_2)]$

$\Delta S^o_f = (1\ mol)(107\ J/(K \cdot mol))$
$- [(1\ mol)(41.4\ J/(K \cdot mol)) + (1\ mol)(31.8\ J/(K \cdot mol)) + (2\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o_f = -376\ J/K = -376\ J/(K \cdot mol)$

$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f$

$$\Delta S^o_f = \frac{\Delta H^o_f - \Delta G^o_f}{T} = \frac{-1434.1\ kJ/mol - (-1321.9\ kJ/mol)}{298\ K} = -0.376\ kJ/(K \cdot mol)$$

$\Delta S^o_f = -376\ J/(K \cdot mol)$

Both calculations lead to the same value of ΔS^o_f.

(c) $2\ C(s) + 3\ H_2(g) + 1/2\ O_2(g) \rightarrow C_2H_5OH(l)$

$\Delta S^o_f = S^o(C_2H_5OH) - [S^o(C) + S^o(H_2) + 1/2\ S^o(O_2)]$

$\Delta S^o_f = (1\ mol)(161\ J/(K \cdot mol))$
$- [(2\ mol)(5.7\ J/(K \cdot mol)) + (3\ mol)(130.6\ J/(K \cdot mol)) + (0.5\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o_f = -345\ J/K = -345\ J/(K \cdot mol)$

$\Delta G^o_f = \Delta H^o_f - T\Delta S^o_f$

$$\Delta S^o_f = \frac{\Delta H^o_f - \Delta G^o_f}{T} = \frac{-277.7\ kJ/mol - (-174.9\ kJ/mol)}{298\ K} = -0.345\ kJ/(K \cdot mol)$$

$\Delta S^o_f = -345\ J/(K \cdot mol)$

Both calculations lead to the same value of ΔS^o_f.

17.105 $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

From Problem 17.102(b)

$\Delta H^o = +101\ kJ; \quad \Delta S^o = 174.8\ J/K = 174.8 \times 10^{-3}\ kJ/K$

The equilibrium pressure of CO_2 is equal to $K_p = P_{CO_2}$. K_p is not affected by the quantities of $MgCO_3$ and MgO present. K_p can be calculated from ΔG^o.

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta G^o = -RT \ln K_p$

(a) $\Delta G^o = 101\ kJ - (298\ K)(174.8 \times 10^{-3}\ kJ/K) = +49\ kJ$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-49\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](298\ K)} = -19.8$$

$K_p = P_{CO_2} = e^{-19.8} = 3 \times 10^{-9}$ atm

(b) $\Delta G^o = 101\ kJ - (553\ K)(174.8 \times 10^{-3}\ kJ/K) = 4.3\ kJ$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-4.3\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](553\ K)} = -0.94$$

$K_p = P_{CO_2} = e^{-0.94} = 0.39$ atm

(c) $P_{CO_2} = 0.39$ atm because the temperature is the same as in (b).

17.106 $\Delta G^o = -RT \ln K_b$

At 20 °C: $\Delta G^o = -[8.314 \times 10^{-3}\ kJ/(K \cdot mol)](293\ K) \ln(1.710 \times 10^{-5}) = +26.74\ kJ/mol$

At 50 °C: $\Delta G^o = -[8.314 \times 10^{-3}\ kJ/(K \cdot mol)](323\ K) \ln(1.892 \times 10^{-5}) = +29.20\ kJ/mol$

$\Delta G^o = \Delta H^o - T\Delta S^o$

$26.74 = \Delta H^o - 293\Delta S^o$

$29.20 = \Delta H^o - 323\Delta S^o$ Solve these two equations simultaneously for ΔH^o and ΔS^o.

$26.74 + 293\Delta S^o = \Delta H^o$

$29.20 + 323\Delta S^o = \Delta H^o$ Set these two equations equal to each other.

$26.74 + 293\Delta S^o = 29.20 + 323\Delta S^o$

$26.74 - 29.20 = 323\Delta S^o - 293\ \Delta S^o$

$-2.46 = 30\Delta S^o$

$\Delta S^o = -2.46/30 = -0.0820 = -0.0820\ kJ/K = -82.0\ J/K$

$26.74 + 293\Delta S^o = 26.74 + 293(-0.0820) = \Delta H^o = +2.71\ kJ$

17.107 (a) $\Delta H^o = 2\ \Delta H^o_f(NH_3) = (2\ mol)(-46.1\ kJ/mol) = -92.2\ kJ$

$\Delta G^o = 2\ \Delta G^o_f(NH_3) = (2\ mol)(-16.5\ kJ/mol) = -33.0\ kJ$

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta H^o - \Delta G^o = T\Delta S^o$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-92.2\ kJ - (-33.0\ kJ)}{298\ K} = -0.199\ kJ/K = -199\ J/K$$

(b) ΔS^o is negative because the number of mol of gas molecules decreases from 4 mol to 2 mol on going from reactants to products.

(c) The reaction is spontaneous because ΔG^o is negative.

(d) $\Delta G^o = \Delta H^o - T\Delta S^o = -92.2\ kJ - (350\ K)(-0.199\ kJ/K) = -22.55\ kJ$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-22.55\ kJ/mol)}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](350\ K)} = 7.749$$

$K_p = e^{7.749} = 2.3 \times 10^3$

$\Delta n = 2 - (1 + 3) = -2$

$K_c = K_p\left(\frac{1}{RT}\right)^{\Delta n} = (2.3 \times 10^3)\left(\frac{1}{RT}\right)^{-2} = (2.3 \times 10^3)(RT)^2$

$K_c = (2.3 \times 10^3)[(0.082\ 06)(350)]^2 = 1.9 \times 10^6$

17.108 (a) $\Delta H^o = [\Delta H^o_f(Ag^+(aq)) + \Delta H^o_f(Br^-(aq))] - \Delta H^o_f(AgBr(s))$

$\Delta H^o = [(1\ mol)(105.6\ kJ/mol) + (1\ mol)(-121.5\ kJ/mol)] - (1\ mol)(-100.4\ kJ/mol) = +84.5\ kJ$

$\Delta S^o = [S^o(Ag^+(aq)) + S^o(Br^-(aq))] - S^o(AgBr(s))$

$\Delta S^o = [(1\ mol)(72.7\ J/(K \cdot mol)) + (1\ mol)(82.4\ J/(K \cdot mol))]$

$- (1\ mol)(107\ J/(K \cdot mol)) = +48.1\ J$

$\Delta G^o = \Delta H^o - T\Delta S^o = 84.5\ kJ - (298\ K)(48.1 \times 10^{-3}\ kJ/K) = +70.2\ kJ$

(b) $\Delta G^o = -RT \ln K_{sp}$

$\ln K_{sp} = \frac{-\Delta G^o}{RT} = \frac{-70.2\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](298\ K)} = -28.3$

$K_{sp} = e^{-28.3} = 5 \times 10^{-13}$

(c) $Q = [Ag^+][Br^-] = (1.00 \times 10^{-5})(1.00 \times 10^{-5}) = 1.00 \times 10^{-10}$

$\Delta G = \Delta G^o + RT\ln Q$

$\Delta G = 70.2\ kJ/mol + [8.314 \times 10^{-3}\ kJ/(K \cdot mol)](298\ K)\ln(1.00 \times 10^{-10}) = 13.2\ kJ/mol$

A positive value of ΔG means that the forward reaction is nonspontaneous under these conditions. The reverse reaction is therefore spontaneous, which is consistent with the fact that $Q > K_{sp}$.

17.109 (a) $\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G^o = -RT \ln K$

Set the two equations equal to each other.

$-RT \ln K = \Delta H^o - T\Delta S^o$

$\ln K = \frac{\Delta H^o - T\Delta S^o}{-RT}$; $\ln K = \frac{-\Delta H^o}{RT} + \frac{T\Delta S^o}{RT}$; $\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$

$\ln K = \frac{-\Delta H^o}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^o}{R}$ This is the equation for a straight line (y = mx + b).

$y = \ln K$; $m = -\frac{\Delta H^o}{R}$ = slope; $x = \frac{1}{T}$; $b = \frac{\Delta S^o}{R}$ = intercept

(b) Plot ln K versus 1/T

$\Delta H^o = -R(\text{slope})$ $\Delta S^o = R(\text{intercept})$

(c) For a reaction where K increases with increasing temperature, the following plot would be obtained:

The slope is negative.

Because ΔH^o = -R(slope), ΔH^o is positive, and the reaction is endothermic.

This prediction is in accord with LeChâtelier's principle because when you add heat (raise the temperature) for an endothermic reaction, the reaction in the forward direction takes place, the product concentrations increase and the reactant concentrations decrease. This results in an increase in K.

17.110 $Br_2(l) \rightleftharpoons Br_2(g)$

$\Delta S^o = S^o(Br_2(g)) - S^o(Br_2(l))$

$\Delta S^o = (1\ mol)(245.4\ J/(K \cdot mol)) - (1\ mol)(152.2\ J/(K \cdot mol)) = 93.2\ J/K = 93.2 \times 10^{-3}\ kJ/K$

$\Delta G = \Delta H^o - T\Delta S^o$

At the boiling point, $\Delta G = 0$.

$0 = \Delta H^o - T_{bp}\Delta S^o$

$$T_{bp} = \frac{\Delta H^o}{\Delta S^o}$$

$\Delta H^o = T_{bp}\,\Delta S^o = (332\ K)(93.2 \times 10^{-3}\ kJ/K) = 30.9\ kJ$

$$K_p = P_{Br_2} = \left(227\ mm\ Hg \times \frac{1\ atm}{760\ mm\ Hg}\right) = 0.299\ atm$$

$\Delta G^o = -RT \ln K_p$ and $\Delta G^o = \Delta H^o - T\Delta S^o$ (set equations equal to each other)

$\Delta H^o - T\Delta S^o = -RT \ln K_p$ (rearrange)

$$\ln K_p = \frac{-\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R}$$ (solve for T)

$$T = \frac{\left(\frac{-\Delta H^o}{R}\right)}{\left(\ln K_p - \frac{\Delta S^o}{R}\right)} = \frac{\left(\frac{-30.9\ kJ/mol}{8.314 \times 10^{-3}\ kJ/(K \bullet mol)}\right)}{\left(\ln(0.299) - \frac{93.2 \times 10^{-3}\ kJ/(K \bullet mol)}{8.314 \times 10^{-3}\ kJ/(K \bullet mol)}\right)} = 299\ K = 26^oC$$

$Br_2(l)$ has a vapor pressure of 227 mm Hg at 26°C.

17.111 For PbI_2, $K_{sp} = [Pb^{2+}][I^-]^2$

	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2\ I^-(aq)$
initial (M)			0		0
equil (M)			x		2x

$K_{sp} = x(2x)^2 = 4x^3$, where x = molar solubility

At 20°C = 20 + 273 = 293 K, $K_{sp} = 4(1.45 \times 10^{-3})^3 = 1.22 \times 10^{-8}$

At 80°C = 80 + 273 = 353 K, $K_{sp} = 4(6.85 \times 10^{-3})^3 = 1.29 \times 10^{-6}$

From problem 17.109, $\ln K = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$

$$\ln K_1 - \ln K_2 = \frac{-\Delta H^o}{RT_1} + \frac{\Delta S^o}{R} - \left(\frac{-\Delta H^o}{RT_2} + \frac{\Delta S^o}{R}\right)$$

$$\ln \frac{K_1}{K_2} = \frac{-\Delta H^o}{RT_1} - \frac{-\Delta H^o}{RT_2} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta H^o = \frac{[\ln K_1 - \ln K_2]R}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

$$\Delta H^o = \frac{[\ln(1.22 \times 10^{-8}) - \ln(1.29 \times 10^{-6})][8.314 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}]}{\left(\frac{1}{353\ \text{K}} - \frac{1}{293\ \text{K}}\right)} = 66.8\ \text{kJ/mol}$$

$\Delta G^o = -RT \ln K_{sp} = -[8.314 \times 10^{-3}\ \text{kJ/(K} \cdot \text{mol)}](293\ \text{K}) \ln(1.22 \times 10^{-8}) = 44.4\ \text{kJ/mol}$

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta H^o - \Delta G^o = T\Delta S^o$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$$

$$\Delta S^o = \frac{66.8\ \text{kJ/mol} - 44.4\ \text{kJ/mol}}{293\ \text{K}} = 0.0765\ \text{kJ/(K} \cdot \text{mol)} = 76.5\ \text{J/(K} \cdot \text{mol)}$$

17.112 $\Delta H^o = [2\ \Delta H^o_f(Cl^-(aq))] - [2\ \Delta H^o_f(Br^-(aq))]$

$\Delta H^o = [(2\ \text{mol})(-167.2\ \text{kJ/mol})] - [(2\ \text{mol})(-121.5\ \text{kJ/mol})] = -91.4\ \text{kJ}$

$\Delta S^o = [S^o(Br_2(l)) + 2\ S^o(Cl^-(aq))] - [2\ S^o(Br^-(aq)) + S^o(Cl_2(g))]$

$\Delta S^o = [(1\ \text{mol})(152.2\ \text{J/(K} \cdot \text{mol)}) + (2\ \text{mol})(56.5\ \text{J/(K} \cdot \text{mol)})]$

$\quad - [(2\ \text{mol})(82.4\ \text{J/(K} \cdot \text{mol)}) + (1\ \text{mol})(223.0\ \text{J/(K} \cdot \text{mol)})] = -122.6\ \text{J/K}$

$80^oC = 80 + 273 = 353\ \text{K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -91.4\ \text{kJ} - (353\ \text{K})(-122.6 \times 10^{-3}\ \text{kJ/K}) = -48.1\ \text{kJ}$

$\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^o}{RT} = \frac{-(-48.1\ \text{kJmol})}{[8.314 \times 10^{-3}\ \text{kJ/(K} \bullet \text{mol)}](353\ \text{K})} = 16.4$$

$K = e^{16.4} = 1.3 \times 10^7$

17.113 $CS_2(l) \rightleftharpoons CS_2(g)$

$\Delta H^o = \Delta H^o_f(CS_2(g)) - \Delta H^o_f(CS_2(l))$

$\Delta H^o = [(1\ \text{mol})(116.7\ \text{kJ/mol})] - [(1\ \text{mol})(89.0\ \text{kJ/mol})] = 27.7\ \text{kJ}$

$\Delta S^o = S^o(CS_2(g)) - S^o(CS_2(l))$

$\Delta S^o = [(1\ \text{mol})(237.7\ \text{J/(K} \cdot \text{mol)})] - [(1\ \text{mol})(151.3\ \text{J/(K} \cdot \text{mol)})] = 86.4\ \text{J/K}$

$\Delta G = \Delta H^o - T\Delta S^o$

At the boiling point, $\Delta G = 0$.

$0 = \Delta H^o - T_{bp}\Delta S^o$

$$T_{bp} = \frac{\Delta H^o}{\Delta S^o} = \frac{27.7\ \text{kJ}}{86.4 \times 10^{-3}\ \text{kJ/K}} = 321\ \text{K}$$

$T_{bp} = 321\ \text{K} = 321 - 273 = 48^oC$

17.114 $35^oC = 35 + 273 = 308\ K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -352\ kJ - (308\ K)(-899 \times 10^{-3}\ kJ/K) = -75.1\ kJ$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-75.1\ kJ/mol)}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](308\ K)} = 29.33$$

$K_p = e^{29.33} = 5.5 \times 10^{12}$

$$K_p = \frac{1}{(P_{H_2O})^6} = 5.5 \times 10^{12}$$

$$P_{H_2O} = \sqrt[6]{\frac{1}{5.5 \times 10^{12}}} = 0.0075\ atm$$

$$P_{H_2O} = 0.0075\ atm \times \frac{760\ mm\ Hg}{1\ atm} = 5.7\ mm\ Hg$$

17.115 $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$

$\Delta H^o = 2\ \Delta H^o_f(KCl) - 2\ \Delta H^o_f(KClO_3)$

$\Delta H^o = (2\ mol)(-436.7\ kJ) - (2\ mol)(-397.7\ kJ) = -78.0\ kJ$

$25^oC = 25 + 273 = 298\ K$

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\Delta H^o - \Delta G^o = T\Delta S^o$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} = \frac{-78.0\ kJ - (-225.8\ kJ)}{298\ K} = 0.496\ kJ/K = 496\ J/K$$

$\Delta S^o = [2\ S^o(KCl) + 3\ S^o(O_2)] - 2\ S^o(KClO_3)$

$496\ J/K = [(2\ mol)(82.6\ J/(K \cdot mol)) + (3\ mol)S^o(O_2)] - (2\ mol)(143\ J/(K \cdot mol))$

$(3\ mol)S^o(O_2) = 496\ J/K - (2\ mol)(82.6\ J/(K \cdot mol)) + (2\ mol)(143\ J/(K \cdot mol))$

$(3\ mol)S^o(O_2) = 616.8\ J/K$

$S^o(O_2) = (616.8\ J/K)/(3\ mol) = 205.6\ J/(K \cdot mol) = 206\ J/(K \cdot mol)$

17.116 $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$\Delta H^o = 2\ \Delta H^o_f(NO_2) - \Delta H^o_f(N_2O_4) = (2\ mol)(33.2\ kJ) - (1\ mol)(9.16\ kJ) = 57.2\ kJ$

$\Delta S^o = 2\ S^o(NO_2) - S^o(N_2O_4) = (2\ mol)(240.0\ J/(K \cdot mol)) - (1\ mol)(304.2\ J/(K \cdot mol))$

$\Delta S^o = 175.8\ J/K = 175.8 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o$ and $\Delta G^o = -RT \ln K_p$; Set these two equations equal to each other and solve for T.

$\Delta H^o - T\Delta S^o = -RT \ln K_p$

$\Delta H^o = T\Delta S^o - RT \ln K_p = T(\Delta S^o - R \ln K_p)$

$$T = \frac{\Delta H^o}{\Delta S^o - R \ln K_p}$$

(a) $P_{N_2O_4} + P_{NO_2} = 1.00\ atm$ and $P_{NO_2} = 2\ P_{N_2O_4}$

$P_{N_2O_4} + 2\ P_{N_2O_4} = 3\ P_{N_2O_4} = 1.00\ atm$

$P_{N_2O_4} = 1.00\ atm/3 = 0.333\ atm$

$P_{NO_2} = 1.00\ atm - P_{N_2O_4} = 1.00 - 0.333 = 0.667\ atm$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.667)^2}{(0.333)} = 1.34$$

$$T = \frac{\Delta H^o}{\Delta S^o - R \ln K_p}$$

$$T = \frac{57.2 \text{ kJ/mol}}{[175.8 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}] - [8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}] \ln (1.34)} = 330 \text{ K}$$

$T = 330 \text{ K} = 330 - 273 = 57^oC$

(b) $P_{N_2O_4} + P_{NO_2} = 1.00$ atm and $P_{NO_2} = P_{N_2O_4}$ so $P_{NO_2} = P_{N_2O_4} = 0.50$ atm

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.500)^2}{(0.500)} = 0.500$$

$$T = \frac{\Delta H^o}{\Delta S^o - R \ln K_p}$$

$$T = \frac{57.2 \text{ kJ/mol}}{[175.8 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}] - [8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}] \ln (0.500)} = 315 \text{ K}$$

$T = 315 \text{ K} = 315 - 273 = 42^oC$

Multi-Concept Problems

17.117 $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$

$\Delta H^o = 2\ \Delta H^o_f(NO_2) - \Delta H^o_f(N_2O_4) = (2 \text{ mol})(33.2 \text{ kJ}) - (1 \text{ mol})(9.16 \text{ kJ}) = 57.2 \text{ kJ}$

$\Delta S^o = 2\ S^o(NO_2) - S^o(N_2O_4) = (2 \text{ mol})(240.0 \text{ J/(K} \cdot \text{mol)}) - (1 \text{ mol})(304.2 \text{ J/(K} \cdot \text{mol)})$

$\Delta S^o = 175.8 \text{ J/K} = 175.8 \times 10^{-3} \text{ kJ/K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = 57.2 \text{ kJ} - (373 \text{ K})(175.8 \times 10^{-3} \text{ kJ/K}) = -8.4 \text{ kJ}$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-8.4 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](373 \text{ K})} = 2.71$$

$K_p = e^{2.71} = 15$

	$N_2O_4(g)$	$\rightleftharpoons$	$2\ NO_2(g)$
initial (atm)	1.00		1.00
change (atm)	-x		+2x
equil (atm)	1.00 - x		1.00 + 2x

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = 15 = \frac{(1.00 + 2x)^2}{(1.00 - x)}$$

$4x^2 + 19x - 14 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(19) \pm \sqrt{(19)^2 - (4)(4)(-14)}}{2(4)} = \frac{-19 \pm 24.2}{8}$$

x = 0.65 and -5.4

Of the two solutions for x, only 0.65 has physical meaning because -5.4 would lead to a negative partial pressure for NO_2.

$P_{N_2O_4}$ = 1.00 - x = 1.00 - 0.65 = 0.35 atm; P_{NO_2} = 1.00 + 2x = 1.00 + 2(0.65) = 2.30 atm

17.118 $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$

$\Delta H^o = 2\,\Delta H^o_f(NH_3) - [\Delta H^o_f(N_2) + 3\,\Delta H^o_f(H_2)] = (2\text{ mol})(-46.1\text{ kJ}) - [0] = -92.2\text{ kJ}$

$\Delta S^o = 2\,S^o(NH_3) - [S^o(N_2) + 3\,S^o(H_2)]$

$\Delta S^o = (2\text{ mol})(192.3\text{ J/(K} \cdot \text{mol)})$

$- [(1\text{ mol})(191.5\text{ J/(K} \cdot \text{mol)}) + (3\text{ mol})(130.6\text{ J/(K} \cdot \text{mol)})] = -198.7\text{ J/K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -92.2\text{ kJ} - (673\text{ K})(-198.7 \times 10^{-3}\text{ kJ/K}) = 41.5\text{ kJ}$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-41.5\text{ kJ/mol}}{[8.314 \times 10^{-3}\text{ kJ/(K} \bullet \text{mol)}](673\text{ K})} = -7.42$$

$K_p = e^{-7.42} = 6.0 \times 10^{-4}$

Because $K_p = K_c(RT)^{\Delta n}$, $K_c = K_p(RT)^{-\Delta n}$

$K_c = K_p(RT)^2 = (6.0 \times 10^{-4})[(0.082\,06)(673)]^2 = 1.83$

N_2, 28.01 amu; H_2, 2.016 amu

Initial concentrations:

$$[N_2] = \frac{(14.0\text{ g})\left(\frac{1\text{ mol}}{28.01\text{ g}}\right)}{5.00\text{ L}} = 0.100\text{ M} \text{ and } [H_2] = \frac{(3.024\text{ g})\left(\frac{1\text{ mol}}{2.016\text{ g}}\right)}{5.00\text{ L}} = 0.300\text{ M}$$

	$N_2(g)$	+	$3\,H_2(g)$	$\rightleftharpoons$	$2\,NH_3(g)$
initial (M)	0.100		0.300		0
change (M)	-x		-3x		+2x
equil (M)	0.100 - x		0.300 - 3x		2x

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2x)^2}{(0.100 - x)(0.300 - 3x)^3} = \frac{4x^2}{27(0.100 - x)^4} = 1.83$$

$$\left(\frac{x}{(0.100 - x)^2}\right)^2 = \frac{(27)(1.83)}{4} = 12.35; \quad \frac{x}{(0.100 - x)^2} = \sqrt{12.35} = 3.515$$

$3.515x^2 - 1.703x + 0.03515 = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(-1.703) \pm \sqrt{(-1.703)^2 - (4)(3.515)(0.03515)}}{2(3.515)} = \frac{1.703 \pm 1.551}{7.030}$$

x = 0.463 and 0.0216

Of the two solutions for x, only 0.0216 has physical meaning because 0.463 would lead to negative concentrations of N_2 and H_2.

$[N_2] = 0.100 - x = 0.100 - 0.0216 = 0.078$ M

$[H_2] = 0.300 - 3x = 0.300 - 3(0.0216) = 0.235$ M

$[NH_3] = 2x = 2(0.0216) = 0.043\ M$

17.119 $2\ SO_2(g) + O_2(g) \_ 2\ SO_3(g)$

$\Delta H^o = 2\ \Delta H^o_f(SO_3) - 2\ \Delta H^o_f(SO_2)$

$\Delta H^o = (2\ mol)(-395.7\ kJ/mol) - (2\ mol)(-296.8\ kJ/mol) = -197.8\ kJ$

$\Delta S^o = 2\ S^o(SO_3) - [2\ S^o(SO_2) + S^o(O_2)]$

$\Delta S^o = (2\ mol)(256.6\ J/(K \cdot mol)) - [(2\ mol)(248.1\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -188.0\ J/K = -188.0 \times 10^{-3}\ kJ/K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -197.8\ kJ - (800\ K)(-188.0 \times 10^{-3}\ kJ/K) = -47.4\ kJ$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-47.4\ kJ/mol)}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](800\ K)} = 7.13$$

$K_p = e^{7.13} = 1249$

SO_2, 64.06 amu; O_2, 32.00 amu

At 800 K:

$$P_{SO_2} = \frac{n\,R\,T}{V} = \frac{\left(192\ g \times \frac{1\ mol}{64.06\ g}\right)\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(800\ K)}{15.0\ L} = 13.1\ atm$$

$$P_{O_2} = \frac{n\,R\,T}{V} = \frac{\left(48.0\ g \times \frac{1\ mol}{32.00\ g}\right)\left(0.08206\ \frac{L \bullet atm}{K \bullet mol}\right)(800\ K)}{15.0\ L} = 6.57\ atm$$

	$2\ SO_2(g)$	+	$O_2(g)$	_	$2\ SO_3(g)$
initial (atm)	13.1		6.57		0
assume complete rxn (atm)	0		0		13.1
assume a small back rxn	+2x		+x		-2x
equil (atm)	2x		x		13.1 - 2x

$$K_p = 1249 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(13.1 - 2x)^2}{(2x)^2(x)} \approx \frac{(13.1)^2}{(2x)^2(x)}$$

Solve for x. $x^3 = 0.0343$; $x = 0.325$

Use successive approximations to solve for x because 2x is not negligible compared with 13.1.

Second approximation:

$$1249 = \frac{[13.1 - (2)(0.325)]^2}{(2x)^2(x)};$$ Solve for x. $x^3 = 0.0310$; $x = 0.314$

Third approximation:

$$1249 = \frac{[13.1 - (2)(0.314)]^2}{(2x)^2(x)};$$ Solve for x. $x^3 = 0.0311$; $x = 0.315$ (x has converged)

P_{SO_2} = 2x = 2(0.315) = 0.63 atm

P_{O_2} = x = 0.32 atm

P_{SO_3} = 13.1 - 2x = 13.1 - 2(0.315) = 12.5 atm

(b) The % yield of SO_3 decreases with increasing temperature because ΔS^o is negative. ΔG^o becomes less negative and K_p gets smaller as the temperature increases.

(c) At 1000 K:

$\Delta G^o = \Delta H^o - T\Delta S^o = -197.8 \text{ kJ} - (1000 \text{ K})(-188.0 \times 10^{-3} \text{ kJ/K}) = -9.8 \text{ kJ}$

$\Delta G^o = -RT \ln K_p$

$$\ln K_p = \frac{-\Delta G^o}{RT} = \frac{-(-9.8 \text{ kJ/mol})}{[8.314 \times 10^{-3} \text{ kJ/(K} \bullet \text{ mol)}](1000 \text{ K})} = 1.179$$

$K_p = e^{1.179} = 3.25$

$$P_{SO_2} = \frac{n R T}{V} = \frac{\left(192 \text{ g} \times \frac{1 \text{ mol}}{64.06 \text{ g}}\right)\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(1000 \text{ K})}{15.0 \text{ L}} = 16.4 \text{ atm}$$

$$P_{O_2} = \frac{n R T}{V} = \frac{\left(48.0 \text{ g} \times \frac{1 \text{ mol}}{32.00 \text{ g}}\right)\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(1000 \text{ K})}{15.0 \text{ L}} = 8.2 \text{ atm}$$

	$2\ SO_2(g)$	+	$O_2(g)$	−	$2\ SO_3(g)$
initial (atm)	16.4		8.2		0
assume complete rxn (atm)	0		0		16.4
assume a small back rxn	+2x		+x		-2x
equil (atm)	2x		x		16.4 - 2x

$$K_p = 3.25 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(16.4 - 2x)^2}{(2x)^2(x)} \approx \frac{(16.4)^2}{(2x)^2(x)}$$

Solve for x. $x^3 = 20.7$; x = 2.7

Use successive approximations to solve for x because 2x is not negligible compared with 16.4.

Second approximation:

$3.25 = \frac{[16.4 - (2)(2.7)]^2}{(2x)^2(x)}$; Solve for x. $x^3 = 9.31$; x = 2.1

Third approximation:

$3.25 = \frac{[16.4 - (2)(2.1)]^2}{(2x)^2(x)}$; Solve for x. $x^3 = 11.4$; x = 2.3

Fourth approximation:

$3.25 = \frac{[16.4 - (2)(2.3)]^2}{(2x)^2(x)}$; Solve for x. $x^3 = 10.7$; x = 2.2 (x has converged)

P_{SO_2} = 2x = 2(2.2) = 4.4 atm

P_{O_2} = x = 2.2 atm

P_{SO_3} = 16.4 - 2x = 16.4 - 2(2.2) = 12.0 atm

$P_{total} = P_{SO_2} + P_{O_2} + P_{SO_3}$ = 4.4 + 2.2 + 12.0 = 18.6 atm

On going from 800 K to 1000 K, P_{total} increases to 18.6 atm (because K_p decreases, but P increases with temperature at constant volume).

17.120 $Pb(s) + PbO_2(s) + 2\ H^+(aq) + 2\ HSO_4^-(aq) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$

(a) $\Delta G^o = [2\ \Delta G^o_f(PbSO_4) + 2\ \Delta G^o_f(H_2O)] - [\Delta G^o_f(PbO_2) + 2\ \Delta G^o_f(HSO_4^-)]$

ΔG^o = (2 mol)(-813.2 kJ/mol) + (2 mol)(-237.2 kJ/mol)]
- [(1 mol)(-217.4 kJ/mol) + (2 mol)(-756.0 kJ/mol)] = -371.4 kJ

(b) $^oC = 5/9(^oF - 32) = 5/9(10 - 32) = -12.2^oC$; $-12.2^oC = 261$ K

$\Delta H^o = [2\ \Delta H^o_f(PbSO_4) + 2\ \Delta H^o_f(H_2O)] - [\Delta H^o_f(PbO_2) + 2\ \Delta H^o_f(HSO_4^-)]$

ΔH^o = [(2 mol)(-919.9 kJ/mol) + (2 mol)(-285.8 kJ/mol)]
- [(1 mol)(-277 kJ/mol) + (2 mol)(-887.3 kJ/mol)] = -359.8 kJ

$\Delta S^o = [2\ S^o(PbSO_4) + 2\ S^o(H_2O)] - [S^o(Pb) + S^o(PbO_2) + 2\ S^o(H^+) + 2\ S^o(HSO_4^-)]$

ΔS^o = [(2 mol)(148.6 J/(K · mol)) + (2 mol)(69.9 J/(K · mol))]
- [(1 mol)(64.8 J/(K · mol)) + (1 mol)(68.6 J/(K · mol))
+ (2 mol)(132 J/(K · mol))] = 39.6 J/K = 39.6 x 10^{-3} kJ/K

$\Delta G^o = \Delta H^o - T\Delta S^o$ = -359.8 kJ -(261 K)(39.6 x 10^{-3} kJ/K) = -370.1 kJ at 261 K

	$HSO_4^-(aq)$ +	$H_2O(l)$ _	$H_3O^+(aq)$ +	$SO_4^{2-}(aq)$
initial (M)	0.100		0.100	0
change (M)	-x		+x	+x
equil (M)	0.100 - x		0.100 + x	x

$$K_{a2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2} = \frac{(0.100 + x)\,x}{0.100 - x}$$

$x^2 + 0.112x - (1.2 \times 10^{-3}) = 0$

Use the quadratic formula to solve for x.

$$x = \frac{-(0.112) \pm \sqrt{(0.112)^2 - (4)(1)(-1.2 \times 10^{-3})}}{2(1)} = \frac{-0.112 \pm 0.132}{2}$$

x = -0.122 and 0.010

Of the two solutions for x, only 0.010 has physical meaning because -0.122 would lead to negative concentrations of H_3O^+ and SO_4^{2-}.

$[H^+] = 0.100 + x = 0.100 + 0.010 = 0.110$ M

$[HSO_4^-] = 0.100 - x = 0.100 - 0.010 = 0.090$ M

$$\Delta G = \Delta G^o + RT \ln \frac{1}{[H^+]^2[HSO_4^-]^2}$$

$$\Delta G = (-370.1 \text{ kJ/mol}) + [8.314 \times 10^{-3} \text{ kJ/(K · mol)}](261 \text{ K}) \ln \frac{1}{(0.110)^2(0.090)^2}$$

ΔG = -350.1 kJ/mol

17.121 $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$\Delta H^o = [\Delta H^o_f(Ca^{2+}) + \Delta H^o_f(CO_3^{2-})] - \Delta H^o_f(CaCO_3)$

$\Delta H^o = [(1\ mol)(-542.8\ kJ/mol) + (1\ mol)(-677.1\ kJ/mol)] - (1\ mol)(-1206.9\ kJ/mol)$

$\Delta H^o = -13.0\ kJ$

$\Delta S^o = [S^o(Ca^{2+}) + S^o(CO_3^{2-})] - S^o(CaCO_3)$

$\Delta S^o = [(1\ mol)(-53.1\ J/(K \cdot mol)) + (1\ mol)(-56.9\ J/(K \cdot mol))] - (1\ mol)(92.9\ J/(K \cdot mol))$

$\Delta S^o = -202.9\ J/K = -202.9 \times 10^{-3}\ kJ/K$

$50^oC = 50 + 273 = 323\ K$

$\Delta G = \Delta H^o - T\Delta S^o = -13.0\ kJ - (323\ K)(-202.9 \times 10^{-3}\ kJ/K) = +52.54\ kJ$

$\Delta G = -RT \ln K_{sp}$

$$\ln K_{sp} = \frac{-\Delta G}{RT} = \frac{-52.54\ kJ/mol}{[8.314 \times 10^{-3}\ kJ/(K \bullet mol)](323\ K)} = -19.56$$

$K_{sp} = e^{-19.56} = 3.2 \times 10^{-9}$

$20^oC = 20 + 273 = 293\ K$

$$n_{CO_2} = \frac{PV}{RT} = \frac{\left(731\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)(1.000\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(293\ K)} = 0.0400\ mol\ CO_2$$

$Ca(OH)_2$, 74.09 amu

$$mol\ Ca(OH)_2 = 3.335\ g\ Ca(OH)_2 \times \frac{1\ mol\ Ca(OH)_2}{74.09\ g\ Ca(OH)_2} = 0.0450\ mol\ Ca(OH)_2$$

$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

	$Ca(OH)_2(aq)$	+ $H_2CO_3(aq)$	$\rightarrow$ $CaCO_3(s)$	+ $2\ H_2O(l)$
before (mol)	0.0450	0.0400	0	
change (mol)	-0.0400	-0.0400	+0.0400	
after (mol)	0.0050	0	0.0400	

$500.0\ mL = 0.5000\ L$

$[Ca(OH)_2] = [Ca^{2+}] = 0.0050\ mol/0.5000\ L = 0.010\ M$

	$CaCO_3(s) \rightleftharpoons$	$Ca^{2+}(aq)$	+ $CO_3^{2-}(aq)$
initial (M)		0.010	0
change (M)		+x	+x
equil (M)		0.010 + x	x

$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 3.2 \times 10^{-9} = (0.010 + x)x \approx 0.010x$

x = molar solubility $= 3.2 \times 10^{-9}/0.010 = 3.2 \times 10^{-7}\ M$

Because ΔH^o is negative (exothermic), the solubility of $CaCO_3$ is lower at 50^oC.

17.122 $PV = nRT$

$$n_{NH_3} = \frac{PV}{RT} = \frac{\left(744\ mm\ Hg\ x \frac{1.00\ atm}{760\ mm\ Hg}\right)(1.00\ L)}{\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(298.1\ K)} = 0.0400\ mol\ NH_3$$

500.0 mL = 0.5000 L

$[NH_3] = 0.0400\ mol/0.5000\ L = 0.0800\ M$

$NH_3(aq) + H_2O(l) \_ NH_4^+(aq) + OH^-(aq)$

$\Delta H^o = [\Delta H^o_f(NH_4^+) + \Delta H^o_f(OH^-)] - [\Delta H^o_f(NH_3) + \Delta H^o_f(H_2O)]$

$\Delta H^o = [(1\ mol)(-132.5\ kJ/mol) + (1\ mol)(-230.0\ kJ/mol)]$
$- [(1\ mol)(-80.3\ kJ/mol) + (1\ mol)(-285.8\ kJ/mol)] = +3.6\ kJ$

$\Delta S^o = [S^o(NH_4^+) + S^o(OH^-)] - [S^o(NH_3) + S^o(H_2O)]$

$\Delta S^o = [(1\ mol)(113\ J/(K \cdot mol)) + (1\ mol)(-10.8\ J/(K \cdot mol))]$
$- [(1\ mol)(111\ J/(K \cdot mol)) + (1\ mol)(69.9\ J/(K \cdot mol))] = -78.7\ J/K$

$T = 2.0^oC = 2.0 + 273.1 = 275.1\ K$

$\Delta G^o = \Delta H^o - T\Delta S^o = 3.6\ kJ - (275.1\ K)(-78.7\ x\ 10^{-3}\ kJ/K) = 25.3\ kJ$

$\Delta G^o = -RT \ln K_b$

$$\ln K_b = \frac{-\Delta G^o}{RT} = \frac{-25.3\ kJ/mol}{[8.314\ x\ 10^{-3}\ kJ/(K \bullet mol)](275.1\ K)} = -11.06$$

$K_b = e^{-11.06} = 1.6\ x\ 10^{-5}$

	$NH_3(aq)$	+ $H_2O(l)$	_ $NH_4^+(aq)$	+ $OH^-(aq)$
initial (M)	0.0800		0	~0
change (M)	-x		+x	+x
equil (M)	0.0800 - x		x	x

$$\text{at } 2^oC,\ K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.6\ x\ 10^{-5} = \frac{x^2}{0.0800 - x} \approx \frac{x^2}{0.0800}$$

$x^2 = (1.6\ x\ 10^{-5})(0.0800)$

$x = [OH^-] = \sqrt{(1.6\ x\ 10^{-5})(0.0800)} = 1.13\ x\ 10^{-3}\ M$

$$[H_3O^+] = \frac{1.0\ x\ 10^{-14}}{1.13\ x\ 10^{-3}} = 8.85\ x\ 10^{-12}\ M$$

$pH = -\log[H_3O^+] = -\log(8.85\ x\ 10^{-12}) = 11.05$

17.123 (a) $I_2(s) \rightarrow 2\ I^-(aq)$

$[I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)] \times 5$ reduction half reaction

$I_2(s) \rightarrow 2\ IO_3^-(aq)$

$I_2(s) + 6\ H_2O(l) \rightarrow 2\ IO_3^-(aq)$

$I_2(s) + 6\ H_2O(l) \rightarrow 2\ IO_3^-(aq) + 12\ H^+(aq)$

$I_2(s) + 6\ H_2O(l) \rightarrow 2\ IO_3^-(aq) + 12\ H^+(aq) + 10\ e^-$ oxidation half reaction

Combine the two half reactions.

$6\ I_2(s) + 6\ H_2O(l) \rightarrow 10\ I^-(aq) + 2\ IO_3^-(aq) + 12\ H^+(aq)$

Divide all coefficients by 2.

$3\ I_2(s) + 3\ H_2O(l) \rightarrow 5\ I^-(aq) + IO_3^-(aq) + 6\ H^+(aq)$

$3\ I_2(s) + 3\ H_2O(l) + 6\ OH^-(aq) \rightarrow 5\ I^-(aq) + IO_3^-(aq) + 6\ H^+(aq) + 6\ OH^-(aq)$

$3\ I_2(s) + 3\ H_2O(l) + 6\ OH^-(aq) \rightarrow 5\ I^-(aq) + IO_3^-(aq) + 6\ H_2O(l)$

$3\ I_2(s) + 6\ OH^-(aq) \rightarrow 5\ I^-(aq) + IO_3^-(aq) + 3\ H_2O(l)$

(b) $\Delta G^o = [5\ \Delta G^o_f(I^-) + \Delta G^o_f(IO_3^-) + 3\ \Delta G^o_f(H_2O(l))] - 6\ \Delta G^o_f(OH^-)$

$\Delta G^o = [(5\text{ mol})(-51.6\text{ kJ/mol}) + (1\text{ mol})(-128.0\text{ kJ/mol}) + (3\text{ mol})(-237.2\text{ kJ/mol})]$
$- (6\text{ mol})(-157.3\text{ kJ/mol}) = -153.8\text{ kJ}$

(c) The reaction is spontaneous because ΔG^o is negative.

(d) $25^oC = 25 + 273 = 298\text{ K}$

$\Delta G^o = -RT \ln K_c$

$$\ln K_c = \frac{-\Delta G^o}{RT} = \frac{-(-153.8\text{ kJ/mol})}{[8.314 \times 10^{-3}\text{ kJ/(K} \bullet \text{mol)}](298\text{ K})} = 62.077$$

$K_c = e^{62.077} = 9.1 \times 10^{26}$

$$K_c = \frac{[I^-]^5[IO_3^-]}{[OH^-]^6} = 9.1 \times 10^{26} = \frac{(0.10)^5(0.50)}{[OH^-]^6}$$

$$[OH^-] = \sqrt[6]{\frac{(0.10)^5(0.50)}{9.1 \times 10^{26}}} = 4.2 \times 10^{-6}\text{ M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-6}} = 2.38 \times 10^{-9}\text{ M}$$

$pH = -\log[H_3O^+] = -\log(2.38 \times 10^{-9}) = 8.62$

18 Electrochemistry

18.1 $2\ Ag^+(aq) + Ni(s) \rightarrow 2\ Ag(s) + Ni^{2+}(aq)$

There is a Ni anode in an aqueous solution of Ni^{2+}, and a Ag cathode in an aqueous solution of Ag^+. A salt bridge connects the anode and cathode compartment. The electrodes are connected through an external circuit.

18.2 $Fe(s)\,|\,Fe^{2+}(aq)\,\|\,Sn^{2+}(aq)\,|\,Sn(s)$

18.3 $Pb(s) + Br_2(l) \rightarrow Pb^{2+}(aq) + 2\ Br^-(aq)$
There is a Pb anode in an aqueous solution of Pb^{2+}. The cathode is a Pt wire that dips into a pool of liquid Br_2 and an aqueous solution that is saturated with Br_2. A salt bridge connects the anode and cathode compartment. The electrodes are connected through an external circuit.

18.4 (a) and (b)

(c) $2\ Al(s) + 3\ Co^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Co(s)$

(d) $Al(s)\,|\,Al^{3+}(aq)\,\|\,Co^{2+}(aq)\,|\,Co(s)$

18.5 $Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$

$$\Delta G^o = -nFE^o = -(3 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(0.92 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = -266{,}340 \text{ J} = -270 \text{ kJ}$$

18.6

oxidation:	$Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-$	$E^o = 1.66$ V
reduction:	$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	$E^o = ?$
overall	$Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$	$E^o = 0.92$ V

The standard reduction potential for the Cr^{3+}/Cr half cell is:
$E^o = 0.92 - 1.66 = -0.74$ V

18.7 (a) $Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$ $E^o = 1.36$ V
$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^o = 0.80$ V

Cl_2 has the greater tendency to be reduced (larger E^o). The species that has the greater tendency to be reduced is the stronger oxidizing agent. Cl_2 is the stronger oxidizing agent.

(b) $Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$ $E^o = -0.45$ V
$Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$ $E^o = -2.37$ V

The second half-reaction has the lesser tendency to occur in the forward direction (more negative E^o) and the greater tendency to occur in the reverse direction. Therefore, Mg is the stronger reducing agent.

18.8 (a) $2\,Fe^{3+}(aq) + 2\,I^-(aq) \rightarrow 2\,Fe^{2+}(aq) + I_2(s)$

reduction:	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	$E^o = 0.77$ V
oxidation:	$2\,I^-(aq) \rightarrow I_2(s) + 2\,e^-$	$E^o = -0.54$ V
		overall $E^o = 0.23$ V

Because E^o for the overall reaction is positive, this reaction can occur under standard-state conditions.

(b) $3\,Ni(s) + 2\,Al^{3+}(aq) \rightarrow 3\,Ni^{2+}(aq) + 2\,Al(s)$

oxidation:	$Ni(s) \rightarrow Ni^{2+}(aq) + 2\,e^-$	$E^o = 0.26$ V
reduction:	$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	$E^o = -1.66$ V
		overall $E^o = -1.40$ V

Because E^o for the overall reaction is negative, this reaction cannot occur under standard-state conditions. This reaction can occur in the reverse direction.

18.9 (a) D is the strongest reducing agent. D^+ has the most negative standard reduction potential. A^{3+} is the strongest oxidizing agent. It has the most positive standard reduction potential.
(b) An oxidizing agent can oxidize any reducing agent that is below it in the table. B^{2+} can oxidize C and D.
A reducing agent can reduce any oxidizing agent that is above it in the table. C can reduce A^{3+} and B^{2+}.

(c) Use the two half-reactions that have the most positive and the most negative standard

reduction potentials, respectively.

$A^{3+} + 2\,e^- \rightarrow A^+$ 1.47 V

$\underline{2 \times (D \rightarrow D^+ + e^-)}$ $\underline{1.38\ V}$

$A^{3+} + 2\,D \rightarrow A^+ + 2\,D^+$ 2.85 V

18.10 $Cu(s) + 2\,Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2\,Fe^{2+}(aq)$

$E^o = E^o_{Cu\ \_\ Cu^{2+}} + E^o_{Fe^{3+}\ \_\ Fe^{2+}} = -0.34\ V + 0.77\ V = 0.43\ V; \quad n = 2\ mol\ e^-$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2} = 0.43\ V - \frac{(0.0592\ V)}{2} \log \frac{(0.25)(0.20)^2}{(1.0 \times 10^{-4})^2} = 0.25\ V$$

18.11 $5\,[Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^-]$ oxidation half reaction

$2\,[5\,e^- + 8\,H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)]$ reduction half reaction

$5\,Cu(s) + 16\,H^+(aq) + 2\,MnO_4^-(aq) \rightarrow 5\,Cu^{2+}(aq) + 2\,Mn^{2+}(aq) + 8\,H_2O(l)$

$$\Delta E = -\frac{0.0592\ V}{n} \log \frac{[Cu^{2+}]^5[Mn^{2+}]^2}{[MnO_4^-]^2[H^+]^{16}}$$

(a) The anode compartment contains Cu^{2+}.

$$\Delta E = -\frac{0.0592\ V}{10} \log \frac{(0.01)^5(1)^2}{(1)^2(1)^{16}} = +0.059\ V$$

(b) The cathode compartment contains Mn^{2+}, MnO_4^-, and H^+.

$$\Delta E = -\frac{0.0592\ V}{10} \log \frac{(1)^5(0.01)^2}{(0.01)^2(0.01)^{16}} = -0.19\ V$$

18.12 $H_2(g) + Pb^{2+}(aq) \rightarrow 2\,H^+(aq) + Pb(s)$

$E^o = E^o_{H_2\ \_\ H^+} + E^o_{Pb^{2+}\ \_\ Pb} = 0\ V + (-0.13\ V) = -0.13\ V; \quad n = 2\ mol\ e^-$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[H_3O^+]^2}{[Pb^{2+}](P_{H_2})}$$

$$0.28\ V = -0.13\ V - \frac{(0.0592\ V)}{2} \log \frac{[H_3O^+]^2}{(1)(1)} = -0.13\ V - (0.0592\ V) \log [H_3O^+]$$

$pH = -\log[H_3O^+]$ therefore $0.28\ V = -0.13\ V + (0.0592\ V)\ pH$

$$pH = \frac{(0.28\ V + 0.13\ V)}{0.0592\ V} = 6.9$$

18.13 $4\,Fe^{2+}(aq) + O_2(g) + 4\,H^+(aq) \rightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$

$E^o = E^o_{Fe^{2+}\ \_\ Fe^{3+}} + E^o_{O_2\ \_\ H_2O} = -0.77\ V + 1.23\ V = 0.46\ V; \quad n = 4\ mol\ e^-$

$$E^o = \frac{0.0592\ V}{n} \log K$$

$$\log K = \frac{nE^o}{0.0592\ V} = \frac{(4)(0.46\ V)}{0.0592\ V} = 31; \quad K = 10^{31} \text{ at } 25^oC$$

18.14 $E^o = \frac{0.0592\ V}{n} \log K = \frac{0.0592\ V}{2} \log (1.8 \times 10^{-5}) = -0.140\ V$

18.15 (a) $Zn(s) + 2\ MnO_2(s) + 2\ NH_4^+(aq) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(l)$
(b) $Zn(s) + 2\ MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$
(c) $Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$
(d) $Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l) \rightarrow Cd(OH)_2(s) + 2\ Ni(OH)_2(s)$

18.16 (a) $[Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-] \times 2$
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$
$2\ Mg(s) + O_2(g) + 4\ H^+(aq) \rightarrow 2\ Mg^{2+}(aq) + 2\ H_2O(l)$
(b) $[Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-] \times 4$
$[O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)] \times 2$
$4\ Fe^{2+}(aq) + O_2(g) + 4\ H^+(aq) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O(l)$
$[2\ Fe^{3+}(aq) + 4\ H_2O(l) \rightarrow Fe_2O_3 \cdot H_2O(s) + 6\ H^+(aq)] \times 2$
$4\ Fe(s) + 3\ O_2(g) + 2\ H_2O(l) \rightarrow 2\ Fe_2O_3 \cdot H_2O(s)$

18.17 (a)

(b)

anode reaction	$4\ OH^-(l) \rightarrow O_2(g) + 2\ H_2O(l) + 4\ e^-$
cathode reaction	$4\ K^+(l) + 4\ e^- \rightarrow 4\ K(l)$
overall reaction	$4\ K^+(l) + 4\ OH^-(l) \rightarrow 4\ K(l) + O_2(g) + 2\ H_2O(l)$

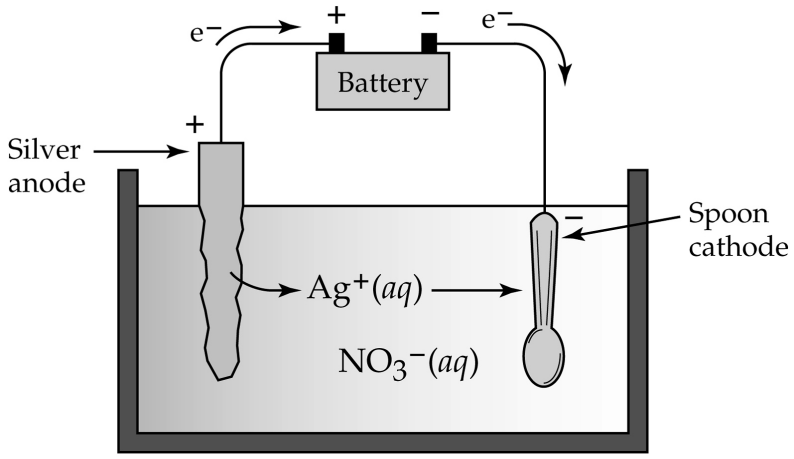
18.18 (a)

anode reaction	$2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$
cathode reaction	$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$
overall reaction	$2\ Cl^-(aq) + 2\ H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2\ OH^-(aq)$

(b)

anode reaction	$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$
cathode reaction	$2\ Cu^{2+}(aq) + 4\ e^- \rightarrow 2\ Cu(s)$
overall reaction	$2\ Cu^{2+}(aq) + 2\ H_2O(l) \rightarrow 2\ Cu(s) + O_2(g) + 4\ H^+(aq)$

18.19



anode reaction $Ag(s) \rightarrow Ag^+(aq) + e^-$
cathode reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$
The overall reaction is transfer of silver metal from the silver anode to the spoon.

18.20 $\text{Charge} = \left(1.00 \times 10^5 \frac{\text{C}}{\text{s}}\right)(8.00\ \text{h})\left(\frac{60\ \text{min}}{\text{h}}\right)\left(\frac{60\ \text{s}}{\text{min}}\right) = 2.88 \times 10^9\ \text{C}$

$\text{Moles of } e^- = (2.88 \times 10^9\ \text{C})\left(\frac{1\ \text{mol } e^-}{96{,}500\ \text{C}}\right) = 2.98 \times 10^4\ \text{mol } e^-$

cathode reaction: $Al^{3+} + 3\,e^- \rightarrow Al$

$\text{mass Al} = (2.98 \times 10^4\ \text{mol } e^-) \times \frac{1\ \text{mol Al}}{3\ \text{mol } e^-} \times \frac{26.98\ \text{g Al}}{1\ \text{mol Al}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 268\ \text{kg Al}$

18.21 $3.00\ \text{g Ag} \times \frac{1\ \text{mol Ag}}{107.9\ \text{g Ag}} = 0.0278\ \text{mol Ag}$

cathode reaction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

$\text{Charge} = (0.0278\ \text{mol Ag})\left(\frac{1\ \text{mol } e^-}{1\ \text{mol Ag}}\right)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol } e^-}\right) = 2682.7\ \text{C}$

$\text{Time} = \frac{\text{C}}{\text{A}} = \left(\frac{2682.7\ \text{C}}{0.100\ \text{C/s}} \times \frac{1\ \text{h}}{3600\ \text{s}}\right) = 7.45\ \text{h}$

18.22 When a beam of white light strikes the anodized surface, part of the light is reflected from the outer TiO_2, while part penetrates through the semitransparent TiO_2 and is reflected from the inner metal. If the two reflections of a particular wavelength are out of phase, they interfere destructively and that wavelength is canceled from the reflected light.
Because $n\lambda = 2d \times \sin\theta$, the canceled wavelength depends on the thickness of the TiO_2 layer.

18.23 $\text{volume} = \left(0.0100\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}\right)(10.0\ \text{cm})^2 = 0.100\ \text{cm}^3$

$\text{mol } Al_2O_3 = (0.100\ \text{cm}^3)(3.97\ \text{g/cm}^3)\frac{1\ \text{mol } Al_2O_3}{102.0\ \text{g } Al_2O_3} = 3.892 \times 10^{-3}\ \text{mol } Al_2O_3$

$\text{mole } e^- = 3.892 \times 10^{-3}\ \text{mol } Al_2O_3 \times \frac{6\ \text{mol } e^-}{1\ \text{mol } Al_2O_3} = 0.02335\ \text{mol } e^-$

$\text{coulombs} = 0.02335\ \text{mol } e^- \times \frac{96{,}500\ \text{C}}{1\ \text{mol } e^-} = 2253\ \text{C}$

$\text{time} = \frac{\text{C}}{\text{A}} = \frac{2253\ \text{C}}{0.600\ \text{C/s}} \times \frac{1\ \text{min}}{60\ \text{s}} = 62.6\ \text{min}$

Understanding Key Concepts

18.24 (a) - (d)

(e) anode reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$
cathode reaction $\underline{Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)}$
overall reaction $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$

18.25 (a) anode is Ni; cathode is Pt
(b) anode reaction $3\ Ni(s) \rightarrow 3\ Ni^{2+}(aq) + 6\ e^-$
cathode reaction $\underline{Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)}$
overall reaction $Cr_2O_7^{2-}(aq) + 3\ Ni(s) + 14\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ Ni^{2+}(aq) + 7\ H_2O(l)$
(c) $Ni(s)\,|\,Ni^{2+}(aq)\,\|\,Cr_2O_7^{2-}(aq), Cr^{3+}\,|\,Pt(s)$

18.26 (a) The three cell reactions are the same except for cation concentrations.

anode reaction	$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$	$E^o = -0.34$ V
cathode reaction	$\underline{2\ Fe^{3+}(aq) + 2\ e^- \rightarrow 2\ Fe^{2+}(aq)}$	$\underline{E^o = 0.77\ \text{V}}$
overall reaction	$Cu(s) + 2\ Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Fe^{2+}(aq)$	$E^o = 0.43$ V

(b)

(c) $E = E^o - \frac{0.0592\ V}{n} \log \frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{2+}]^2}$; $n = 2$ mol e^-

(1) $E = E^o = 0.43$ V because all cation concentrations are 1 M.

(2) $E = E^o - \frac{0.0592\ V}{2} \log \frac{(1)(5)^2}{(1)^2} = 0.39$ V

(3) $E = E^o - \frac{0.0592\ V}{2} \log \frac{(0.1)(0.1)^2}{(0.1)^2} = 0.46$ V

Cell (3) has the largest potential, while cell (2) has the smallest as calculated from the Nernst equation.

18.27 (a) - (b)

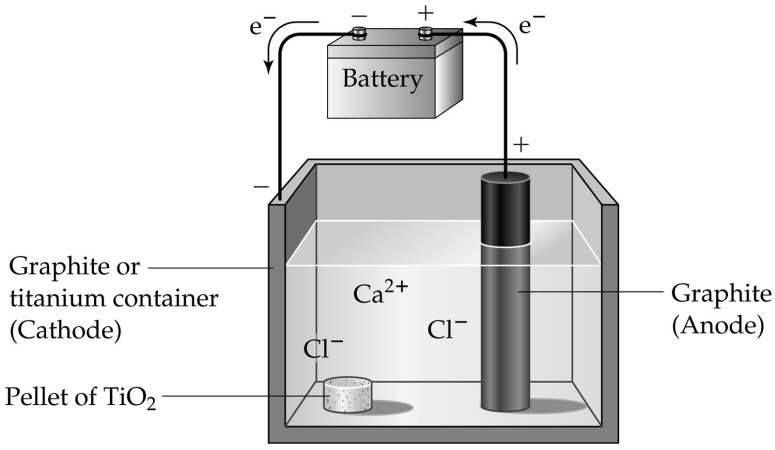
(c) anode reaction $2\ Br^-(aq) \rightarrow Br_2(aq) + 2\ e^-$
cathode reaction $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$
overall reaction $Cu^{2+}(aq) + 2\ Br^-(aq) \rightarrow Cu(s) + Br_2(aq)$

18.28 (a) This is an electrolytic cell that has a battery connected between two inert electrodes.

(b)

(c) anode reaction $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$
cathode reaction $\underline{Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)}$
overall reaction $2\ Ni^{2+}(aq) + 2\ H_2O(l) \rightarrow 2\ Ni(s) + O_2(g) + 4\ H^+(aq)$

18.29 (a) & (b)



(c) anode reaction $2\ O^{2-} \rightarrow O_2(g) + 4\ e^-$
cathode reaction $\underline{TiO_2(s) + 4\ e^- \rightarrow Ti(s) + 2\ O^{2-}}$
overall reaction $TiO_2(s) \rightarrow Ti(s) + O_2(g)$

18.30 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$; $E = E^o - \dfrac{0.0592\ V}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

(a) E increases because increasing $[Cu^{2+}]$ decreases $\log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$.

(b) E will decrease because addition of H_2SO_4 increases the volume which decreases

$[Cu^{2+}]$ and increases $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$.

(c) E decreases because increasing $[Zn^{2+}]$ increases $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$.

(d) Because there is no change in $[Zn^{2+}]$, there is no change in E.

18.31 $Cu(s) + 2\ Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s); \quad E = E^o - \frac{0.0592\ V}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$

(a) E decreases because addition of NaCl precipitates AgCl which decreases $[Ag^+]$ and increases $\log \frac{[Cu^{2+}]}{[Ag^+]^2}$.

(b) E increases because addition of NaCl increases the volume which decreases $[Cu^{2+}]$ and decreases $\log \frac{[Cu^{2+}]}{[Ag^+]^2}$.

(c) E decreases because addition of NH_3 complexes Ag^+, yielding $Ag(NH_3)_2{}^+$, which decreases $[Ag^+]$ and increases $\log \frac{[Cu^{2+}]}{[Ag^+]^2}$.

(d) E increases because addition of NH_3 complexes Cu^{2+}, yielding $Cu(NH_3)_4{}^{2+}$, which decreases $[Cu^{2+}]$ and decreases $\log \frac{[Cu^{2+}]}{[Ag^+]^2}$.

Additional Problems
Galvanic Cells

18.32 The electrode where oxidation takes place is called the anode. For example, the lead electrode in the lead storage battery.
The electrode where reduction takes place is called the cathode. For example, the PbO_2 electrode in the lead storage battery.

18.33 The oxidizing agent gets reduced and reduction takes place at the cathode.

18.34 The cathode of a galvanic cell is considered to be the positive electrode because electrons flow through the external circuit toward the positive electrode (the cathode).

18.35 The salt bridge maintains charge neutrality in both the anode and cathode compartments of a galvanic cell.

18.36 (a) $Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$

(b) $2\ Al(s) + 3\ Cd^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cd(s)$

(c) $6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

18.37 (a) $3\ Cu^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Cu(s) + 2\ Cr^{3+}(aq)$

(b) $Pb(s) + 2\ H^{+}(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$

(c) $Cl_2(g) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ Cl^{-}(aq)$

18.38 (a) $Cd(s)\,|\,Cd^{2+}(aq)\,\|\,Sn^{2+}(aq)\,|\,Sn(s)$
(b) $Al(s)\,|\,Al^{3+}(aq)\,\|\,Cd^{2+}(aq)\,|\,Cd(s)$
(c) $Pt(s)\,|\,Fe^{2+}(aq),\ Fe^{3+}(aq)\,\|\,Cr_2O_7^{2-}(aq),\ Cr^{3+}(aq)\,|\,Pt(s)$

18.39 (a) $Cr(s)\,|\,Cr^{3+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$
(b) $Pb(s)\,|\,Pb^{2+}(aq)\,\|\,H^{+}(aq)\,|\,H_2(g)\,|\,Pt(s)$
(c) $Pt(s)\,|\,Sn^{2+}(aq),\ Sn^{4+}(aq)\,\|\,Cl_2(g)\,|\,Cl^{-}(aq)\,|\,Pt(s)$

18.40 (a)

(b) anode reaction $H_2(g) \rightarrow 2\,H^{+}(aq) + 2\,e^{-}$
cathode reaction $2\,Ag^{+}(aq) + 2\,e^{-} \rightarrow 2\,Ag(s)$
overall reaction $H_2(g) + 2\,Ag^{+}(aq) \rightarrow 2\,H^{+}(aq) + 2\,Ag(s)$

(c) $Pt(s)\,|\,H_2(g)\,|\,H^{+}(aq)\,\|\,Ag^{+}(aq)\,|\,Ag(s)$

18.41 (a)

(b) anode reaction $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$
cathode reaction $\underline{Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)}$
overall reaction $Zn(s) + Cl_2(g) \rightarrow Zn^{2+}(aq) + 2\ Cl^-(aq)$
(c) $Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cl_2(g)\,|\,Cl^-(aq)\,|\,C(s)$

18.42 (a) anode reaction $Co(s) \rightarrow Co^{2+}(aq) + 2\ e^-$
cathode reaction $\underline{Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)}$
overall reaction $Co(s) + Cu^{2+}(aq) \rightarrow Co^{2+}(aq) + Cu(s)$

(b) anode reaction $2\ Fe(s) \rightarrow 2\ Fe^{2+}(aq) + 4\ e^-$
cathode reaction $\underline{O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)}$
overall reaction $2\ Fe(s) + O_2(g) + 4\ H^+(aq) \rightarrow 2\ Fe^{2+}(aq) + 2\ H_2O(l)$

18.43 (a) anode reaction $Mn(s) \rightarrow Mn^{2+}(aq) + 2\ e^-$

cathode reaction $\underline{Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)}$

overall reaction $Mn(s) + Pb^{2+}(aq) \rightarrow Mn^{2+}(aq) + Pb(s)$

(b) anode reaction $H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$

cathode reaction $\underline{2\ AgCl(s) + 2\ e^- \rightarrow 2\ Ag(s) + 2\ Cl^-(aq)}$

overall reaction $H_2(g) + 2\ AgCl(s) \rightarrow 2\ Ag(s) + 2\ H^+(aq) + 2\ Cl^-(aq)$

Cell Potentials and Free-Energy Changes; Standard Reduction potentials

18.44 The SI unit of electrical potential is the volt (V).
The SI unit of charge is the coulomb (C).
The SI unit of energy is the joule (J).
1 J = 1 C · 1 V

18.45 $\Delta G = -nFE$; ΔG is the free energy change for the cell reaction
n is the number of moles of e^-
F is the Faraday (96,500 C/mol e^-)
E is the galvanic cell potential

18.46 E is the standard cell potential (E^o) when all reactants and products are in their standard states--solutes at 1 M concentrations, gases at a partial pressure of 1 atm, solids and liquids in pure form, all at 25°C.

18.47 The standard reduction potential is the potential of the reduction half reaction in a galvanic cell where the other electrode is the standard hydrogen electrode.

18.48 $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2\ Ag(s)$; n = 2 mol e^-

$$\Delta G = -nFE = -(2 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(1.60 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = -308{,}800 \text{ J} = -309 \text{ kJ}$$

18.49 $Pb(s) + PbO_2(s) + 2\ H^+(aq) + 2\ HSO_4^-(aq) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$

n = 2 mol e^-

$$\Delta G^o = -nFE^o = -(2 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(1.924 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = -371{,}300 \text{ J} = -371 \text{ kJ}$$

18.50 $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$; n = 4 mol e^- and 1 V = 1 J/C

$\Delta G^o = 2\ \Delta G^o_f(H_2O(l)) = (2 \text{ mol})(-237.2 \text{ kJ/mol}) = -474.4 \text{ kJ}$

$\Delta G^o = -nFE^o$

$$E^o = \frac{-\Delta G^o}{nF} = \frac{-(-474{,}400 \text{ J})}{(4 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)} = +1.23 \text{ J/C} = +1.23 \text{ V}$$

18.51 $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$; n = 8 mol e^- and 1 V = 1 J/C

$\Delta G^o = [\Delta G^o_f(CO_2) + 2\ \Delta G^o_f(H_2O(l))] - \Delta G^o_f(CH_4)$

$\Delta G^o = [(1 \text{ mol})(-394.4 \text{ kJ/mol}) + (2 \text{ mol})(-237.2 \text{ kJ/mol})]$
$- (1 \text{ mol})(-50.8 \text{ kJ/mol}) = -818.0 \text{ kJ}$

$\Delta G^o = -nFE^o$ $\qquad$ $$E^o = \frac{-\Delta G^o}{nF} = \frac{-(-818{,}000 \text{ J})}{(8 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)} = +1.06 \text{ J/C} = +1.06 \text{ V}$$

18.52

oxidation:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$	$E^o = 0.76$ V
reduction:	$Eu^{3+}(aq) + e^- \rightarrow Eu^{2+}(aq)$	$E^o = ?$
overall	$Zn(s) + 2\ Eu^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2\ Eu^{2+}(aq)$	$E^o = 0.40$ V

The standard reduction potential for the Eu^{3+}/Eu^{2+} half cell is:

$E^o = 0.40 - 0.76 = -0.36$ V

18.53

oxidation:	$2\ Ag(s) + 2\ Br^-(aq) \rightarrow 2\ AgBr(s) + 2\ e^-$	$E^o = ?$
reduction:	$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	$E^o = 0.34$ V
overall	$Cu^{2+}(aq) + 2\ Ag(s) + 2\ Br^-(aq) \rightarrow Cu(s) + 2\ AgBr(s)$	$E^o = 0.27$ V

E^o for the oxidation half reaction = 0.27 - 0.34 = -0.07 V

For $AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$, $E^o = -(-0.07 \text{ V}) = +0.07$ V

18.54 $Sn^{4+}(aq) < Br_2(l) < MnO_4^-$

18.55 $Pb(s) < Fe(s) < Al(s)$

18.56 $Cr_2O_7^{2-}(aq)$ is highest in the table of standard reduction potentials, therefore it is the strongest oxidizing agent.

$Fe^{2+}(aq)$ is lowest in the table of standard reduction potentials, therefore it is the weakest oxidizing agent.

18.57 From Table 18.1:

Sn^{2+} is the strongest reducing agent and Fe^{2+} is the weakest reducing agent.

18.58 (a) $Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$

oxidation: $Cd(s) \rightarrow Cd^{2+}(aq) + 2\ e^-$ $E^o = 0.40$ V

reduction: $Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$ $\underline{E^o = -0.14\ V}$

overall $E^o = 0.26$ V

$n = 2$ mol e^-

$$\Delta G^o = -nFE^o = -(2\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(0.26\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -50{,}180\ \text{J} = -50\ \text{kJ}$$

(b) $2\ Al(s) + 3\ Cd^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cd(s)$

oxidation: $2\ Al(s) \rightarrow 2\ Al^{3+}(aq) + 6\ e^-$ $E^o = 1.66$ V

reduction: $3\ Cd^{2+}(aq) + 6\ e^- \rightarrow 3\ Cd(s)$ $\underline{E^o = -0.40\ V}$

overall $E^o = 1.26$ V

$n = 6$ mol e^-

$$\Delta G^o = -nFE^o = -(6\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(1.26\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -729{,}540\ \text{J} = -730\ \text{kJ}$$

(c) $6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

oxidation: $6\ Fe^{2+}(aq) \rightarrow 6\ Fe^{3+}(aq) + 6\ e^-$ $E^o = -0.77$ V

reduction: $Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- + \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ $\underline{E^o = 1.33\ V}$

overall $E^o = 0.56$ V

$n = 6$ mol e^-

$$\Delta G^o = -nFE^o = -(6\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(0.56\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -324{,}240\ \text{J} = -324\ \text{kJ}$$

18.59 (a) $3\ Cu^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Cu(s) + 2\ Cr^{3+}(aq)$

oxidation $2\ Cr(s) \rightarrow 2\ Cr^{3+}(aq) + 6\ e^-$ $E^o = 0.74$ V

reduction $3\ Cu^{2+}(aq) + 6\ e^- \rightarrow 3\ Cu(s)$ $\underline{E^o = 0.34\ V}$

overall $E^o = 1.08$ V

$n = 6$ mol e^-

$$\Delta G^o = -nFE^o = -(6\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(1.08\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -625{,}320\ \text{J} = -625\ \text{kJ}$$

(b) $Pb(s) + 2\ H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$

oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2\ e^-$ $E^o = 0.13$ V

reduction: $2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$ $\underline{E^o = 0.00\ V}$

overall $E^o = 0.13$ V

$n = 2$ mol e^-

$$\Delta G^o = -nFE^o = -(2\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(0.13\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -25{,}090\ \text{J} = -25\ \text{kJ}$$

(c) $Cl_2(g) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ Cl^-(aq)$

oxidation $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ e^-$ $E^o = -0.15$ V

reduction $Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ $\underline{E^o = 1.36\ V}$

overall $E^o = 1.21$ V

n = 2 mol e^-

$$\Delta G^o = -nFE^o = -(2 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(1.21 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = -233{,}530 \text{ J} = -234 \text{ kJ}$$

18.60 (a) $2\ Fe^{2+}(aq) + Pb^{2+}(aq) \rightarrow 2\ Fe^{3+}(aq) + Pb(s)$

oxidation: $2\ Fe^{2+}(aq) \rightarrow 2\ Fe^{3+}(aq) + 2\ e^-$ $E^o = -0.77$ V

reduction: $Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$ $E^o = -0.13$ V

overall $E^o = -0.90$ V

Because E^o is negative, this reaction is nonspontaneous.

(b) $Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$

oxidation: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\ e^-$ $E^o = 2.37$ V

reduction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $E^o = -0.26$ V

overall $E^o = 2.11$ V

Because E^o is positive, this reaction is spontaneous.

18.61 (a) $5\ Ag^+(aq) + Mn^{2+}(aq) + 4\ H_2O(l) \rightarrow 5\ Ag(s) + MnO_4^-(aq) + 8\ H^+(aq)$

oxidation: $Mn^{2+}(aq) + 4\ H_2O(l) \rightarrow MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$ $E^o = -1.51$ V

reduction: $5\ Ag^+(aq) + 5\ e^- \rightarrow 5\ Ag(s)$ $E^o = 0.80$ V

overall $E^o = -0.71$ V

Because E^o is negative, this reaction is nonspontaneous.

(b) $2\ H_2O_2(aq) \rightarrow O_2(g) + 2\ H_2O(l)$

oxidation: $H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2\ e^-$ $E^o = -0.70$ V

reduction: $H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$ $E^o = 1.78$ V

overall $E^o = 1.08$ V

Because E^o is positive, this reaction is spontaneous.

18.62 (a) oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ e^-$ $E^o = -0.15$ V

reduction: $Br_2(l) + 2\ e^- \rightarrow 2\ Br^-(aq)$ $E^o = 1.09$ V

overall $E^o = +0.94$ V

Because the overall E^o is positive, $Sn^{2+}(aq)$ can be oxidized by $Br_2(l)$.

(b) oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ e^-$ $E^o = -0.15$ V

reduction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $E^o = -0.26$ V

overall $E^o = -0.41$ V

Because the overall E^o is negative, $Ni^{2+}(aq)$ cannot be reduced by $Sn^{2+}(aq)$.

(c) oxidation: $2\ Ag(s) \rightarrow 2\ Ag^+(aq) + 2\ e^-$ $E^o = -0.80$ V

reduction: $Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$ $E^o = -0.13$ V

overall $E^o = -0.93$ V

Because the overall E^o is negative, Ag(s) cannot be oxidized by $Pb^{2+}(aq)$.

(d) oxidation: $H_2SO_3(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$ $E^o = -0.17$ V

reduction: $I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)$ $E^o = 0.54$ V

overall $E^o = +0.37$ V

Because the overall E^o positive, $I_2(s)$ can be reduced by H_2SO_3.

18.63 (a) oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$ $E^o = 0.76$ V
reduction: $Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$ $\underline{E^o = -0.13\ V}$
overall $E^o = 0.63$ V

$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$
The reaction is spontaneous because E^o is positive.

(b) oxidation: $4\ Fe^{2+}(aq) \rightarrow 4\ Fe^{3+}(aq) + 4\ e^-$ $E^o = -0.77$ V
reduction: $O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$ $\underline{E^o = 1.23\ V}$
overall $E^o = 0.46$ V

$4\ Fe^{2+}(aq) + O_2(g) + 4\ H^+(aq) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O(l)$
The reaction is spontaneous because E^o is positive.

(c) oxidation: $2\ Ag(s) \rightarrow 2\ Ag^+(aq) + 2\ e^-$ $E^o = -0.80$ V
reduction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $\underline{E^o = -0.26\ V}$
overall $E^o = -1.06$ V

There is no reaction because E^o is negative.

(d) oxidation: $H_2(g) \rightarrow 2\ H^+(aq) + 2\ e^-$ $E^o = 0.00$ V
reduction: $Cd^{2+}(aq) + 2\ e^- \rightarrow Cd(s)$ $\underline{E^o = -0.40\ V}$
overall $E^o = -0.40$ V

There is no reaction because E^o is negative.

The Nernst Equation

18.64 $2\ Ag^+(aq) + Sn(s) \rightarrow 2\ Ag(s) + Sn^{2+}(aq)$
oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2\ e^-$ $E^o = 0.14$ V
reduction: $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$ $\underline{E^o = 0.80\ V}$
overall $E^o = 0.94$ V

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Sn^{2+}]}{[Ag^+]^2} = 0.94\ V - \frac{(0.0592\ V)}{2} \log \frac{(0.020)}{(0.010)^2} = 0.87\ V$$

18.65 $2\ Fe^{2+}(aq) + Cl_2(g) \rightarrow 2\ Fe^{3+}(aq) + 2\ Cl^-(aq)$
oxidation: $2\ Fe^{2+}(aq) \rightarrow 2\ Fe^{3+}(aq) + 2\ e^-$ $E^o = -0.77$ V
reduction: $Cl_2(g) + 2\ e^- \rightarrow 2\ Cl^-(aq)$ $\underline{E^o = 1.36\ V}$
overall $E^o = 0.59$ V

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Fe^{3+}]^2[Cl^-]^2}{[Fe^{2+}]^2 P_{Cl_2}} = 0.59\ V - \frac{(0.0592\ V)}{2} \log \frac{(0.0010)^2(0.0030)^2}{(1.0)^2(0.50)} = 0.91\ V$$

18.66 $Pb(s) + Cu^{2+}(aq) \rightarrow Pb^{2+}(aq) + Cu(s)$
oxidation: $Pb(s) \rightarrow Pb^{2+}(aq) + 2\ e^-$ $E^o = 0.13$ V
reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $\underline{E^o = 0.34\ V}$
overall $E^o = 0.47$ V

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Pb^{2+}]}{[Cu^{2+}]} = 0.47\ V - \frac{(0.0592\ V)}{2} \log \frac{1.0}{(1.0 \times 10^{-4})} = 0.35\ V$$

When E = 0, $0 = E^o - \frac{0.0592\ V}{n}\log\frac{[Pb^{2+}]}{[Cu^{2+}]} = 0.47\ V - \frac{(0.0592\ V)}{2}\log\frac{1.0}{[Cu^{2+}]}$

$0 = 0.47\ V + \frac{(0.0592\ V)}{2}\log[Cu^{2+}]$

$\log[Cu^{2+}] = (-0.47\ V)\left(\frac{2}{0.0592\ V}\right) = -15.88; \qquad [Cu^{2+}] = 10^{-15.88} = 1 \times 10^{-16}\ M$

18.67 $Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$

oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$ $\qquad E^o = 0.45\ V$

reduction: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $\qquad \underline{E^o = 0.34\ V}$

overall $E^o = 0.79\ V$

$E = 0.67\ V = E^o - \frac{0.0592\ V}{n}\log\frac{[Fe^{2+}]}{[Cu^{2+}]} = 0.79\ V - \frac{(0.0592\ V)}{2}\log\left(\frac{0.10}{[Cu^{2+}]}\right)$

$0.67\ V = 0.79\ V - \frac{(0.0592\ V)}{2}(\log\ (0.10) - \log\ [Cu^{2+}])$

$\log[Cu^{2+}] = -5.05; \qquad [Cu^{2+}] = 10^{-5.05} = 8.9 \times 10^{-6}\ M$

18.68 (a) $E = E^o - \frac{0.0592\ V}{n}\log\ [I^-]^2 = 0.54\ V - \frac{(0.0592\ V)}{2}\log\ (0.020)^2 = 0.64\ V$

(b) $E = E^o - \frac{0.0592\ V}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.77\ V - \frac{(0.0592\ V)}{1}\log\left(\frac{0.10}{0.10}\right) = 0.77\ V$

(c) $E = E^o - \frac{0.0592\ V}{n}\log\frac{[Sn^{4+}]}{[Sn^{2+}]} = -0.15\ V - \frac{(0.0592\ V)}{2}\log\left(\frac{0.40}{0.0010}\right) = -0.23\ V$

(d) $E = E^o - \frac{0.0592\ V}{n}\log\frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2} = -1.33\ V - \frac{(0.0592\ V)}{6}\log\left(\frac{(1.0)(0.010)^{14}}{1.0}\right)$

$E = -1.33\ V - \frac{(0.0592\ V)}{6}(14)\log\ (0.010) = -1.05\ V$

18.69 $E = E^o - \frac{0.0592\ V}{n}\log\frac{P_{H_2}}{[H_3O^+]^2}$; $\quad E^o = 0$, n = 2 mol e^-, and $P_{H_2} = 1$ atm

(a) $[H_3O^+] = 1.0\ M; \quad E = -\frac{0.0592\ V}{2}\log\frac{1}{(1.0)^2} = 0$

(b) pH = 4.00, $[H_3O^+] = 10^{-4.00} = 1.0 \times 10^{-4}\ M$

$E = -\frac{0.0592\ V}{2}\log\frac{1}{(1.0 \times 10^{-4})^2} = -0.24\ V$

(c) $[H_3O^+] = 1.0 \times 10^{-7}\ M; \quad E = -\frac{0.0592\ V}{2}\log\frac{1}{(1.0 \times 10^{-7})^2} = -0.41\ V$

(d) $[OH^-] = 1.0\ M$; $[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\ M$

$$E = -\frac{0.0592\ V}{2} \log \frac{1}{(1.0 \times 10^{-14})^2} = -0.83\ V$$

18.70 $H_2(g) + Ni^{2+}(aq) \rightarrow 2\ H^+(aq) + Ni(s)$

$E^o = E^o_{H_2\ -\ H^+} + E^o_{Ni^{2+}\ -\ Ni} = 0\ V + (-0.26\ V) = -0.26\ V$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[H_3O^+]^2}{[Ni^{2+}](P_{H_2})}$$

$$0.27\ V = -0.26\ V - \frac{(0.0592\ V)}{2} \log \frac{[H_3O^+]^2}{(1)(1)}$$

$0.27\ V = -0.26\ V - (0.0592\ V) \log [H_3O^+]$

$pH = -\log [H_3O^+]$ therefore $0.27\ V = -0.26\ V + (0.0592\ V)\ pH$

$$pH = \frac{(0.27\ V + 0.26\ V)}{0.0592\ V} = 9.0$$

18.71 $Zn(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

$E^o = E^o_{H^+\ -\ H_2} + E^o_{Zn\ -\ Zn^{2+}} = 0\ V + 0.76\ V = 0.76\ V$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Zn^{2+}](P_{H_2})}{[H_3O^+]^2}$$

$$0.58\ V = 0.76\ V - \frac{(0.0592\ V)}{2} \log \frac{(1)(1)}{[H_3O^+]^2}$$

$0.58\ V = 0.76\ V + (0.0592\ V) \log [H_3O^+]$

$pH = -\log [H_3O^+]$ therefore $0.58\ V = 0.76\ V - (0.0592\ V)\ pH$

$$pH = \frac{-(0.58\ V - 0.76\ V)}{0.0592\ V} = 3.0$$

Standard Cell Potentials and Equilibrium Constants

18.72 $\Delta G^o = -nFE^o$

Because n and F are always positive, ΔG^o is negative when E^o is positive because of the negative sign in the equation.

$$E^o = \frac{0.0592\ V}{n} \log K; \quad \log K = \frac{n\ E^o}{0.0592\ V}; \quad K = 10^{\frac{n\ E^o}{0.0592}}$$

If E^o is positive, the exponent is positive (because n is positive), and K is greater than 1.

18.73 If $K < 1$, $E^o < 0$. When $E^o = 0$, $K = 1$.

18.74 $Ni(s) + 2\ Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2\ Ag(s)$

oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2\ e^-$ $\qquad E^o = 0.26\ V$

reduction: $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$ $\underline{E^o = 0.80\ V}$

overall $E^o = 1.06\ V$

$$E^o = \frac{0.0592\ V}{n} \log K;\ \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(2)(1.06\ V)}{0.0592\ V} = 35.8;\quad K = 10^{35.8} = 6 \times 10^{35}$$

18.75 $2\ MnO_4^-(aq) + 10\ Cl^-(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ Cl_2(g) + 8\ H_2O(l)$

oxidation: $10\ Cl^-(aq) \rightarrow 5\ Cl_2(g) + 10\ e^-$ $E^o = -1.36\ V$

reduction: $2\ MnO_4^-(aq) + 16\ H^+(aq) + 10\ e^- \rightarrow 2\ Mn^{2+}(aq) + 8\ H_2O(l)$ $\underline{E^o = 1.51\ V}$

overall $E^o = 0.15\ V$

$$E^o = \frac{0.0592\ V}{n} \log K;\ \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(10)(0.15\ V)}{0.0592\ V} = 25.3;\quad K = 10^{25.3} = 2 \times 10^{25}$$

18.76 E^o and n are from Problem 18.58.

$$E^o = \frac{0.0592\ V}{n} \log K; \qquad \log K = \frac{n\ E^o}{0.0592\ V}$$

(a) $Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$; $E^o = 0.26\ V$ and $n = 2$ mol e^-

$$\log K = \frac{(2)(0.26\ V)}{0.0592\ V} = 8.8; \qquad K = 10^{8.8} = 6 \times 10^8$$

(b) $2\ Al(s) + 3\ Cd^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Cd(s)$; $E^o = 1.26\ V$ and $n = 6$ mol e^-

$$\log K = \frac{(6)(1.26\ V)}{0.0592\ V} = 128; \qquad K = 10^{128}$$

(c) $6\ Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\ H^+(aq) \rightarrow 6\ Fe^{3+}(aq) + 2\ Cr^{3+}(aq) + 7\ H_2O(l)$

$E^o = 0.56\ V$ and $n = 6$ mol e^-

$$\log K = \frac{(6)(0.56\ V)}{0.0592\ V} = 57; \qquad K = 10^{57}$$

18.77 E^o and n are from Problem 18.59.

$$E^o = \frac{0.0592\ V}{n} \log K; \qquad \log K = \frac{n\ E^o}{0.0592\ V}$$

(a) $3\ Cu^{2+}(aq) + 2\ Cr(s) \rightarrow 3\ Cu(s) + 2\ Cr^{3+}(aq)$; $E^o = 1.08\ V$ and $n = 6$ mol e^-

$$\log K = \frac{(6)(1.08\ V)}{0.0592\ V} = 109; \qquad K = 10^{109}$$

(b) $Pb(s) + 2\ H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$; $E^o = 0.13\ V$ and $n = 2$ mol e^-

$$\log K = \frac{(2)(0.13\ V)}{0.0592\ V} = 4.4; \qquad K = 10^{4.4} = 3 \times 10^4$$

(c) $Cl_2(g) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\ Cl^-(aq)$; $E^o = 1.21\ V$ and $n = 2$ mol e^-

$$\log K = \frac{(2)(1.21\ V)}{0.0592\ V} = 40.9; \qquad K = 10^{40.9} = 8 \times 10^{40}$$

18.78 $Hg_2^{2+}(aq) \rightarrow Hg(l) + Hg^{2+}(aq)$

oxidation: $\frac{1}{2}[Hg_2^{2+}(aq) \rightarrow 2\ Hg^{2+}(aq) + 2\ e^-]$ $E^o = -0.92\ V$

reduction: $\frac{1}{2}[Hg_2^{2+}(aq) + 2\ e^- \rightarrow 2\ Hg(l)]$ $\underline{E^o = 0.80\ V}$

overall $E^o = -0.12\ V$

$$E^o = \frac{0.0592\ V}{n} \log K$$

$$\log K = \frac{n E^o}{0.0592\ V} = \frac{(1)(-0.12\ V)}{0.0592\ V} = -2.027; \qquad K = 10^{-2.027} = 9 \times 10^{-3}$$

18.79 $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

oxidation: $H_2O_2(aq) \rightarrow O_2(g) + 2\ H^+(aq) + 2e^-$ $E^o = -0.70\ V$

reduction: $H_2O_2(aq) + 2\ H^+(aq) + 2e^- \rightarrow 2\ H_2O(l)$ $\underline{E^o = 1.78\ V}$

overal $E^o = 1.08\ V$

$$E^o = \frac{0.0592\ V}{n} \log K;\ \log K = \frac{n E^o}{0.0592\ V} = \frac{(2)(1.08\ V)}{0.0592\ V} = 36.5; \quad K = 10^{36.5} = 3 \times 10^{36}$$

Batteries; Corrosion

18.80 Rust is a hydrated form of iron(III) oxide ($Fe_2O_3 \cdot H_2O$). Rust forms from the oxidation of Fe in the presence of O_2 and H_2O. Rust can be prevented by coating Fe with Zn (galvanizing).

18.81 Cr forms a protective oxide coating similar to Al.

18.82 Cathodic protection is the attachment of a more easily oxidized metal to the metal you want to protect. This forces the metal you want to protect to be the cathode, hence the name, cathodic protection.
Zn and Al can offer cathodic protection to Fe (Ni and Sn cannot).

18.83 A sacrificial anode is a metal used for cathodic protection. It behaves as an anode and is more easily oxidized than the metal it is protecting.
An example of a sacrificial anode is Zn for protecting Fe (galvanizing).

18.84 (a)

(b) Anode: $Pb(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2\ e^-$ $E^o = 0.296\ V$

Cathode: $\underline{PbO_2(s) + 3\ H^+(aq) + HSO_4^-(aq) + 2\ e^- \rightarrow PbSO_4(s) + 2\ H_2O(l)}$ $\underline{E^o = 1.628\ V}$

Overall $Pb(s) + PbO_2(s) + 2\ H^+(aq) + 2\ HSO_4^-(aq) \rightarrow 2\ PbSO_4(s) + 2\ H_2O(l)$ $E^o = 1.924\ V$

(c) $E^o = \dfrac{0.0592\ V}{n} \log K$; $\log K = \dfrac{n\ E^o}{0.0592\ V} = \dfrac{(2)(1.924\ V)}{0.0592\ V} = 65.0$; $K = 1 \times 10^{65}$

(d) When the cell reaction reaches equilibrium the cell voltage = 0.

18.85

oxidation:	$2\ H_2(g) + 4\ OH^-(aq) \rightarrow 4\ H_2O(l) + 4\ e^-$	$E^o = 0.83\ V$
reduction:	$\underline{O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)}$	$\underline{E^o = 0.43\ V}$
	$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$	$E^o = 1.23\ V$

n = 4 mol e^- and 1 J = 1 C x 1 V

$$\Delta G^o = -nFE^o = -(4\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.23\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -474{,}780\ J = -475\ kJ$$

$$E^o = \frac{0.0592\ V}{n} \log K; \quad \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(4)(1.23\ V)}{0.0592\ V} = 83.1; \quad K = 10^{83.1} = 1 \times 10^{83}$$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{1}{(P_{H_2})^2 (P_{O_2})} = 1.23\ V - \frac{0.0592\ V}{4} \log \frac{1}{(25)^2 (25)} = 1.29\ V$$

18.86 $Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$; Zn, 65.39 amu; HgO, 216.59 amu

$$\text{mass HgO} = 2.00\ g\ Zn \times \frac{1\ mol\ Zn}{65.39\ g\ Zn} \times \frac{1\ mol\ HgO}{1\ mol\ Zn} \times \frac{216.59\ g\ HgO}{1\ mol\ HgO} = 6.62\ g\ HgO$$

18.87 $Cd(OH)_2(s) + 2\ Ni(OH)_2(s) \rightarrow Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(l)$

$Ni(OH)_2$, 92.71 amu; Cd, 112.41 amu

$$\text{mass Cd} = 10.0\ g\ Ni(OH)_2 \times \frac{1\ mol\ Ni(OH)_2}{92.71\ g\ Ni(OH)_2} \times \frac{1\ mol\ Cd}{2\ mol\ Ni(OH)_2} \times \frac{112.41\ g\ Cd}{1\ mol\ Cd} = 6.06\ g\ Cd$$

Electrolysis

18.88 (a)

(b) anode: $2\ Cl^-(l) \rightarrow Cl_2(g) + 2\ e^-$
cathode: $\underline{Mg^{2+}(l) + 2\ e^- \rightarrow Mg(l)}$
overall: $Mg^{2+}(l) + 2\ Cl^-(l) \rightarrow Mg(l) + Cl_2(g)$

18.89 (a)

(b) anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$
cathode: $\underline{4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2(g)}$
overall: $2\ H_2O(l) \rightarrow O_2(g) + 2\ H_2(g)$

18.90 possible anode reactions:

$2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$
$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

possible cathode reactions:

$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$
$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$

actual reactions:

anode: $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$
cathode: $2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

This anode reaction takes place instead of $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$ because of a high overvoltage for formation of gaseous O_2.

This cathode reaction takes place instead of $Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$ because H_2O is easier to reduce than Mg^{2+}.

18.91 (a) K(l) and $Cl_2(g)$ (b) $H_2(g)$ and $Cl_2(g)$. Solvent H_2O is reduced in preference to K^+.

18.92 (a) NaBr

anode: $2\ Br^-(aq) \rightarrow Br_2(l) + 2\ e^-$

cathode: $2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

overall: $2\ H_2O(l) + 2\ Br^-(aq) \rightarrow Br_2(l) + H_2(g) + 2\ OH^-(aq)$

(b) $CuCl_2$

anode: $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$

cathode: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

overall: $Cu^{2+}(aq) + 2\ Cl^-(aq) \rightarrow Cu(s) + Cl_2(g)$

(c) LiOH

anode: $4\ OH^-(aq) \rightarrow O_2(g) + 2\ H_2O(l) + 4\ e^-$

cathode: $4\ H_2O(l) + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-(aq)$

overall: $2\ H_2O(l) \rightarrow O_2(g) + 2\ H_2(g)$

18.93 (a) Ag_2SO_4

anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ e^-$

cathode: $4\ Ag^+(aq) + 4\ e^- \rightarrow 4\ Ag(s)$

overall: $4\ Ag^+(aq) + 2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4\ Ag(s)$

(b) $Ca(OH)_2$

anode: $4\ OH^-(aq) \rightarrow O_2(g) + 2\ H_2O(l) + 4\ e^-$

cathode: $4\ H_2O(l) + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-(aq)$

overall: $2\ H_2O(l) \rightarrow O_2(g) + 2\ H_2(g)$

(c) KI

anode: $2\ I^-(aq) \rightarrow I_2(s) + 2\ e^-$

cathode: $2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$

overall: $2\ I^-(aq) + 2\ H_2O(l) \rightarrow I_2(s) + H_2(g) + 2\ OH^-(aq)$

18.94 $Ag^+(aq) + e^- \rightarrow Ag(s)$; 1 A = 1 C/s

$$\text{mass Ag} = 2.40\ \frac{\text{C}}{\text{s}} \times 20.0\ \text{min} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{1\ \text{mol}\ e^-}{96{,}500\ \text{C}} \times \frac{1\ \text{mol Ag}}{1\ \text{mol}\ e^-} \times \frac{107.87\ \text{g Ag}}{1\ \text{mol Ag}} =$$

3.22 g

18.95 $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$

$$\text{mol}\ e^- = 100.0\ \frac{\text{C}}{\text{s}} \times 24.0\ \text{h} \times \frac{60\ \text{min}}{\text{h}} \times \frac{60\ \text{s}}{\text{min}} \times \frac{1\ \text{mol}\ e^-}{96{,}500\ \text{C}} = 89.5\ \text{mol}\ e^-$$

$$\text{mass Cu} = 89.5\ \text{mol}\ e^- \times \frac{1\ \text{mol Cu}}{2\ \text{mol}\ e^-} \times \frac{63.54\ \text{g Cu}}{1\ \text{mol Cu}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 2.84\ \text{kg Cu}$$

18.96 $2\ Na^+(l) + 2\ Cl^-(l) \rightarrow 2\ Na(l) + Cl_2(g)$

$Na^+(l) + e^- \rightarrow Na(l)$; 1 A = 1 C/s; 1.00×10^3 kg = 1.00×10^6 g

$$\text{Charge} = 1.00 \times 10^6 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1 \text{ mol e}^-}{1 \text{ mol Na}} \times \frac{96{,}500 \text{ C}}{1 \text{ mol e}^-} = 4.20 \times 10^9 \text{ C}$$

$$\text{Time} = \frac{4.20 \times 10^9 \text{ C}}{30{,}000 \text{ C/s}} \times \frac{1 \text{ h}}{3600 \text{ s}} = 38.9 \text{ h}$$

$$1.00 \times 10^6 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} \times \frac{1 \text{ mol } Cl_2}{2 \text{ mol Na}} = 21{,}748.6 \text{ mol } Cl_2$$

$$PV = nRT$$

$$V = \frac{nRT}{P} = \frac{(21{,}748.6 \text{ mol})\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(273.15 \text{ K})}{1.00 \text{ atm}} = 4.87 \times 10^5 \text{ L } Cl_2$$

18.97 $Al^{3+} + 3\ e^- \rightarrow Al$; 40.0 kg = 40,000 g; 1 h = 3600 s

$$\text{Charge} = 40{,}000 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Al}} \times \frac{96{,}500 \text{ C}}{1 \text{ mol e}^-} = 4.29 \times 10^8 \text{ C}$$

$$\text{Current} = \frac{4.29 \times 10^8 \text{ C}}{3600 \text{ s}} = 1.19 \times 10^5 \text{ A}$$

18.98 $PbSO_4(s) + H^+(aq) + 2\ e^- \rightarrow Pb(s) + HSO_4^-(aq)$

mass $PbSO_4$

$$= 10.0 \frac{\text{C}}{\text{s}} \times 1.50 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{1 \text{ mol e}^-}{96{,}500 \text{ C}} \times \frac{1 \text{ mol } PbSO_4}{2 \text{ mol e}^-} \times \frac{303.3 \text{ g } PbSO_4}{1 \text{ mol } PbSO_4}$$

mass $PbSO_4 = 84.9$ g $PbSO_4$

18.99 $Cr^{3+}(aq) + 3\ e^- \rightarrow Cr(s)$

$$\text{Charge} = 125 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} \times \frac{3 \text{ mol e}^-}{1 \text{ mol Cr}} \times \frac{96{,}500 \text{ C}}{1 \text{ mol e}^-} = 6.96 \times 10^5 \text{ C}$$

$$\text{Time} = \frac{6.96 \times 10^5 \text{ C}}{200.0 \text{ C/s}} \times \frac{1 \text{ min}}{60 \text{ s}} = 58.0 \text{ min}$$

General Problems

18.100 (a) $2\ MnO_4^-(aq) + 16\ H^+(aq) + 5\ Sn^{2+}(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ Sn^{4+}(aq) + 8\ H_2O(l)$

(b) MnO_4^- is the oxidizing agent; Sn^{2+} is the reducing agent.

(c) $E^o = 1.51 \text{ V} + (-0.15 \text{ V}) = 1.36 \text{ V}$

18.101 $2\ Mn^{3+}(aq) + 2\ H_2O(l) \rightarrow Mn^{2+}(aq) + MnO_2(s) + 4\ H^+(aq)$

$E^o = 1.51 \text{ V} + (-0.95 \text{ V}) = +0.56 \text{ V}$

Because E^o is positive, the disproportionation is spontaneous under standard-state conditions.

18.102 (a) Ag^+ is the strongest oxidizing agent because Ag^+ has the most positive standard reduction potential.

Pb is the strongest reducing agent because Pb^{2+} has the most negative standard reduction potential.

(b)

(c) $Pb(s) + 2\ Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2\ Ag(s)$; $n = 2$ mol e^-

$E^o = E^o_{ox} + E^o_{red} = 0.13\ V + 0.80\ V = 0.93\ V$

$$\Delta G^o = -nFE^o = -(2\ \text{mol}\ e^-)\left(\frac{96{,}500\ C}{1\ \text{mol}\ e^-}\right)(0.93\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -179{,}490\ J = -180\ kJ$$

$$E^o = \frac{0.0592\ V}{n}\log K; \quad \log K = \frac{n E^o}{0.0592\ V} = \frac{(2)(0.93\ V)}{0.0592\ V} = 31; \quad K = 10^{31}$$

$$\text{(d) } E = E^o - \frac{0.0592\ V}{n}\log\frac{[Pb^{2+}]}{[Ag^+]^2} = 0.93\ V - \frac{0.0592\ V}{2}\log\left(\frac{0.01}{(0.01)^2}\right) = 0.87\ V$$

18.103 For Pb^{2+}, $E = -0.13 - \frac{0.0592\ V}{2}\log\frac{1}{[Pb^{2+}]}$

For Cd^{2+}, $E = -0.40 - \frac{0.0592\ V}{2}\log\frac{1}{[Cd^{2+}]}$

Set these two equations for E equal to each other and solve for $[Cd^{2+}]/[Pb^{2+}]$.

$$-0.13 - \frac{0.0592\ V}{2}\log\frac{1}{[Pb^{2+}]} = -0.40 - \frac{0.0592\ V}{2}\log\frac{1}{[Cd^{2+}]}$$

$$0.27 = \frac{0.0592\ V}{2}(\log[Cd^{2+}] - \log[Pb^{2+}]) = \frac{0.0592\ V}{2}\ \log\ \frac{[Cd^{2+}]}{[Pb^{2+}]}$$

$$\log\frac{[Cd^{2+}]}{[Pb^{2+}]} = \frac{(0.27)(2)}{0.0592} = 9.1;\ \frac{[Cd^{2+}]}{[Pb^{2+}]} = 10^{9.1} = 1 \times 10^{9}$$

18.104 (a)

(b) $2\ Al(s) + 6\ H^{+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ H_2(g)$

$E^o = E^o_{ox} + E^o_{red} = 1.66\ V + 0.00\ V = 1.66\ V$

(c)

$$E = E^o - \frac{0.0592\ V}{n}\ \log\ \frac{[Al^{3+}]^2(P_{H_2})^3}{[H^+]^6} = 1.66\ V\ -\ \frac{(0.0592\ V)}{6}\ \log\left(\frac{(0.10)^2(10.0)^3}{(0.10)^6}\right) = 1.59\ V$$

(d) $\Delta G^o = -nFE^o = -(6\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.66\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -961{,}140\ J = -961\ kJ$

$$E^o = \frac{0.0592\ V}{n}\ \log\ K;\quad \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(6)(1.66\ V)}{0.0592\ V} = 168;\quad K = 10^{168}$$

(e) $$\text{mass Al} = 10.0\ \frac{C}{s}\ x\ 25.0\ min\ x\ \frac{60\ s}{1\ min}\ x\ \frac{1\ mol\ e^-}{96{,}500\ C}\ x\ \frac{1\ mol\ Al}{3\ mol\ e^-}\ x\ \frac{26.98\ g\ Al}{1\ mol\ Al} =$$

1.40 g

18.105 $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

$$\text{mass Zn} = 0.100\ \frac{C}{s}\ x\ 200.0\ h\ x\ \frac{60\ min}{h}\ x\ \frac{60\ s}{min}\ x\ \frac{1\ mol\ e^-}{96{,}500\ C}\ x\ \frac{1\ mol\ Zn}{2\ mol\ e^-}\ x\ \frac{65.39\ g\ Zn}{1\ mol\ Zn}$$

mass Zn = 24.4 g

18.106 $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$

13 million tons = 13×10^6 tons; Cl_2, 70.91 amu

$$13 \times 10^6\ tons\ x\ \frac{907{,}200\ g}{1\ ton}\ x\ \frac{1\ mol\ Cl_2}{70.91\ g\ Cl_2} = 1.66 \times 10^{11}\ mol\ Cl_2$$

$$\text{Charge} = 1.66 \times 10^{11}\ mol\ Cl_2\ x\ \frac{2\ mol\ e^-}{1\ mol\ Cl_2}\ x\ \frac{96{,}500\ C}{1\ mol\ e^-} = 3.20 \times 10^{16}\ C$$

1 J = 1 C x 1 V; Energy = $(3.20 \times 10^{16}\ C)(4.5\ V) = 1.44 \times 10^{17}\ J$

$$\text{kWh} = (1.44 \times 10^{17}\ \text{J})\left(\frac{1\ \text{kWh}}{3.6 \times 10^{6}\ \text{J}}\right) = 4.0 \times 10^{10}\ \text{kWh}$$

18.107 (a) From: $B + A^+ \rightarrow B^+ + A$, A^+ is reduced more easily than B^+
From: $C + A^+ \rightarrow C^+ + A$, A^+ is reduced more easily than C^+
From: $B + C^+ \rightarrow B^+ + C$, C^+ is reduced more easily than B^+
$A^+ + e^- \rightarrow A$
$C^+ + e^- \rightarrow C$
$B^+ + e^- \rightarrow B$
(b) A^+ is the strongest oxidizing agent; B is the strongest reducing agent
(c) $A^+ + B \rightarrow B^+ + A$

18.108 (a) oxidizing agents: PbO_2, H^+, $Cr_2O_7^{2-}$; reducing agents: Al, Fe, Ag
(b) PbO_2 is the strongest oxidizing agent. H^+ is the weakest oxidizing agent.
(c) Al is the strongest reducing agent. Ag is the weakest reducing agent.
(d) oxidized by Cu^{2+}: Fe and Al; reduced by H_2O_2: PbO_2 and $Cr_2O_7^{2-}$

18.109 From Appendix D:
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$ $E^o = 0.07$ V
(a) oxidation: $C_6H_4(OH)_2(aq) \rightarrow C_6H_4O_2(aq) + 2\ H^+(aq) + 2\ e^-$ $E^o = -0.699$ V
reduction: $2[AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)]$ $E^o = 0.07$ V
overall: $2\ AgBr(s) + C_6H_4(OH)_2(aq) \rightarrow 2\ Ag(s) + 2\ Br^-(aq) + C_6H_4O_2(aq) + 2\ H^+(aq)$
overall $E^o = -0.699\ V + 0.07\ V = -0.63\ V$
Because the overall E^o is negative, the reaction is nonspontaneous when $[H^+] = 1.0$ M.

(b) $E^o(\text{in 1.0 M } OH^-) = E^o(\text{in 1.0 M } H^+) - \dfrac{0.0592\ V}{n} \log \dfrac{[Br^-]^2[H^+]^2[C_6H_4O_2]}{[C_6H_4(OH)_2]}$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\ \text{M}$$

$$E^o(\text{in 1.0 M } OH^-) = -0.63\ V - \frac{(0.0592\ V)}{2} \log \frac{(1)^2(10^{-14})^2(1)}{(1)} = +0.20\ V$$

18.110 (a) $3\ CH_3CH_2OH(aq) + 2\ Cr_2O_7^{2-}(aq) + 16\ H^+(aq) \rightarrow 3\ CH_3CO_2H(aq) + 4\ Cr^{3+}(aq) + 11\ H_2O(l)$
oxidation:
$3\ CH_3CH_2OH(aq) + 3\ H_2O(l) \rightarrow 3\ CH_3CO_2H(aq) + 12\ H^+(aq) + 12\ e^-$ $E^o = -0.058$V
reduction:
$2\ Cr_2O_7^{2-}(aq) + 28\ H^+(aq) + 12\ e^- + \rightarrow 4\ Cr^{3+}(aq) + 14\ H_2O(l)$ $E^o = 1.33$ V
overall $E^o = 1.27$ V

(b) $E = E^o - \frac{0.0592\ V}{n} \log \frac{[CH_3CO_2H]^3[Cr^{3+}]^4}{[CH_3CH_2OH]^3[Cr_2O_7^{2-}]^2[H^+]^{16}}$

pH = 4.00, $[H^+] = 0.000\ 10$ M

$E = 1.27\ V - \frac{(0.0592\ V)}{12} \log \left(\frac{(1.0)^3(1.0)^4}{(1.0)^3(1.0)^2(0.00010)^{16}} \right)$

$E = 1.27\ V - \frac{(0.0592\ V)}{12} \log \frac{1}{(0.00010)^{16}} = 0.95\ V$

18.111 (a) $\Delta G^o = -nFE^o$

$\Delta G^o_3 = \Delta G^o_1 + \Delta G^o_2$ therefore $-n_3FE^o_3 = -n_1FE^o_1 + (-n_2FE^o_2)$

$n_3E^o_3 = n_1E^o_1 + n_2E^o_2$

$E^o_3 = \frac{n_1E^o_1 + n_2E^o_2}{n_3}$

(b) $E^o_3 = \frac{(3)(-0.04\ V) + (2)(0.45\ V)}{1} = 0.78\ V$

(c) E^o values would be additive ($E^o_3 = E^o_1 + E^o_2$) if reaction (3) is an overall cell reaction because the electrons in the two half reactions, (1) and (2), cancel. That is, $n_1 = n_2 = n_3$ in the equation for E^o_3.

18.112

anode: $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$

cathode: $\underline{Ag^+(aq) + e^- \rightarrow Ag(s)}$

overall: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ $\quad E^o = 0.578\ V$

For $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $\quad E^o = -0.578\ V$

$E^o = \frac{0.0592\ V}{n} \log K$; $\quad \log K = \frac{n E^o}{0.0592\ V} = \frac{(1)(-0.578\ V)}{0.0592\ V} = -9.76$

$K = K_{sp} = 10^{-9.76} = 1.7 \times 10^{-10}$

18.113 (a)

anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$ $\quad E^o = -0.34\ V$

cathode: $\underline{2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)}$ $\quad \underline{E^o = 0.80\ V}$

overall: $2\ Ag^+(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$ $\quad E^o = 0.46\ V$

$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2} = 0.46\ V - \frac{(0.0592\ V)}{2} \log \left(\frac{1.0}{(0.050)^2} \right) = 0.38\ V$

(b) $[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{5.4 \times 10^{-13}}{1.0\ M} = 5.4 \times 10^{-13}$ M

$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2} = 0.46\ V - \frac{(0.0592\ V)}{2} \log \left(\frac{1.0}{(5.4 \times 10^{-13})^2} \right) = -0.27\ V$

The cell potential for the spontaneous reaction is E = 0.27 V.

The spontaneous reaction is: $Cu^{2+}(aq) + 2\ Ag(s) + 2\ Br^-(aq) \rightarrow 2\ AgBr(s) + Cu(s)$

(c) $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $E^o = 0.34$ V

$2\ Ag(s) + 2\ Br^-(aq) \rightarrow 2\ AgBr(s) + 2\ e^-$ $E^o = ?$

$Cu^{2+}(aq) + 2\ Ag(s) + 2\ Br^-(aq) \rightarrow 2\ AgBr(s) + Cu(s)$ $E^o = 0.27$ V

$E^o = ? = 0.27\ V - 0.34\ V = -0.07\ V$

For: $AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$

the standard reduction potential is $E^o = 0.07$ V

18.114 $4\ Fe^{2+}(aq) + O_2(g) + 4\ H^+(aq) \rightarrow 4\ Fe^{3+}(aq) + 2\ H_2O(l)$

oxidation $4\ Fe^{2+}(aq) \rightarrow 4\ Fe^{3+}(aq) + 4\ e^-$ $E^o = -0.77$ V

reduction $O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$ $E^o = 1.23$ V

overall $E^o = 0.46$ V

$$P_{O_2} = 160\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg} = 0.211\ atm$$

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[Fe^{3+}]^4}{[Fe^{2+}]^4[H^+]^4(P_{O_2})}$$

$$E = 0.46\ V - \frac{0.0592\ V}{4} \log \frac{(1 \times 10^{-7})^4}{(1 \times 10^{-7})^4(1 \times 10^{-7})^4(0.211)}$$

$E = 0.46\ V - 0.42\ V = 0.04\ V$

Because E is positive, the reaction is spontaneous.

18.115 $H_2MoO_4(aq) + As(s) \rightarrow Mo^{3+}(aq) + H_3AsO_4(aq)$

$H_2MoO_4(aq) \rightarrow Mo^{3+}(aq)$

$H_2MoO_4(aq) \rightarrow Mo^{3+}(aq) + 4\ H_2O(l)$

$6\ H^+(aq) + H_2MoO_4(aq) \rightarrow Mo^{3+}(aq) + 4\ H_2O(l)$

$[3\ e^- + 6\ H^+(aq) + H_2MoO_4(aq) \rightarrow Mo^{3+}(aq) + 4\ H_2O(l)] \times 5$ (reduction half reaction)

$As(s) \rightarrow H_3AsO_4(aq)$

$As(s) + 4\ H_2O(l) \rightarrow H_3AsO_4(aq)$

$As(s) + 4\ H_2O(l) \rightarrow H_3AsO_4(aq) + 5\ H^+(aq)$

$[As(s) + 4\ H_2O(l) \rightarrow H_3AsO_4(aq) + 5\ H^+(aq) + 5\ e^-] \times 3$ (oxidation half reaction)

Combine the two half reactions.

$30\ H^+(aq) + 5\ H_2MoO_4(aq) + 3\ As(s) + 12\ H_2O(l) \rightarrow 5\ Mo^{3+}(aq) + 3\ H_3AsO_4(aq) + 15\ H^+(aq) + 20\ H_2O(l)$

$15\ H^+(aq) + 5\ H_2MoO_4(aq) + 3\ As(s) \rightarrow 5\ Mo^{3+}(aq) + 3\ H_3AsO_4(aq) + 8\ H_2O(l)$

$5 \times [H_2MoO_4(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow MoO_2(s) + 2\ H_2O(l)]$ $E^o = +0.646$ V

$5 \times [MoO_2(s) + 4\ H^+(aq) + e^- \rightarrow Mo^{3+}(aq) + 2\ H_2O(l)]$ $E^o = -0.008$ V

$3 \times [As(s) + 3\ H_2O(l) \rightarrow H_3AsO_3(aq) + 3\ H^+(aq) + 3\ e^-]$ $E^o = -0.240$ V
$3 \times [H_3AsO_3(aq) + H_2O(l) \rightarrow H_3AsO_4(aq) + 2\ H^+(aq) + 2\ e^-]$ $E^o = -0.560$ V

$15\ H^+(aq) + 5\ H_2MoO_4(aq) + 3\ As(s) \rightarrow 5\ Mo^{3+}(aq) + 3\ H_3AsO_4(aq) + 8\ H_2O(l)$

$$\Delta G^o = -nFE^o = -(10 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(0.646 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = -623{,}390 \text{ J} = -623.4 \text{ kJ}$$

$$\Delta G^o = -nFE^o = -(5 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(-0.008 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = 3{,}860 \text{ J} = +3.9 \text{ kJ}$$

$$\Delta G^o = -nFE^o = -(9 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(-0.240 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = 208{,}440 \text{ J} = +208.4 \text{ kJ}$$

$$\Delta G^o = -nFE^o = -(6 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)(-0.560 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C} \bullet \text{V}}\right) = 324{,}240 \text{ J} = +324.2 \text{ kJ}$$

ΔG^o(total) = -623.4 kJ + 3.9 kJ + 208.4 kJ + 324.2 kJ = -86.9 kJ = -86,900 J
1 V = 1 J/C

$$\Delta G^o = -nFE^o;\ E^o = \frac{-\Delta G^o}{nF} = \frac{-(-86{,}900 \text{ J})}{(15 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)} = +0.060 \text{ J/C} = +0.060 \text{ V}$$

18.116 First calculate E^o for the galvanic cell in order to determine E^o_1.

anode: $5\ [2\ Hg(l) + 2\ Br^-(aq) \rightarrow Hg_2Br_2(s) + 2\ e^-]$ $E^o_1 = ?$
cathode: $\underline{2\ [MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)]}$ $E^o_2 = 1.51$ V
overall: $2\ MnO_4^-(aq) + 10\ Hg(l) + 10\ Br^-(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 5\ Hg_2Br_2(s) + 8\ H_2O(l)$

n = 10 mol e^-

$$E = E^o - \frac{0.0592 \text{ V}}{n} \log \frac{[Mn^{2+}]^2}{[Br^-]^{10}[MnO_4^-]^2[H^+]^{16}}$$

$$1.214 \text{ V} = E^o - \frac{(0.0592 \text{ V})}{10} \log \left(\frac{(0.10)^2}{(0.10)^{10}(0.10)^2(0.10)^{16}}\right)$$

$$1.214 \text{ V} = E^o - \frac{(0.0592 \text{ V})}{10} \log \frac{1}{(0.10)^{26}} = E^o - 0.154 \text{ V}$$

$E^o = 1.214 + 0.154 = 1.368$ V
$E^o_1 + E^o_2 = 1.368$ V; $E^o_1 + 1.51$ V $= 1.368$ V; $E^o_1 = 1.368$ V $- 1.51$ V $= -0.142$ V
oxidation: $2\ Hg(l) \rightarrow Hg_2^{2+}(aq) + 2\ e^-$ $E^o = -0.80$ V (Appendix D)
reduction: $\underline{Hg_2Br_2(s) + 2\ e^- \rightarrow 2\ Hg(l) + 2\ Br^-(aq)}$ $\underline{E^o = -0.142 \text{ V}}$ (from E^o_1)
overall: $Hg_2Br_2(s) \rightarrow Hg_2^{2+}(aq) + 2\ Br^-(aq)$ $E^o = -0.658$ V

$$E^o = \frac{0.0592 \text{ V}}{n} \log K;\quad \log K = \frac{n E^o}{0.0592 \text{ V}} = \frac{(2)(-0.658 \text{ V})}{0.0592 \text{ V}} = -22.2$$

$K = K_{sp} = 10^{-22.2} = 6 \times 10^{-23}$

18.117 oxidation: $Cu^+(aq) \rightarrow Cu^{2+}(aq) + e^-$ $E^o = -0.15$ V

reduction: $\underline{Cu^{2+}(aq) + 2\,CN^-(aq) + e^- \rightarrow Cu(CN)_2^-(aq)}$ $\underline{E^o = 1.103\ V}$

overall: $Cu^+(aq) + 2\,CN^-(aq) \rightarrow Cu(CN)_2^-(aq)$ $E^o = 0.953\ V$

$$E^o = \frac{0.0592\ V}{n}\log K; \quad \log K = \frac{n\,E^o}{0.0592\ V} = \frac{(1)(0.953\ V)}{0.0592\ V} = 16.1$$

$$K = K_f = 10^{16.1} = 1 \times 10^{16}$$

18.118 (a) anode: $4[Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-]$ $E^o = 1.66\ V$

cathode: $\underline{3[O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)]}$ $\underline{E^o = 1.23\ V}$

overall: $4\,Al(s) + 3\,O_2(g) + 12\,H^+(aq) \rightarrow 4\,Al^{3+}(aq) + 6\,H_2O(l)$ $E^o = 2.89\ V$

(b) & (c) $$E = E^o - \frac{2.303\,R\,T}{n\,F}\log\frac{[Al^{3+}]^4}{(P_{O_2})^3[H^+]^{12}}$$

$$E = 2.89\ V - \frac{(2.303)\left(8.314 \times 10^{-3}\ \frac{kJ}{K \bullet mol}\right)(310\ K)}{(12\ mol\ e^-)(96{,}500\ C/mol\ e^-)}\log\left(\frac{(1.0 \times 10^{-9})^4}{(0.20)^3(1.0 \times 10^{-7})^{12}}\right)$$

$$E = 2.89\ V - 0.257\ V = 2.63\ V$$

18.119 $$E_1 = E^o{}_1 - \frac{0.0592\ V}{6}\log\frac{[Cu^{2+}]^3(P_{NO})^2}{[NO_3^-]^2[H^+]^8} \text{ and } E_2 = E^o{}_2 - \frac{0.0592\ V}{2}\log\frac{[Cu^{2+}](P_{NO_2})^2}{[NO_3^-]^2[H^+]^4}$$

(a) $$E_1 = 0.62\ V - \frac{0.0592\ V}{6}\log\frac{(0.10)^3(1.0 \times 10^{-3})^2}{(1.0)^2(1.0)^8} = 0.71\ V$$

$$E_2 = 0.45\ V - \frac{0.0592\ V}{2}\log\frac{(0.10)(1.0 \times 10^{-3})^2}{(1.0)^2(1.0)^4} = 0.66\ V$$

Reaction (1) has the greater thermodynamic tendency to occur because of the larger positive potential.

(b) $$E_1 = 0.62\ V - \frac{0.0592\ V}{6}\log\frac{(0.10)^3(1.0 \times 10^{-3})^2}{(10.0)^2(10.0)^8} = 0.81\ V$$

$$E_2 = 0.45\ V - \frac{0.0592\ V}{2}\log\frac{(0.10)(1.0 \times 10^{-3})^2}{(10.0)^2(10.0)^4} = 0.83\ V$$

Reaction (2) has the greater thermodynamic tendency to occur because of the larger positive potential.

(c) Set the two equations equal to each other and solve for x.

$$0.62\ V - \frac{0.0592\ V}{6}\log\frac{(0.10)^3(1.0 \times 10^{-3})^2}{(x)^2(x)^8} = 0.45\ V - \frac{0.0592\ V}{2}\log\frac{(0.10)(1.0 \times 10^{-3})^2}{(x)^2(x)^4}$$

$$0.17 - \frac{0.0592\ V}{6}[(-9) - 10\log x] = -\frac{0.0592\ V}{2}[(-7) - 6\log x]$$

$$0.0516 = 0.0789\log x; \quad \frac{0.0516}{0.0789} = \log x; \quad 0.654 = \log x$$

$$[HNO_3] = x = 10^{0.654} = 4.5\ M$$

Multi-Concept Problems

18.120 (a) $4\ CH_2{=}CHCN\ +\ 2\ H_2O\ \rightarrow\ 2\ NC(CH_2)_4CN\ +\ O_2$

(b) mol e^- = 3000 C/s x 10.0 h x $\frac{3600\ s}{1\ h}$ x $\frac{1\ mol\ e^-}{96{,}500\ C}$ = 1119.2 mol e^-

mass adiponitrile =

1119.2 mol e^- x $\frac{1\ mol\ adiponitrile}{2\ mol\ e^-}$ x $\frac{108.14\ g\ adiponitrile}{1\ mol\ adiponitrile}$ x $\frac{1.0\ kg}{1000\ g}$ = 60.5 kg

(c) 1119.2 mol e^- x $\frac{1\ mol\ O_2}{4\ mol\ e^-}$ = 279.8 mol O_2

PV = nRT

$$V = \frac{nRT}{P} = \frac{(279.8\ mol)\left(0.082\ 06\ \frac{L \bullet atm}{K \bullet mol}\right)(298\ K)}{\left(740\ mm\ Hg\ x\ \frac{1\ atm}{760\ mm\ Hg}\right)} = 7030\ L\ O_2$$

18.121 (a) $2\ MnO_4^-(aq)\ +\ 5\ H_2C_2O_4(aq)\ +\ 6\ H^+(aq)\ \rightarrow$
$2\ Mn^{2+}(aq)\ +\ 10\ CO_2(g)\ +\ 8\ H_2O(l)$

(b) oxidation: $5[H_2C_2O_4(aq) \rightarrow 2\ CO_2(g) + 2\ H^+(aq) + 2\ e^-]$ $E^o = 0.49$ V

reduction: $2[MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)]$ $E^o = 1.51$ V

overall $E^o = 2.00$ V

(c)

$$\Delta G^o = -nFE^o = -(10\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(2.00\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -1{,}930{,}000\ J = -1{,}930\ kJ$$

$$E^o = \frac{0.0592\ V}{n}\ \log K; \quad \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(10)(2.00\ V)}{0.0592\ V} = 338; \quad K = 10^{338}$$

(d) $Na_2C_2O_4$, 134.0 amu

1.200 g $Na_2C_2O_4$ x $\frac{1\ mol\ Na_2C_2O_4}{134.0\ g\ Na_2C_2O_4}$ x $\frac{2\ mol\ KMnO_4}{5\ mol\ Na_2C_2O_4}$ = 3.582×10^{-3} mol $KMnO_4$

molarity = $\frac{3.582 \times 10^{-3}\ mol}{0.032\,50\ L}$ = 0.1102 M

18.122 (a) $Cr_2O_7^{2-}(aq)\ +\ 6\ Fe^{2+}(aq)\ +\ 14\ H^+(aq)\ \rightarrow\ 2\ Cr^{3+}(aq)\ +\ 6\ Fe^{3+}(aq)\ +\ 7\ H_2O(l)$

(b) The two half reactions are:

oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ $E^o = -0.77$ V

reduction: $Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$ $E^o = 1.33$ V

At the equivalence point the potential is given by either of the following expressions:

(1) $E = 1.33\ V - \frac{0.0592\ V}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$

(2) $E = 0.77\ V - \frac{0.0592\ V}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$

where E is the same in both because equilibrium is reached and the solution can have only one potential. Multiplying (1) by 6, adding it to (2), and using some stoichiometric relationships at the equivalence point will simplify the log term.

$$7E = [(6 \times 1.33\ V) + 0.77\ V] - (0.0592\ V)\log\frac{[Fe^{2+}][Cr^{3+}]^2}{[Fe^{3+}][Cr_2O_7^{2-}][H^+]^{14}}$$

At the equivalence point, $[Fe^{2+}] = 6[Cr_2O_7^{2-}]$ and $[Fe^{3+}] = 3[Cr^{3+}]$. Substitute these equalities into the previous equation.

$$7E = [(6 \times 1.33\ V) + 0.77\ V] - (0.0592\ V)\log\frac{6[Cr_2O_7^{2-}][Cr^{3+}]^2}{3[Cr^{3+}][Cr_2O_7^{2-}][H^+]^{14}}$$

Cancel identical terms.

$$7E = [(6 \times 1.33\ V) + 0.77\ V] - (0.0592\ V)\log\frac{6[Cr^{3+}]}{3[H^+]^{14}}$$

mol Fe^{2+} = (0.120 L)(0.100 mol/L) = 0.0120 mol Fe^{2+}

mol $Cr_2O_7^{2-}$ = 0.0120 mol Fe^{2+} x $\frac{1\ mol\ Cr_2O_7^{2-}}{6\ mol\ Fe^{2+}}$ = 0.00200 mol $Cr_2O_7^{2-}$

volume $Cr_2O_7^{2-}$ = 0.00200 mol x $\frac{1\ L}{0.120\ mol}$ = 0.0167 L

At the equivalence point assume mol Fe^{3+} = initial mol Fe^{2+} = 0.0120 mol

Total volume at the equivalence point is 0.120 L + 0.0167 L = 0.1367 L

$[Fe^{3+}] = \frac{0.0120\ mol}{0.1367\ L}$ = 0.0878 M; $[Cr^{3+}] = [Fe^{3+}]/3 = (0.0878\ M)/3 = 0.0293\ M$

$[H^+] = 10^{-pH} = 10^{-2.00} = 0.010\ M$

$$7E = [(6 \times 1.33\ V) + 0.77\ V] - (0.0592\ V)\log\frac{6(0.0293)}{3(0.010)^{14}} = 8.75 - 1.585 = 7.165\ V$$

$E = \frac{7.165\ V}{7}$ = 1.02 V at the equivalence point.

18.123 $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

(a) $\Delta H^o = 2\ \Delta H^o_f(H_2O) = (2\ mol)(-285.8\ kJ/mol) = -571.6\ kJ$

$\Delta S^o = 2\ S^o(H_2O) - [2\ S^o(H_2) + S^o(O_2)]$

$\Delta S^o = (2\ mol)(69.9\ J/(K \cdot mol)) - [(2\ mol)(130.6\ J/(K \cdot mol)) + (1\ mol)(205.0\ J/(K \cdot mol))]$

$\Delta S^o = -326.4\ J/K = -0.3264\ kJ/K$

$95^oC = 368\ K$

$\Delta G^o = \Delta H^o - T\Delta S^o = -571.6\ kJ - (368\ K)(-0.3264\ kJ/K) = -451.5\ kJ$

1 V = 1 J/C

$\Delta G^o = -nFE^o$; $E^o = -\frac{\Delta G^o}{nF} = -\frac{-451.5 \times 10^3 \text{ J}}{(4)(96{,}500 \text{ C})} = 1.17 \text{ J/C} = 1.17 \text{ V}$

(b) $E = E^o - \frac{2.303\,R\,T}{n\,F}\log\frac{1}{(P_{H_2})^2(P_{O_2})}$

$E = 1.17 \text{ V} - \frac{(2.303)\left(8.314 \times 10^{-3} \frac{\text{kJ}}{\text{mol} \bullet \text{K}}\right)(368 \text{ K})}{(4 \text{ mol } e^-)(96{,}500 \text{ C/mol } e^-)} \log\left(\frac{1}{(25)^2(25)}\right)$

$E = 1.17 \text{ V} + 0.077 \text{ V} = 1.25 \text{ V}$

18.124 (a) $Zn(s) + 2\,Ag^+(aq) + H_2O(l) \rightarrow ZnO(s) + 2\,Ag(s) + 2\,H^+(aq)$

$\Delta H^o_{rxn} = \Delta H^o_f(ZnO) - [2\,\Delta H^o_f(Ag^+) + \Delta H^o_f(H_2O)]$

$\Delta H^o_{rxn} = [(1 \text{ mol})(-348.3 \text{ kJ/mol})] - [(2 \text{ mol})(105.6 \text{ kJ/mol}) + (1 \text{ mol})(-285.8 \text{ kJ/mol})]$

$\Delta H^o_{rxn} = -273.7 \text{ kJ}$

$\Delta S^o = [S^o(ZnO) + 2\,S^o(Ag)] - [S^o(Zn) + 2\,S^o(Ag^+) + S^o(H_2O)]$

$\Delta S^o = [(1 \text{ mol})(43.6 \text{ J/(K}\cdot\text{ mol)}) + (2 \text{ mol})(42.6 \text{ J/(K}\cdot\text{ mol)})]$
$- [(1 \text{ mol})(41.6 \text{ J/(K}\cdot\text{ mol)}) + (2 \text{ mol})(72.7 \text{ J/(K}\cdot\text{ mol)}) + (1 \text{ mol})(69.9 \text{ J/(K}\cdot\text{ mol)})$

$\Delta S^o = -128.1 \text{ J/K}$

$\Delta G^o = \Delta H^o - T\Delta S^o = -273.7 \text{ kJ} - (298 \text{ K})(-128.1 \times 10^{-3} \text{ kJ/K}) = -235.5 \text{ kJ}$

(b) 1 V = 1 J/C

$\Delta G^o = -nFE^o \quad E^o = \frac{-\Delta G^o}{nF} = \frac{-(-235.5 \times 10^3 \text{ J})}{(2 \text{ mol } e^-)\left(\frac{96{,}500 \text{ C}}{1 \text{ mol } e^-}\right)} = 1.220 \text{ J/C} = 1.220 \text{ V}$

$E^o = \frac{0.0592 \text{ V}}{n}\log K; \quad \log K = \frac{n\,E^o}{0.0592 \text{ V}} = \frac{(2)(1.220 \text{ V})}{0.0592 \text{ V}} = 41.22$

$K = 10^{41.22} = 2 \times 10^{41}$

(c) $E = E^o - \frac{0.0592 \text{ V}}{n}\log\frac{[H^+]^2}{[Ag^+]^2}$

The addition of NH_3 to the cathode compartment would result in the formation of the $Ag(NH_3)_2^+$ complex ion which results in a decrease in Ag^+ concentration. The log term in the Nernst equation becomes larger and the cell voltage decreases.

On mixing equal volumes of two solutions, the concentrations of both solutions are cut in half.

	$Ag^+(aq)$	+	$2\,NH_3(aq)$	⇌	$Ag(NH_3)_2^+(aq)$
before reaction (M)	0.0500		2.00		0
assume 100% reaction	-0.0500		-2(0.0500)		+0.0500
after reaction (M)	0		1.90		0.0500
assume small back rxn	+x		+2x		-x
equil (M)	x		1.90 + 2x		0.0500 - x

$K_f = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.0500 - x)}{(x)(1.90 + 2x)^2} \approx \frac{0.0500}{(x)(1.90)^2}$

Solve for x. $x = [Ag^+] = 8.15 \times 10^{-10}$ M

$$E = E^o - \frac{0.0592\ V}{n} \log \frac{[H^+]^2}{[Ag^+]^2} = 1.220\ V - \frac{0.0592\ V}{2} \log \frac{(1.00\ M)^2}{(8.15 \times 10^{-10}\ M)^2} = 0.682\ V$$

(d) Calculate new initial concentrations because of dilution to 110.0 mL.

$$M_i \times V_i = M_f \times V_f; \quad M_f = [Cl^-] = \frac{M_i \times V_i}{V_f} = \frac{0.200\ M \times 10.0\ mL}{110.0\ mL} = 0.0182\ M$$

$$M_i \times V_i = M_f \times V_f; \quad M_f = [Ag^+] = \frac{M_i \times V_i}{V_f} = \frac{0.0500\ M \times 100.0\ mL}{110.0\ mL} = 0.0455\ M$$

$$M_i \times V_i = M_f \times V_f; \quad M_f = [NH_3] = \frac{M_i \times V_i}{V_f} = \frac{2.00\ M \times 100.0\ mL}{110.0\ mL} = 1.82\ M$$

Now calculate the $[Ag^+]$ as a result of the following equilibrium:

	$Ag^+(aq)$	+	$2\ NH_3(aq)$	_	$Ag(NH_3)_2^+(aq)$
before reaction (M)	0.0455		1.82		0
assume 100% reaction	-0.0455		-2(0.0455)		+0.0455
after reaction (M)	0		1.73		0.0455
assume small back rxn	+x		+2x		-x
equil (M)	x		1.73 + 2x		0.0455 - x

$$K_f = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.0455\ \_\ x)}{(x)(1.73\ +\ 2x)^2} \approx \frac{0.0455}{(x)(1.73)^2}$$

Solve for x. $x = [Ag^+] = 8.94 \times 10^{-10}$ M

For AgCl, $K_{sp} = 1.8 \times 10^{-10}$

$IP = [Ag^+][Cl^-] = (8.94 \times 10^{-10}\ M)(0.0182\ M) = 1.6 \times 10^{-11}$

$IP < K_{sp}$, AgCl will not precipitate.

Now calculate new initial concentrations because of dilution to 120.0 mL.

$$M_i \times V_i = M_f \times V_f; \quad M_f = [Br^-] = \frac{M_i \times V_i}{V_f} = \frac{0.200\ M \times 10.0\ mL}{120.0\ mL} = 0.0167\ M$$

$$M_i \times V_i = M_f \times V_f; \quad M_f = [Ag^+] = \frac{M_i \times V_i}{V_f} = \frac{0.0500\ M \times 100.0\ mL}{120.0\ mL} = 0.0417\ M$$

$$M_i \times V_i = M_f \times V_f; \quad M_f = [NH_3] = \frac{M_i \times V_i}{V_f} = \frac{2.00\ M \times 100.0\ mL}{120.0\ mL} = 1.67\ M$$

Now calculate the $[Ag^+]$ as a result of the following equilibrium:

	$Ag^+(aq)$	+	$2\ NH_3(aq)$	_	$Ag(NH_3)_2^+(aq)$
before reaction (M)	0.0417		1.67		0
assume 100% reaction	-0.0417		-2(0.0417)		+0.0417
after reaction (M)	0		1.59		0.0417
assume small back rxn	+x		+2x		-x
equil (M)	x		1.59 + 2x		0.0417 - x

$$K_f = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{(0.0417\ \_\ x)}{(x)(1.59\ +\ 2x)^2} \approx \frac{0.0417}{(x)(1.59)^2}$$

Solve for x. $x = [Ag^+] = 9.70 \times 10^{-10}$ M

For AgBr, $K_{sp} = 5.4 \times 10^{-13}$
IP = $[Ag^+][Br^-] = (9.70 \times 10^{-10}\ M)(0.0167\ M) = 1.6 \times 10^{-11}$
IP > K_{sp}, AgBr will precipitate.

18.125 (a) anode: $Fe(s) + 2\ OH^-(aq) \rightarrow Fe(OH)_2(s) + 2\ e^-$
cathode: $2 \times [NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq)]$
overall: $Fe(s) + 2\ NiO(OH)(s) + 2\ H_2O(l) \rightarrow Fe(OH)_2(s) + 2\ Ni(OH)_2(s)$

(b)

$$\Delta G^o = -nFE^o = -(2\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.37\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -264{,}410\ J = -264\ kJ$$

$$E^o = \frac{0.0592\ V}{n}\ \log K; \quad \log K = \frac{n\ E^o}{0.0592\ V} = \frac{(2)(1.37\ V)}{0.0592\ V} = 46.3$$

$K = 10^{46.3} = 2 \times 10^{46}$

(c) It would still be 1.37 V because OH^- does not appear in the overall cell reaction. The overall cell reaction contains only solids and one liquid, therefore the cell voltage does not change because there are no concentration changes.

(d) $Fe(OH)_2$, 89.86 amu; 1 A = 1 C/s

$$mol\ e^- = (0.250\ C/s)(40.0\ min)\left(\frac{60\ s}{1\ min}\right)\left(\frac{1\ mol\ e^-}{96{,}500\ C}\right) = 6.22 \times 10^{-3}\ mol\ e^-$$

$$mass\ Fe(OH)_2 = (6.22 \times 10^{-3}\ mol\ e^-) \times \frac{1\ mol\ Fe(OH)_2}{2\ mol\ e^-} \times \frac{89.86\ g\ Fe(OH)_2}{1\ mol\ Fe(OH)_2} = 0.279\ g$$

H_2O molecules consumed =

$$(6.22 \times 10^{-3}\ mol\ e^-) \times \frac{2\ mol\ H_2O}{2\ mol\ e^-} \times \frac{6.022 \times 10^{23}\ H_2O\ molecules}{1\ mol\ H_2O} = 3.75 \times 10^{21}\ H_2O\ molecules$$

18.126 (a) Oxidation half reaction: $2\ [C_4H_{10}(g) + 13\ O^{2-}(s) \rightarrow 4\ CO_2(g) + 5\ H_2O(l) + 26\ e^-]$
Reduction half reaction: $13\ [O_2(g) + 4\ e^- \rightarrow 2\ O^{2-}(s)]$
Cell reaction: $2\ C_4H_{10}(g) + 13\ O_2(g) \rightarrow 8\ CO_2(g) + 10\ H_2O(l)$

(b) $\Delta H^o = [8\ \Delta H^o_f(CO_2)) + 10\ \Delta H^o_f(H_2O)] - [2\ \Delta H^o_f(C_4H_{10})]$
$\Delta H^o = [(8\ mol)(-393.5\ kJ/mol) + (10\ mol)(-285.8\ kJ/mol)]$
$- [(2\ mol)(-126\ kJ/mol)] = -5754\ kJ$
$\Delta S^o = [8\ S^o(CO_2) + 10\ S^o(H_2O)] - [2\ S^o(C_4H_{10}) + 13\ S^o(O_2)]$
$\Delta S^o = [(8\ mol)(213.6\ J/(K \cdot mol)) + (10\ mol)(69.9\ J/(K \cdot mol))]$
$- [(2\ mol)(310\ J/(K \cdot mol)) + (13\ mol)(205\ J/(K \cdot mol))] = -877.2\ J/K$
$\Delta G^o = \Delta H^o - T\Delta S^o = -5754\ kJ - (298\ K)(-877.2 \times 10^{-3}\ kJ/K) = -5493\ kJ$
1 V = 1 J/C

$$\Delta G^o = -nFE^o; \quad E^o = -\frac{\Delta G^o}{nF} = -\frac{-5493 \times 10^3\ J}{(52)(96{,}500\ C)} = 1.09\ J/C = 1.09\ V$$

$\Delta G^o = -RT \ln K$

$$\ln K = \frac{-\Delta G^{o}}{RT} = \frac{-(-5493\ kJ)}{(8.314\ x\ 10^{-3}\ kJ/K)(298\ K)} = 2217$$

$K = e^{2217} = 7 \times 10^{962}$

On raising the temperature, both K and E^o will decrease because the reaction is exothermic ($\Delta H^o < 0$).

(c) C_4H_{10}, 58.12 amu; 10.5 A = 10.5 C/s

$$\text{mass } C_4H_{10} = 10.5\ C/s \times 8\ hr \times \frac{60\ min}{1\ hr} \times \frac{60\ s}{1\ min} \times \frac{1\ mol\ e^-}{96{,}500\ C} \times \frac{2\ mol\ C_4H_{10}}{52\ mol\ e^-} \times \frac{58.12\ g\ C_4H_{10}}{1\ mol\ C_4H_{10}} = 7.00\ g\ C_4H_{10}$$

$$n = 7.00\ g\ C_4H_{10} \times \frac{1\ mol\ C_4H_{10}}{58.12\ g\ C_4H_{10}} = 0.120\ mol\ C_4H_{10}$$

$20^oC = 20 + 273 = 293\ K$

$PV = nRT$

$$V = \frac{nRT}{P} = \frac{(0.120\ mol)\left(0.082\,06\ \frac{L \bullet atm}{K \bullet mol}\right)(293\ K)}{\left(815\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg}\right)} = 2.69\ L$$

18.127 cathode:

(1) $MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Mn^{2+}(aq) + 2\ H_2O(l)$ $\quad E^o = +1.22\ V$

(2) $Mn(OH)_2(s) + OH^-(aq) \rightarrow MnO(OH)(s) + H_2O(l) + e^-$ $\quad E^o = +0.380\ V$

(3) $Mn^{2+}(aq) + 2\ OH^-(aq) \rightarrow Mn(OH)_2(s)$ $\quad K = 1/K_{sp} = 1/(2.1 \times 10^{-13}) = 4.8 \times 10^{12}$

(4) $\underline{4 \times [H_2O(l) \rightarrow H^+(aq) + OH^-(aq)]}$ $\quad K = (K_w)^4 = (1.0 \times 10^{-14})^4 = 1.0 \times 10^{-56}$

$MnO_2(s) + H_2O(l) + e^- \rightarrow MnO(OH)(s) + OH^-(aq)$

$$\Delta G^o_1 = -nFE^o = -(2\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.22\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -235{,}460\ J = -235.5\ kJ$$

$$\Delta G^o_2 = -nFE^o = -(1\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(0.380\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -36{,}670\ J = -36.7\ kJ$$

$\Delta G^o_3 = -RT \ln K = -(8.314 \times 10^{-3}\ kJ/K)(298\ K) \ln (4.8 \times 10^{12}) = -72.3\ kJ$

$\Delta G^o_4 = -RT \ln K = -(8.314 \times 10^{-3}\ kJ/K)(298\ K) \ln (1.0 \times 10^{-56}) = +319.5\ kJ$

$\Delta G^o(total) = -235.5\ kJ - 36.7\ kJ - 72.3\ kJ + 319.5\ kJ = -25.0\ kJ = -25{,}000\ J$

$1\ V = 1\ J/C$

$$\Delta G^o = -nFE^o;\ E^o = \frac{-\Delta G^{o}}{nF} = \frac{-(-25{,}000\ J)}{(1\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)} = +0.259\ J/C = +0.259\ V$$

$E^o_{cathode} = +0.259\ V$

anode:

(1) $Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$ $\quad E^o = +0.76$ V

(2) $\underline{Zn^{2+}(aq) + 2\ OH^-(aq) \rightarrow Zn(OH)_2(s)}$ $\quad K = 1/K_{sp} = 1/(4.1 \times 10^{-17}) = 2.4 \times 10^{16}$

$Zn(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_2(s) + 2\ e^-$

$$\Delta G^o_1 = -nFE^o = -(2\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)(0.76\ \text{V})\left(\frac{1\ \text{J}}{1\ \text{C} \bullet \text{V}}\right) = -146{,}680\ \text{J} = -146.7\ \text{kJ}$$

$\Delta G^o_2 = -RT \ln K = -(8.314 \times 10^{-3}\ \text{kJ/K})(298\ \text{K}) \ln (2.4 \times 10^{16}) = -93.4$ kJ

$\Delta G^o(\text{total}) = -146.7\ \text{kJ} - 93.4\ \text{kJ} = -240.1\ \text{kJ} = -240{,}100$ J

1 V = 1 J/C

$$\Delta G^o = -nFE^o;\ E^o = \frac{-\Delta G^o}{nF} = \frac{-(-240{,}100\ \text{J})}{(2\ \text{mol}\ e^-)\left(\frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-}\right)} = +1.24\ \text{J/C} = +1.24\ \text{V}$$

$E^o_{anode} = +1.24$ V

$E^o_{cell} = E^o_{cathode} + E^o_{anode} = 0.259\ \text{V} + 1.24\ \text{V} = 1.50$ V

(b) $FeO_4^{2-}(aq) \rightarrow Fe(OH)_3(s)$

$FeO_4^{2-}(aq) \rightarrow Fe(OH)_3(s) + H_2O(l)$

$FeO_4^{2-}(aq) + 5\ H^+(aq) \rightarrow Fe(OH)_3(s) + H_2O(l)$

$FeO_4^{2-}(aq) + 5\ H^+(aq) + 3\ e^- \rightarrow Fe(OH)_3(s) + H_2O(l)$

$FeO_4^{2-}(aq) + 5\ H^+(aq) + 5\ OH^-(aq) + 3\ e^- \rightarrow Fe(OH)_3(s) + H_2O(l) + 5\ OH^-(aq)$

$FeO_4^{2-}(aq) + 5\ H_2O(l) + 3\ e^- \rightarrow Fe(OH)_3(s) + H_2O(l) + 5\ OH^-(aq)$

$FeO_4^{2-}(aq) + 4\ H_2O(l) + 3\ e^- \rightarrow Fe(OH)_3(s) + 5\ OH^-(aq)$

(c) K_2FeO_4, 198.04 amu; MnO_2, 86.94 amu

$$\text{coulombs} = 10.00\ \text{g}\ K_2FeO_4 \times \frac{1\ \text{mol}\ K_2FeO_4}{198.04\ \text{g}\ K_2FeO_4} \times \frac{3\ \text{mol}\ e^-}{1\ \text{mol}\ K_2FeO_4} \times \frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-} =$$

1.46×10^4 C from 10.00 g K_2FeO_4

$$\text{coulombs} = 10.00\ \text{g}\ MnO_2 \times \frac{1\ \text{mol}\ MnO_2}{86.94\ \text{g}\ MnO_2} \times \frac{1\ \text{mol}\ e^-}{1\ \text{mol}\ MnO_2} \times \frac{96{,}500\ \text{C}}{1\ \text{mol}\ e^-} =$$

1.11×10^4 C from 10.00 g MnO_2

18.128 (a) $4\ [Au(s) + 2\ CN^-(aq) \rightarrow Au(CN)_2^-(aq) + e^-]$ oxidation half reaction

$O_2(g) \rightarrow 2\ H_2O(l)$

$O_2(g) + 4\ H^+(aq) \rightarrow 2\ H_2O(l)$

$4\ e^- + O_2(g) + 4\ H^+(aq) \rightarrow 2\ H_2O(l)$ reduction half reaction

Combine the two half reactions.

$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 4\ H^+(aq) \rightarrow 4\ Au(CN)_2^-(aq) + 2\ H_2O(l)$

$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 4\ H^+(aq) + 4\ OH^-(aq)$

$\rightarrow 4\ Au(CN)_2^-(aq) + 2\ H_2O(l) + 4\ OH^-(aq)$

$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 4\ H_2O(l) \rightarrow 4\ Au(CN)_2^-(aq) + 2\ H_2O(l) + 4\ OH^-(aq)$

$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ Au(CN)_2^-(aq) + 4\ OH^-(aq)$

(b) Add the following five reactions together. ΔG^o is calculated below each reaction.

$4\ [Au^+(aq) + 2\ CN^-(aq) \rightarrow Au(CN)_2^-(aq)]$ $\quad K = (K_f)^4$

$\Delta G^o = -RT \ln K = -(8.314 \times 10^{-3}\ kJ/K)(298\ K) \ln (6.2 \times 10^{38})^4 = -885.2\ kJ$

$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$ $\quad E^o = 1.229\ V$

$$\Delta G^o = -nFE^o = -(4\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.229\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -474{,}394\ J = -474.4\ kJ$$

$4\ [H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)]$ $\quad K = (K_w)^4$

$\Delta G^o = -RT \ln K = -(8.314 \times 10^{-3}\ kJ/K)(298\ K) \ln (1.0 \times 10^{-14})^4 = +319.5\ kJ$

$4\ [Au(s) \rightarrow Au^{3+}(aq) + 3\ e^-]$ $\quad E^o = -1.498\ V$

$$\Delta G^o = -nFE^o = -(12\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(-1.498\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = +1{,}734{,}684\ J = +1{,}734.7\ kJ$$

$4\ [Au^{3+}(aq) + 2\ e^- \rightarrow Au^+(aq)]$ $\quad E^o = 1.401\ V$

$$\Delta G^o = -nFE^o = -(8\ mol\ e^-)\left(\frac{96{,}500\ C}{1\ mol\ e^-}\right)(1.401\ V)\left(\frac{1\ J}{1\ C \bullet V}\right) = -1{,}081{,}572\ J = -1{,}081.6\ kJ$$

Overall reaction:

$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ Au(CN)_2^-(aq) + 4\ OH^-(aq)$

$\Delta G^o = -885.2\ kJ - 474.4\ kJ + 319.5\ kJ + 1{,}734.7\ kJ - 1{,}081.6\ kJ = -387.0\ kJ$

18.129 The overall cell reaction is:

$2\ Fe^{3+}(aq) + 2\ Hg(l) + 2\ Cl^-(aq) \rightarrow 2\ Fe^{2+}(aq) + Hg_2Cl_2(s)$

The Nernst equation can be applied to separate half reactions.

One half reaction is for the calomel reference electrode.

$2\ Hg(l) + 2\ Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2\ e^-$ $\quad E^o = -0.28\ V$

When $[Cl^-] = 2.9\ M$,

$$E_{calomel} = E^o - \frac{0.0592\ V}{n}\log\frac{1}{[Cl^-]^2} = -0.28\ V - \frac{0.0592\ V}{2}\log\frac{1}{(2.9)^2} = -0.25\ V$$

Balance the titration redox reaction: $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$

$[Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-] \times 5$

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$

$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

$MnO_4^-(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$

Combine the two half reactions.

$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H^+(aq) \rightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 4\ H_2O(l)$

initial mol Fe^{2+} = (0.010 mol/L)(0.1000 L) = 0.0010 mol Fe^{2+}
mL MnO_4^- needed to reach endpoint =

$$0.0010 \text{ mol } Fe^{2+} \times \frac{1 \text{ mol } MnO_4^-}{5 \text{ mol } Fe^{2+}} \times \frac{1.00 \text{ L}}{0.010 \text{ mol } MnO_4^-} \times \frac{1000 \text{ mL}}{1.00 \text{ L}} = 20.0 \text{ mL}$$

(a) initial mol Fe^{2+} = (0.010 mol/L)(0.1000 L) = 0.0010 mol Fe^{2+}
mol MnO_4^- in 5.0 mL = (0.010 mol/L)(0.0050 L) = 0.000 050 mol MnO_4^-

	$MnO_4^-(aq)$	+ 5 $Fe^{2+}(aq)$	+ 8 $H^+(aq)$	→ $Mn^{2+}(aq)$	+ 5 $Fe^{3+}(aq)$	+ 4 $H_2O(l)$
before (mol)	0.000 050	0.0010			0	
change (mol)	-0.000 050	-5(0.000 050)			(0.000 050)	
after (mol)	0	0.000 75			0.000 25	

Again, the Nernst equation can be applied to separate half reactions.
The other half reaction is: $Fe^{3+}(aq) + e^- \rightarrow 2\ Fe^{2+}(aq)$ $\quad E^o = +0.77$ V
E for the half reaction after adding 5.0 mL of MnO_4^- is

$$E_{Fe^{3+}/Fe^{2+}} = E^o - \frac{0.0592 \text{ V}}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.77 \text{ V} - \frac{0.0592 \text{ V}}{1} \log \frac{(0.000\ 75)}{(0.000\ 25)} = 0.74 \text{ V}$$

(Note in the Nernst equation above, we are taking a ratio of Fe^{2+} to Fe^{3+} so we can ignore volumes and just use moles instead of molarity.)

$E_{cell} = E_{Fe^{3+}/Fe^{2+}} + E_{calomel} = 0.74 \text{ V} + (-0.25 \text{ V}) = 0.49 \text{ V}$

(b) initial mol Fe^{2+} = (0.010 mol/L)(0.1000 L) = 0.0010 mol Fe^{2+}
mol MnO_4^- in 10.0 mL = (0.010 mol/L)(0.0100 L) = 0.000 10 mol MnO_4^-

	$MnO_4^-(aq)$	+ 5 $Fe^{2+}(aq)$	+ 8 $H^+(aq)$	→ $Mn^{2+}(aq)$	+ 5 $Fe^{3+}(aq)$	+ 4 $H_2O(l)$
before (mol)	0.000 10	0.0010			0	
change (mol)	-0.000 10	-5(0.000 10)			+5(0.000 10)	
after (mol)	0	0.000 50			0.000 50	

E for the half reaction after adding 10.0 mL of MnO_4^- is

$$E_{Fe^{3+}/Fe^{2+}} = E^o - \frac{0.0592 \text{ V}}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.77 \text{ V} - \frac{0.0592 \text{ V}}{1} \log \frac{(0.000\ 50)}{(0.000\ 50)} = 0.77 \text{ V}$$

$E_{cell} = E_{Fe^{3+}/Fe^{2+}} + E_{calomel} = 0.77 \text{ V} + (-0.25 \text{ V}) = 0.52 \text{ V}$

(c) initial mol Fe^{2+} = (0.010 mol/L)(0.1000 L) = 0.0010 mol Fe^{2+}
mol MnO_4^- in 19.0 mL = (0.010 mol/L)(0.0190 L) = 0.000 19 mol MnO_4^-

	$MnO_4^-(aq)$	+ 5 $Fe^{2+}(aq)$	+ 8 $H^+(aq)$	→ $Mn^{2+}(aq)$	+ 5 $Fe^{3+}(aq)$	+ 4 $H_2O(l)$
before (mol)	0.000 19	0.0010			0	
change (mol)	-0.000 19	-5(0.000 19)			+5(0.000 19)	
after (mol)	0	0.000 05			0.000 95	

E for the half reaction after adding 19.0 mL of MnO_4^- is

$$E_{Fe^{3+}/Fe^{2+}} = E^o - \frac{0.0592 \text{ V}}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]} = 0.77 \text{ V} - \frac{0.0592 \text{ V}}{1} \log \frac{(0.000\ 05)}{(0.000\ 95)} = 0.85 \text{ V}$$

$E_{cell} = E_{Fe^{3+}/Fe^{2+}} + E_{calomel} = 0.85 \text{ V} + (-0.25 \text{ V}) = 0.60 \text{ V}$

(d) 21.0 mL is past the endpoint so the MnO_4^- is in excess and all of the Fe^{2+} is consumed.
initial mol Fe^{2+} = (0.010 mol/L)(0.1000 L) = 0.0010 mol Fe^{2+}
mol MnO_4^- in 21.0 mL = (0.010 mol/L)(0.0210 L) = 0.000 21 mol MnO_4^-

	$MnO_4^-(aq)$ +	$5\ Fe^{2+}(aq)$ +	$8\ H^+(aq)$ →	$Mn^{2+}(aq)$ +	$5\ Fe^{3+}(aq)$ +	$4\ H_2O(l)$
before (mol)	0.000 21	0.0010		0	0	
change (mol)	-0.000 20	-5(0.000 20)			+5(0.000 20)	
after (mol)	0.000 01	0		0.000 20	0.0010	

Because the Fe^{2+} is totally consumed, there is a new half reaction:
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ $\quad E^o = 1.51$ V
The total volume = 100.0 mL + 21.0 mL = 121.0 mL = 0.1210 L
$[MnO_4^-]$ = 0.000 01 mol/0.1210 L = 0.000 083 M
$[Mn^{2+}]$ = 0.000 20 mol/0.1210 L = 0.001 65 M
We need to determine $[H^+]$ in order to determine the half reaction potential.
$[H_2SO_4]_{dil} \cdot 121.0\ mL = [H_2SO_4]_{conc} \cdot 100.0\ mL$
$[H_2SO_4]_{dil}$ = [(1.50 M)(100.0 mL)]/121.0 mL = 1.24 M
We can ignore the small amount of H^+ consumed by the titration itself, because the H_2SO_4 concentration is so large.
Consider the dissociation of H_2SO_4. From the complete dissociation of the first proton, $[H^+] = [HSO_4^-]$ = 1.24 M.
For the dissociation of the second proton, the following equilibrium must be considered:

	$HSO_4^-(aq)$ _	$H^+(aq)$ +	$SO_4^{2-}(aq)$
initial (M)	1.24	1.24	0
change (M)	-x	+x	+x
equil (M)	1.24 - x	1.24 + x	x

$$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2} = \frac{(1.24 + x)(x)}{1.24 - x}$$

$x^2 + 1.252x - 0.0149 = 0$
Use the quadratic formula to solve for x.

$$x = \frac{-(1.252) \pm \sqrt{(1.252)^2 - 4(1)(-0.0149)}}{2(1)} = \frac{-1.252 \pm 1.276}{2}$$

x = -1.264 and 0.012
Of the two solutions for x, only the positive value of x has physical meaning, since x is the $[SO_4^{2-}]$.
$[H^+] = 1.24 + x = 1.24 + 0.012 = 1.25$ M

$$E_{MnO_4^-/Mn^{2+}} = E^o - \frac{0.0592\ V}{n} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= 1.51\ V - \frac{0.0592\ V}{5} \log \frac{(0.001\ 65)}{(0.000\ 083)(1.25)^8} = 1.50\ V$$

$E_{cell} = E_{MnO_4^-/Mn^{2+}} + E_{calomel} = 1.50\ V + (-0.25\ V) = 1.25\ V$

Notice that there is a dramatic change in the potential at the equivalence point.

22 Nuclear Chemistry

22.1 (a) In beta emission, the mass number is unchanged, and the atomic number increases by one. $^{106}_{44}\text{Ru} \rightarrow {}^{0}_{-1}\text{e} + {}^{106}_{45}\text{Rh}$

(b) In alpha emission, the mass number decreases by four, and the atomic number decreases by two. $^{189}_{83}\text{Bi} \rightarrow {}^{4}_{2}\text{He} + {}^{185}_{81}\text{Tl}$

(c) In electron capture, the mass number is unchanged, and the atomic number decreases by one. $^{204}_{84}\text{Po} + {}^{0}_{-1}\text{e} \rightarrow {}^{204}_{83}\text{Bi}$

22.2 The mass number decreases by four, and the atomic number decreases by two. This is characteristic of alpha emission. $^{214}_{90}\text{Th} \rightarrow {}^{210}_{88}\text{Ra} + {}^{4}_{2}\text{He}$

22.3 $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.08 \text{ x } 10^{-2} \text{ h}^{-1}} = 64.2 \text{ h}$$

22.4 $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \text{ x } 10^{-4} \text{ y}^{-1}$$

22.5 $$\ln\left(\frac{N}{N_0}\right) = -0.693\left(\frac{t}{t_{1/2}}\right) = -0.693\left(\frac{16{,}230 \text{ y}}{5730 \text{ y}}\right) = -1.963$$

$$\frac{N}{N_0} = e^{-1.963} = 0.140; \qquad \frac{N}{100\%} = 0.140; \qquad N = 14.0\%$$

22.6 $$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at t = 0}}$$

$$\ln\left(\frac{10{,}860}{16{,}800}\right) = (-0.693)\left(\frac{28.0 \text{ d}}{t_{1/2}}\right); \qquad -0.436 = (-0.693)\left(\frac{28.0 \text{ d}}{t_{1/2}}\right)$$

$$t_{1/2} = \frac{(-0.693)(28.0 \text{ d})}{(-0.436)} = 44.5 \text{ d}$$

22.7 $\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right)$

$\ln\left(\frac{10}{100}\right) = (-0.693)\left(\frac{10\ d}{t_{1/2}}\right)$; $\quad -2.303 = (-0.693)\left(\frac{10\ d}{t_{1/2}}\right)$

$t_{1/2} = \frac{(-0.693)(10\ d)}{(-2.303)} = 3.0\ d$

22.8 $^{59}_{29}Cu \rightarrow {}^{0}_{1}e + {}^{59}_{28}Ni$

16 $^{59}Cu \rightarrow$ 8 $^{59}Cu \rightarrow$ 4 $^{59}Cu \rightarrow$ 2 ^{59}Cu; three half-lives have passed.

22.9 ^{199}Au has a higher neutron/proton ratio and decays by beta emission. ^{173}Au has a lower neutron/proton ratio and decays by alpha emission.

22.10 The shorter arrow pointing right is for beta emission. The longer arrow pointing left is for alpha emission.

A = $^{153+97}_{97}X = {}^{250}_{97}Bk$

B = $^{152+98}_{98}X = {}^{250}_{98}Cf$

C = $^{150+96}_{96}X = {}^{246}_{96}Cm$

D = $^{148+94}_{94}X = {}^{242}_{94}Pu$

E = $^{146+92}_{92}X = {}^{238}_{92}U$

22.11 For $^{16}_{8}O$:

First, calculate the total mass of the nucleons (8 n + 8 p)

Mass of 8 neutrons = (8)(1.008 66 amu) = 8.069 28 amu

Mass of 8 protons = (8)(1.007 28 amu) = 8.058 24 amu

Mass of 8 n + 8 p = 16.127 52 amu

Next, calculate the mass of a ^{16}O nucleus by subtracting the mass of 8 electrons from the mass of a ^{16}O atom.

Mass of ^{16}O atom	= 15.994 92 amu
-Mass of 8 electrons = -(8)(5.486 x 10^{-4} amu)	= -0.004 39 amu
Mass of ^{16}O nucleus	= 15.990 53 amu

Then subtract the mass of the ^{16}O nucleus from the mass of the nucleons to find the mass defect:

Mass defect = mass of nucleons - mass of nucleus

= (16.127 52 amu) - (15.990 53 amu) = 0.136 99 amu

Mass defect in g/mol:

(0.136 99 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.136 99 g/mol

Now, use the Einstein equation to convert the mass defect into the binding energy.

$\Delta E = \Delta mc^2$ = (0.136 99 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2

$\Delta E = 1.233 \times 10^{13}$ J/mol = 1.233 x 10^{10} kJ/mol

$$\Delta E = \frac{1.233 \times 10^{13} \text{ J/mol}}{6.022 \times 10^{23} \text{ nuclei/mol}} \times \frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \times \frac{1 \text{ nucleus}}{16 \text{ nucleons}} = 8.00 \frac{\text{MeV}}{\text{nucleon}}$$

22.12 $\Delta E = -852 \text{ kJ/mol} = -852 \times 10^3 \text{ J/mol}$; $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$

$$\Delta E = \Delta mc^2; \quad \Delta m = \frac{\Delta E}{c^2} = \frac{\left(-852 \times 10^3 \frac{\text{kg} \bullet \text{m}^2}{\text{s}^2 \bullet \text{mol}}\right)}{(3.00 \times 10^8 \text{ m/s})^2} = -9.47 \times 10^{-12} \text{ kg/mol}$$

$$\Delta m = -9.47 \times 10^{-12} \frac{\text{kg}}{\text{mol}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = -9.47 \times 10^{-9} \text{ g/mol}$$

22.13 $^{1}_{0}n + {}^{235}_{92}U \rightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\ {}^{1}_{0}n$

mass $^{235}_{92}U$	235.0439	amu
mass $^{1}_{0}n$	1.008 66	amu
-mass $^{137}_{52}Te$	-136.9254	amu
-mass $^{97}_{40}Zr$	-96.9110	amu
-mass $2\ {}^{1}_{0}n$	-(2)(1.008 66)	amu
mass change	0.1988 amu	

$(0.1988 \text{ amu})(1.660\ 54 \times 10^{-24} \text{ g/amu})(6.022 \times 10^{23} \text{ mol}^{-1}) = 0.1988 \text{ g/mol}$
$\Delta E = \Delta mc^2 = (0.1988 \text{ g/mol})(10^{-3} \text{ kg/g})(3.00 \times 10^8 \text{ m/s})^2$
$\Delta E = 1.79 \times 10^{13} \text{ J/mol} = 1.79 \times 10^{10} \text{ kJ/mol}$

22.14 $^{1}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He$

mass ^{1}H	1.007 83 amu
mass ^{2}H	2.014 10 amu
-mass ^{3}He	-3.016 03 amu
mass change	0.005 90 amu

$(0.005\ 90 \text{ amu})(1.660\ 54 \times 10^{-24} \text{ g/amu})(6.022 \times 10^{23} \text{ mol}^{-1}) = 0.005\ 90 \text{ g/mol}$
$\Delta E = \Delta mc^2 = (0.005\ 90 \text{ g/mol})(10^{-3} \text{ kg/g})(3.00 \times 10^8 \text{ m/s})^2$
$\Delta E = 5.31 \times 10^{11} \text{ J/mol} = 5.31 \times 10^8 \text{ kJ/mol}$

22.15 $^{40}_{18}Ar + {}^{1}_{1}p \rightarrow {}^{40}_{19}K + {}^{1}_{0}n$

22.16 $^{238}_{92}U + {}^{2}_{1}H \rightarrow {}^{238}_{93}Np + 2\ {}^{1}_{0}n$

22.17 $\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right)$; $\quad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$

$$\ln\left(\frac{2.4}{15.3}\right) = (\_\ 0.693)\left(\frac{t}{5730\ y}\right); \qquad t = 1.53 \times 10^4\ y$$

22.18 Elements heavier than iron arise from nuclear reactions occuring as a result of supernova explosions.

Understanding Key Concepts

22.19 $16\ ^{40}K \rightarrow 8\ ^{40}K \rightarrow 4\ ^{40}K$; two half-lives have passed.

22.20 The isotope contains 8 neutrons and 6 protons. The isotope symbol is ${}^{14}_{6}C$.
${}^{14}_{6}C$ would decay by beta emission because the n/p ratio is high.

22.21 ${}^{148}_{69}Tm$ decays to ${}^{148}_{68}Er$ by either positron emission or electron capture.

22.22 The shorter arrow pointing right is for beta emission. The longer arrow pointing left is for alpha emission.

A = ${}^{147+94}_{94}X = {}^{241}_{94}Pu$

B = ${}^{146+95}_{95}X = {}^{241}_{95}Am$

C = ${}^{144+93}_{93}X = {}^{237}_{93}Np$

D = ${}^{142+91}_{91}X = {}^{233}_{91}Pa$

E = ${}^{141+92}_{92}X = {}^{233}_{92}U$

22.23 The half-life is approximately 3 years.

Additional Problems
Nuclear Reactions and Radioactivity

22.24 Positron emission is the conversion of a proton in the nucleus into a neutron plus an ejected positron.
Electron capture is the process in which a proton in the nucleus captures an inner-shell electron and is thereby converted into a neutron.

22.25 An alpha particle $\left({}^{4}_{2}He^{2+}\right)$ is a helium nucleus. The He atom has two electrons and is neutral.

22.26 Alpha particles move relatively slowly and can be stopped by the skin. However, inside the body, alpha particles give up their energy to the immediately surrounding tissue.
Gamma rays move at the speed of light and are very penetrating. Therefore they are equally hazardous internally and externally.

22.27 "Neutron rich" nuclides emit beta particles to decrease the number of neutrons and

increase the number of protons in the nucleus.
"Neutron poor" nuclides decrease the number of protons and increase the n/p ratio by either alpha emission, positron emission, or electron capture.

22.28 There is no radioactive "neutralization" reaction like there is an acid-base neutralization reaction.

22.29 The nuclei of ^{24}Na and $^{24}Na^{+}$ are identical so their nuclear reactions must be the same even though their chemical reactions are completely different.

22.30 (a) $^{126}_{50}Sn \rightarrow {}^{0}_{-1}e + {}^{126}_{51}Sb$ (b) $^{210}_{88}Ra \rightarrow {}^{4}_{2}He + {}^{206}_{86}Rn$
(c) $^{77}_{37}Rb \rightarrow {}^{0}_{1}e + {}^{77}_{36}Kr$ (d) $^{76}_{36}Kr + {}^{0}_{-1}e \rightarrow {}^{76}_{35}Br$

22.31 (a) $^{90}_{38}Sr \rightarrow {}^{0}_{-1}e + {}^{90}_{39}Y$ (b) $^{247}_{100}Fm \rightarrow {}^{4}_{2}He + {}^{243}_{98}Cf$
(c) $^{49}_{25}Mn \rightarrow {}^{0}_{1}e + {}^{49}_{24}Cr$ (d) $^{37}_{18}Ar + {}^{0}_{-1}e \rightarrow {}^{37}_{17}Cl$

22.32 (a) $^{188}_{80}Hg \rightarrow {}^{188}_{79}Au + {}^{0}_{1}e$ (b) $^{218}_{85}At \rightarrow {}^{214}_{83}Bi + {}^{4}_{2}He$
(c) $^{234}_{90}Th \rightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e$

22.33 (a) $^{24}_{11}Na \rightarrow {}^{24}_{12}Mg + {}^{0}_{-1}e$ (b) $^{135}_{60}Nd \rightarrow {}^{135}_{59}Pr + {}^{0}_{1}e$
(c) $^{170}_{78}Pt \rightarrow {}^{166}_{76}Os + {}^{4}_{2}He$

22.34 (a) $^{162}_{75}Re \rightarrow {}^{158}_{73}Ta + {}^{4}_{2}He$ (b) $^{138}_{62}Sm + {}^{0}_{-1}e \rightarrow {}^{138}_{61}Pm$
(c) $^{188}_{74}W \rightarrow {}^{188}_{75}Re + {}^{0}_{-1}e$ (d) $^{165}_{73}Ta \rightarrow {}^{165}_{72}Hf + {}^{0}_{1}e$

22.35 (a) $^{157}_{63}Eu \rightarrow {}^{157}_{64}Gd + {}^{0}_{-1}e$ (b) $^{126}_{56}Ba + {}^{0}_{-1}e \rightarrow {}^{126}_{55}Cs$
(c) $^{146}_{62}Sm \rightarrow {}^{142}_{60}Nd + {}^{4}_{2}He$ (d) $^{125}_{56}Ba \rightarrow {}^{125}_{55}Cs + {}^{0}_{1}e$

22.36 ^{160}W is neutron poor and decays by alpha emission. ^{185}W is neutron rich and decays by beta emission.

22.37 $^{136}_{53}I$ is neutron rich and decays by beta emission.
$^{122}_{53}I$ is neutron poor and decays by positron emission.

22.38 $^{241}_{95}Am \rightarrow {}^{237}_{93}Np + {}^{4}_{2}He$
$^{237}_{93}Np \rightarrow {}^{233}_{91}Pa + {}^{4}_{2}He$
$^{233}_{91}Pa \rightarrow {}^{233}_{92}U + {}^{0}_{-1}e$
$^{233}_{92}U \rightarrow {}^{229}_{90}Th + {}^{4}_{2}He$
$^{229}_{90}Th \rightarrow {}^{225}_{88}Ra + {}^{4}_{2}He$
$^{225}_{88}Ra \rightarrow {}^{225}_{89}Ac + {}^{0}_{-1}e$
$^{225}_{89}Ac \rightarrow {}^{221}_{87}Fr + {}^{4}_{2}He$

$^{221}_{87}Fr \_ {}^{217}_{85}At + {}^{4}_{2}He$

$^{217}_{85}At \_ {}^{213}_{83}Bi + {}^{4}_{2}He$

$^{213}_{83}Bi \_ {}^{213}_{84}Po + {}^{0}_{-1}e$

$^{213}_{84}Po \_ {}^{209}_{82}Pb + {}^{4}_{2}He$

$^{209}_{82}Pb \_ {}^{209}_{83}Bi + {}^{0}_{-1}e$

22.39 $^{222}_{86}Rn \_ {}^{218}_{84}Po + {}^{4}_{2}He$

$^{218}_{84}Po \_ {}^{214}_{82}Pb + {}^{4}_{2}He$

$^{214}_{82}Pb \_ {}^{210}_{80}Hg + {}^{4}_{2}He$

$^{210}_{80}Hg \_ {}^{210}_{81}Tl + {}^{0}_{-1}e$

$^{210}_{81}Tl \_ {}^{210}_{82}Pb + {}^{0}_{-1}e$

22.40 Each alpha emission decreases the mass number by four and the atomic number by two. Each beta emission increases the atomic number by one.

$^{232}_{90}Th \_ {}^{208}_{82}Pb$

$$\text{Number of } \alpha \text{ emissions} = \frac{\text{Th mass number} \_ \text{Pb mass number}}{4}$$

$$= \frac{232 \_ 208}{4} = 6\ \alpha \text{ emissions}$$

The atomic number decreases by 12 as a result of 6 alpha emissions. The resulting atomic number is (90 - 12) = 78.

Number of β emissions = Pb atomic number - 78 = 82 - 78 = 4 β emissions

22.41 Each alpha emission decreases the mass number by four and the atomic number by two. Each beta emission increases the atomic number by one.

$^{235}_{92}U \_ {}^{207}_{82}Pb$

$$\text{Number of } \alpha \text{ emissions} = \frac{\text{U mass number} \_ \text{Pb mass number}}{4}$$

$$= \frac{235 \_ 207}{4} = 7\ \alpha \text{ emissions}$$

The atomic number decreases by 14 as a result of 7 alpha emissions. The resulting atomic number is (92 - 14) = 78.

Number of β emissions = Pb atomic number - 78 = 82 - 78 = 4 β emissions

Radioactive Decay Rates

22.42 If the half-life of ^{59}Fe is 44.5 d, it takes 44.5 days for half of the original amount of ^{59}Fe to decay.

22.43 The half-life is the time it takes for one-half of a radioactive sample to decay.

The decay constant is the rate constant for the first order radioactive decay.

$$k = \frac{0.693}{t_{1/2}}$$

22.44 $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.805\ \text{d}} = 0.247\ \text{d}^{-1}$$

22.45 $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{78.25\ \text{h}} = 8.86 \times 10^{-3}\ \text{h}^{-1}$$

22.46 $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.228\ \text{d}^{-1}} = 3.04\ \text{d}$$

22.47 $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.88 \times 10^{-5}\ \text{y}^{-1}} = 2.41 \times 10^{4}\ \text{y}$$

22.48 After 65 d: $$\ln\left(\frac{N}{N_0}\right) = -0.693\left(\frac{t}{t_{1/2}}\right) = -0.693\left(\frac{\left[\frac{65\ \text{d}}{365\ \text{d/y}}\right]}{432.2\ \text{y}}\right) = -0.000\ 285\ 5$$

$$\frac{N}{N_0} = e^{-0.0002855} = 0.9997; \qquad \frac{N}{100\%} = 0.9997; \qquad N = 99.97\%$$

After 65 y: $$\ln\left(\frac{N}{N_0}\right) = -0.693\left(\frac{t}{t_{1/2}}\right) = -0.693\left(\frac{65\ \text{y}}{432.2\ \text{y}}\right) = -0.1042$$

$$\frac{N}{N_0} = e^{-0.1042} = 0.9010; \qquad \frac{N}{100\%} = 0.9010; \qquad N = 90.10\%$$

After 650 y: $$\ln\left(\frac{N}{N_0}\right) = -0.693\left(\frac{t}{t_{1/2}}\right) = -0.693\left(\frac{650\ \text{y}}{432.2\ \text{y}}\right) = -1.042$$

$$\frac{N}{N_0} = e^{-1.042} = 0.3527; \qquad \frac{N}{100\%} = 0.3527; \qquad N = 35.27\%$$

22.49 After 24 min: $$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right) = (-0.693)\left(\frac{24\ \text{min}}{109.8\ \text{min}}\right) = -0.1515$$

$$\frac{N}{N_0} = e^{-0.1515} = 0.8594; \qquad \frac{N}{100\%} = 0.8594; \qquad N = 85.94\%$$

After 24 h: $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{24\ h\ x\ \frac{60\ min}{1\ h}}{109.8\ min}\right) = -9.089$

$\frac{N}{N_0} = e^{-9.089} = 0.000\ 113\ 0;$ $\frac{N}{100\%} = 0.000\ 113\ 0;$ $N = 0.011\ 30\%$

After 24 d: $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{24\ d\ x\ \frac{24\ h}{1\ d}\ x\ \frac{60\ min}{1\ h}}{109.8\ min}\right) = -218.1$

$\frac{N}{N_0} = e^{-218.1} = 1.861\ x\ 10^{-95};$ $\frac{N}{100\%} = 1.861\ x\ 10^{-95};$ $N = 1.861\ x\ 10^{-93}\%$

22.50 $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right);$ $\ln(0.43) = (\_\ 0.693)\left(\frac{t}{5730\ y}\right);$ $t = 6980\ y$

22.51 Assume a sample of $^{40}_{19}K$ containing 100 atoms.

$^{40}_{19}K + {}^{0}_{-1}e\ \_\ {}^{40}_{18}Ar$

before decay (atoms)	100	0
after decay (atoms)	100 - x	x

$\frac{^{40}Ar}{^{40}K} = \frac{x}{100\ \_\ x} = 1.15;$ Solve for x. x = 53.5

$\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right)$

N = 100 - x = 100 - 53.5 = 46.5, the amount of ^{40}K at time t.

N_0 = 100, the original amount of ^{40}K.

$\ln\left(\frac{46.5}{100}\right) = (\_\ 0.693)\left(\frac{t}{1.28\ x\ 10^{9}\ y}\right);$ $t = 1.41\ x\ 10^{9}\ y$

22.52 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.89\ x\ 10^{-3}\ d^{-1}} = 87.83\ d$

$\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{185\ d}{87.83\ d}\right) = -1.4597$

$\frac{N}{N_0} = e^{-1.4597} = 0.2323;$ $\frac{N}{100\%} = 0.2323;$ $N = 23.2\%$

22.53 $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.88\ x\ 10^{-5}\ y^{-1}} = 2.41\ x\ 10^{4}\ y$

After 1000 y: $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{1000\ y}{2.41\ x\ 10^4\ y}\right) = -0.028\ 76$

$\frac{N}{N_0} = e^{-0.02876} = 0.9717; \qquad \frac{N}{100\%} = 0.9717; \qquad N = 97.17\%$

After 25,000 y: $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{25{,}000\ y}{2.41\ x\ 10^4\ y}\right) = -0.7189$

$\frac{N}{N_0} = e^{-0.7189} = 0.4873; \qquad \frac{N}{100\%} = 0.4873; N = 48.73\%$

After 100,000 y: $\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right) = (\_\ 0.693)\left(\frac{100{,}000\ y}{2.41\ x\ 10^4\ y}\right) = -2.876$

$\frac{N}{N_0} = e^{-2.876} = 0.0564; \qquad \frac{N}{100\%} = 0.0564; \qquad N = 5.64\%$

22.54 $t_{1/2} = (102\ y)(365\ d/y)(24\ h/d)(3600\ s/h) = 3.2167\ x\ 10^9\ s$

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.2167\ x\ 10^9\ s} = 2.1544\ x\ 10^{-10}\ s^{-1}$

$N = (1.0\ x\ 10^{-9}\ g)\left(\frac{1\ mol\ Po}{209\ g\ Po}\right)(6.022\ x\ 10^{23}\ atoms/mol) = 2.881\ x\ 10^{12}\ atoms$

Decay rate = kN = $(2.1544\ x\ 10^{-10}\ s^{-1})(2.881\ x\ 10^{12}\ atoms) = 6.21\ x\ 10^2\ s^{-1}$

621 α particles are emitted in 1.0 s.

22.55 $t_{1/2} = (3.0\ x\ 10^5\ y)(365\ d/y)(24\ h/d)(60\ min/h) = 1.6\ x\ 10^{11}\ min$

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.6\ x\ 10^{11}\ min} = 4.3\ x\ 10^{-12}\ min^{-1}$

$N = (5.0\ x\ 10^{-3}\ g)\left(\frac{1\ mol\ {}^{36}Cl}{36\ g}\right)(6.022\ x\ 10^{23}\ atoms/mol) = 8.4\ x\ 10^{19}\ atoms$

Decay rate = kN = $(4.3\ x\ 10^{-12}\ min^{-1})(8.4\ x\ 10^{19}\ atoms) = 3.6\ x\ 10^8\ min^{-1}$

Curies = $(3.6\ x\ 10^8/min)\left(\frac{1\ min}{60\ s}\right)\left(\frac{1\ Ci}{3.7\ x\ 10^{10}/s}\right) = 1.6\ x\ 10^{-4}\ Ci$

22.56 Decay rate = kN

$N = (1.0\ x\ 10^{-3}\ g)\left(\frac{1\ mol\ {}^{79}Se}{79\ g}\right)(6.022\ x\ 10^{23}\ atoms/mol) = 7.6\ x\ 10^{18}\ atoms$

$k = \frac{Decay\ rate}{N} = \frac{1.5\ x\ 10^5/s}{7.6\ x\ 10^{18}} = 2.0\ x\ 10^{-14}\ s^{-1}$

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.0\ x\ 10^{-14}\ s^{-1}} = 3.5\ x\ 10^{13}\ s$

$$t_{1/2} = (3.5 \times 10^{13}\ \text{s})\left(\frac{1\ \text{h}}{3600\ \text{s}}\right)\left(\frac{1\ \text{d}}{24\ \text{h}}\right)\left(\frac{1\ \text{y}}{365\ \text{d}}\right) = 1.1 \times 10^{6}\ \text{y}$$

22.57 Decay rate = kN

$$N = (1.0 \times 10^{-9}\ \text{g})\left(\frac{1\ \text{mol Ti}}{44\ \text{g Ti}}\right)(6.022 \times 10^{23}\ \text{atoms/mol}) = 1.37 \times 10^{13}\ \text{atoms}$$

$$k = \frac{\text{Decay rate}}{N} = \frac{4.8 \times 10^{3}\ \text{s}^{-1}}{1.37 \times 10^{13}} = 3.50 \times 10^{-10}\ \text{s}^{-1}$$

$$k = (3.50 \times 10^{-10}\ \text{s}^{-1})(3600\ \text{s/h})(24\ \text{h/d})(365\ \text{d/y}) = 1.10 \times 10^{-2}\ \text{y}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.10 \times 10^{-2}\ \text{y}^{-1}} = 63\ \text{y}$$

22.58 $$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$$

$$\ln\left(\frac{6990}{8540}\right) = (-0.693)\left(\frac{10.0\ \text{d}}{t_{1/2}}\right); \qquad t_{1/2} = 34.6\ \text{d}$$

22.59 $$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$$

$$\ln\left(\frac{10{,}980}{53{,}500}\right) = (-0.693)\left(\frac{48.0\ \text{h}}{t_{1/2}}\right); \quad t_{1/2} = 21.0\ \text{h}$$

Energy Changes During Nuclear Reactions

22.60 The loss in mass that occurs when protons and neutrons combine to form a nucleus is called the mass defect. The lost mass is converted into the binding energy that is used to hold the nucleons together.

22.61 Energy (heat) is absorbed in an endothermic reaction. The energy is converted to mass. The mass of the products is slightly larger than the mass of the reactants.

22.62 $$E = (1.50\ \text{MeV})\left(\frac{1.60 \times 10^{-13}\ \text{J}}{1\ \text{MeV}}\right) = 2.40 \times 10^{-13}\ \text{J}$$

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34}\ \text{Jcdot s})(3.00 \times 10^{8}\ \text{m/s})}{2.40 \times 10^{-13}\ \text{J}} = 8.28 \times 10^{-13}\ \text{m} = 0.000\ 828\ \text{nm}$$

22.63 $$E = (6.82\ \text{keV})\left(\frac{1\ \text{MeV}}{10^{3}\ \text{keV}}\right)\left(\frac{1.60 \times 10^{-13}\ \text{J}}{1\ \text{MeV}}\right) = 1.09 \times 10^{-15}\ \text{J}$$

$$\nu = \frac{E}{h} = \frac{1.09 \text{ x } 10^{-15} \text{ J}}{6.626 \text{ x } 10^{-34} \text{ J} \bullet \text{ s}} = 1.65 \text{ x } 10^{18}/\text{s} = 1.65 \text{ x } 10^{18} \text{ Hz}$$

22.64 (a) For $^{52}_{26}\text{Fe}$:

First, calculate the total mass of the nucleons (26 n + 26 p)
Mass of 26 neutrons = (26)(1.008 66 amu) = 26.225 16 amu
Mass of 26 protons = (26)(1.007 28 amu) = 26.189 28 amu
Mass of 26 n + 26 p = 52.414 44 amu
Next, calculate the mass of a ^{52}Fe nucleus by subtracting the mass of 26 electrons from the mass of a ^{52}Fe atom.

Mass of ^{52}Fe atom	= 51.948 11 amu
-Mass of 26 electrons = -(26)(5.486 x 10^{-4} amu)	= -0.014 26 amu
Mass of ^{52}Fe nucleus	= 51.933 85 amu

Then subtract the mass of the ^{52}Fe nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (52.414 44 amu) - (51.933 85 amu) = 0.480 59 amu
Mass defect in g/mol:
(0.480 59 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.480 59 g/mol

(b) For $^{92}_{42}\text{Mo}$:

First, calculate the total mass of the nucleons (50 n + 42 p)
Mass of 50 neutrons = (50)(1.008 66 amu) = 50.433 00 amu
Mass of 42 protons = (42)(1.007 28 amu) = 42.305 76 amu
Mass of 50 n + 42 p = 92.738 76 amu
Next, calculate the mass of a ^{92}Mo nucleus by subtracting the mass of 42 electrons from the mass of a ^{92}Mo atom.

Mass of ^{92}Mo atom	= 91.906 81 amu
-Mass of 42 electrons = -(42)(5.486 x 10^{-4} amu)	= -0.023 04 amu
Mass of ^{92}Mo nucleus	= 91.883 77 amu

Then subtract the mass of the ^{92}Mo nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (92.738 76 amu) - (91.883 77 amu) = 0.854 99 amu
Mass defect in g/mol:
(0.854 99 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.854 99 g/mol

22.65 (a) For $^{32}_{16}\text{S}$:

First, calculate the total mass of the nucleons (16 n + 16 p)
Mass of 16 neutrons = (16)(1.008 66 amu) = 16.138 56 amu
Mass of 16 protons = (16)(1.007 28 amu) = 16.116 48 amu
Mass of 16 n + 16 p = 32.255 04 amu
Next, calculate the mass of a ^{32}S nucleus by subtracting the mass of 16 electrons from the mass of a ^{32}S atom.

Mass of ^{32}S = 31.972 07 amu
Mass of 16 electrons = -(16)(5.486 x 10^{-4} amu) = -0.008 78 amu
Mass of ^{32}S nucleus = 31.963 29 amu
Then subtract the mass of the ^{32}S nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (32.255 04 amu) - (31.963 29 amu) = 0.291 75 amu
Mass defect in g/mol:
(0.291 75 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.291 74 g/mol

(b) For $^{40}_{20}Ca$:
First, calculate the total mass of the nucleons (20 n + 20 p)
Mass of 20 neutrons = (20)(1.008 66 amu) = 20.173 20 amu
Mass of 20 protons = (20)(1.007 28 amu) = 20.145 60 amu
Mass of 20 n + 20 p = 40.318 80 amu
Next, calculate the mass of a ^{40}Ca nucleus by subtracting the mass of 20 electrons from the mass of a ^{40}Ca atom.
Mass of ^{40}Ca = 39.962 59 amu
-Mass of 20 electrons = -(20)(5.486 x 10^{-4} amu) = -0.010 97 amu
Mass of ^{40}Ca nucleus = 39.951 62 amu
Then substract the mass of the ^{40}Ca nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (40.318 80 amu) - (39.951 62 amu) = 0.367 18 amu
Mass defect in g/mol:
(0.367 18 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.367 17 g/mol

22.66 (a) For $^{58}_{28}Ni$:
First, calculate the total mass of the nucleons (30 n + 28 p)
Mass of 30 neutrons = (30)(1.008 66 amu) = 30.259 80 amu
Mass of 28 protons = (28)(1.007 28 amu) = 28.203 84 amu
Mass of 30 n + 28 p = 58.463 64 amu
Next, calculate the mass of a ^{58}Ni nucleus by subtracting the mass of 28 electrons from the mass of a ^{58}Ni atom.
Mass of ^{58}Ni atom = 57.935 35 amu
-Mass of 28 electrons = -(28)(5.486 x 10^{-4} amu) = -0.015 36 amu
Mass of ^{58}Ni nucleus = 57.919 99 amu
Then subtract the mass of the ^{58}Ni nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (58.463 64 amu) - (57.919 99 amu) = 0.543 65 amu

Mass defect in g/mol:
(0.543 65 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.543 65 g/mol
Now, use the Einstein equation to convert the mass defect into the binding energy.
$\Delta E = \Delta mc^2$ = (0.543 65 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 4.893 x 10^{13} J/mol = 4.893 x 10^{10} kJ/mol

$$\Delta E = \frac{4.893 \times 10^{13}\ \text{J/mol}}{6.022 \times 10^{23}\ \text{nuclei/mol}} \times \frac{1\ \text{MeV}}{1.60 \times 10^{-13}\ \text{J}} \times \frac{1\ \text{nucleus}}{58\ \text{nucleons}} = 8.76\ \frac{\text{MeV}}{\text{nucleon}}$$

(b) For $^{84}_{36}\text{Kr}$:
First, calculate the total mass of the nucleons (48 n + 36 p)
Mass of 48 neutrons = (48)(1.008 66 amu) = 48.415 68 amu
Mass of 36 protons = (36)(1.007 28 amu) = 36.262 08 amu
Mass of 48 n + 36 p = 84.677 76 amu
Next, calculate the mass of a ^{84}Kr nucleus by subtracting the mass of 36 electrons from the mass of a ^{84}Kr atom.
Mass of ^{84}Kr atom = 83.911 51 amu
-Mass of 36 electrons = -(36)(5.486 x 10^{-4} amu) = -0.019 75 amu
Mass of ^{84}Kr nucleus = 83.891 76 amu
Then subtract the mass of the ^{84}Kr nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (84.677 76 amu) - (83.891 76 amu) = 0.786 00 amu
Mass defect in g/mol:
(0.786 00 amu)(1.660 54 x 10^{-24} g/mol)(6.022 x 10^{23} mol^{-1}) = 0.786 00 g/mol
Now, use the Einstein equation to convert the mass defect into the binding energy.
$\Delta E = \Delta mc^2$ = (0.786 00 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 7.074 x 10^{13} J/mol = 7.074 x 10^{10} kJ/mol

$$\Delta E = \frac{7.074 \times 10^{13}\ \text{J/mol}}{6.022 \times 10^{23}\ \text{nuclei/mol}} \times \frac{1\ \text{MeV}}{1.60 \times 10^{-13}\ \text{J}} \times \frac{1\ \text{nucleus}}{84\ \text{nucleons}} = 8.74\ \frac{\text{MeV}}{\text{nucleon}}$$

22.67 (a) For $^{63}_{29}\text{Cu}$:
First, calculate the total mass of the nucleons (34 n + 29 p)
Mass of 34 neutrons = (34)(1.008 66 amu) = 34.294 44 amu
Mass of 29 protons = (29)(1.007 28 amu) = 29.211 12 amu
Mass of 34 n + 29 p = 63.505 56 amu
Next calculate the mass of a ^{63}Cu nucleus by subtracting the mass of 29 electrons from the mass of a ^{63}Cu atom.
Mass of ^{63}Cu atom = 62.939 60 amu
-Mass of 29 electrons = -(29)(5.486 x 10^{-4}amu) = -0.015 91 amu
Mass of ^{63}Cu nucleus = 62.923 69 amu
Then subtract the mass of the ^{63}Cu nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (63.505 56 amu) - (62.923 69 amu) = 0.581 87 amu

Mass defect in g/mol:
(0.581 87 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.581 86 g/mol
Now, use the Einstein equation to convert the mass defect into the binding energy.
$\Delta E = \Delta mc^2$ = (0.581 86 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 5.237 x 10^{13} J/mol = 5.237 x 10^{10} kJ/mol

$$\Delta E = \frac{5.237 \times 10^{13} \text{ J/mol}}{6.022 \times 10^{23} \text{ nuclei/mol}} \times \frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \times \frac{1 \text{ nucleus}}{63 \text{ nucleons}} = 8.63 \frac{\text{MeV}}{\text{nucleon}}$$

(b) For $^{84}_{38}Sr$:
First, calculate the total mass of the nucleons (46 n + 38 p)
Mass of 46 neutrons = (46)(1.008 66 amu) = 46.398 36 amu
Mass of 38 protons = (38)(1.007 28 amu) = 38.276 64 amu
Mass of 46 n + 38 p = 84.675 00 amu
Next, calculate the mass of a ^{84}Sr nucleus by subtracting the mass of 38 electrons from the mass of a ^{84}Sr atom.
Mass of ^{84}Sr atom = 83.913 43 amu
-Mass of 38 electrons = -(38)(5.486 x 10^{-4} amu) = -0.020 85 amu
Mass of ^{84}Sr nucleus = 83.892 58 amu
Then subtract the mass of the ^{84}Sr nucleus from the mass of the nucleons to find the mass defect:
Mass defect = mass of nucleons - mass of nucleus
= (84.675 00 amu) - (83.892 58 amu) = 0.782 42 amu
Mass defect in g/mol:
(0.782 42 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.782 40 g/mol
Now, use the Einstein equation to convert the mass defect into the binding energy.
$\Delta E = \Delta mc^2$ = (0.782 40 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 7.042 x 10^{13} J/mol = 7.042 x 10^{10} kJ/mol

$$\Delta E = \frac{7.042 \times 10^{13} \text{ J/mol}}{6.022 \times 10^{23} \text{ nuclei/mol}} \times \frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \times \frac{1 \text{ nucleus}}{84 \text{ nucleons}} = 8.70 \frac{\text{MeV}}{\text{nucleon}}$$

22.68 $^{174}_{77}Ir \rightarrow {}^{170}_{75}Re + {}^{4}_{2}He$

mass $^{174}_{77}Ir$	173.966 66 amu
-mass $^{170}_{75}Re$	-169.958 04 amu
-mass $^{4}_{2}He$	- 4.002 60 amu
mass change	0.006 02 amu

(0.006 02 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.006 02 g/mol
$\Delta E = \Delta mc^2$ = (0.006 02 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 5.42 x 10^{11} J/mol = 5.42 x 10^8 kJ/mol

22.69 $^{28}_{12}Mg \rightarrow {}^{28}_{13}Al + {}^{0}_{-1}e$

Reactant: $^{28}_{12}$Mg nucleus = $^{28}_{12}$Mg atom - 12 e^-
Product: $^{28}_{13}$Al nucleus + e^- = ($^{28}_{13}$Al nucleus - 13 e^-) + e^- = $^{28}_{13}$Al nucleus - 12 e^-

Change : ($^{28}_{12}$Mg atom - 12 e^-) - ($^{28}_{13}$Al nucleus - 12 e^-) = $^{28}_{12}$Mg atom - $^{28}_{13}$Al atom
(electrons cancel)
Mass change = 27.983 88 amu - 27.981 91 amu = 0.001 97 amu

(0.001 97 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.001 97 g/mol
$\Delta E = \Delta mc^2$ = (0.001 97 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 1.77 x 10^{11} J/mol = 1.77 x 10^8 kJ/mol

22.70 $\Delta m = \frac{\Delta E}{c^2} = \frac{92.2 \text{ x } 10^3 \text{ J}}{(3.00 \text{ x } 10^8 \text{ m/s})^2} = \frac{92.2 \text{ x } 10^3 \text{ kg} \bullet \text{m}^2/\text{s}^2}{(3.00 \text{ x } 10^8 \text{ m/s})^2} = 1.02 \text{ x } 10^{-12} \text{ kg}$
Δm = 1.02 x 10^{-9} g

22.71 $\Delta m = \frac{\Delta E}{c^2} = \frac{131 \text{ x } 10^3 \text{ J}}{(3.00 \text{ x } 10^8 \text{ m/s})^2} = \frac{131 \text{ x } 10^3 \text{ kg} \bullet \text{m}^2/\text{s}^2}{(3.00 \text{ x } 10^8 \text{ m/s})^2} = 1.46 \text{ x } 10^{-12} \text{ kg}$
Δm = 1.46 x 10^{-9} g

22.72 Mass of positron and electron
= 2(9.109 x 10^{-31} kg)(6.022 x 10^{23} mol^{-1}) = 1.097 x 10^{-6} kg/mol
$\Delta E = \Delta mc^2$ = (1.097 x 10^{-6} kg/mol)(3.00 x 10^8 m/s)^2
ΔE = 9.87 x 10^{10} J/mol = 9.87 x 10^7 kJ/mol

22.73 2 $^2_1$H _ $^3_2$He + $^1_0$n

mass 2 $^2_1$H	2(2.0141) amu
-mass $^3_2$He	-3.0160 amu
-mass $^1_0$n	-1.008 66 amu
mass change	0.003 54 amu

(0.003 54 amu)(1.660 54 x 10^{-24} g/mol)(6.022 x 10^{23} mol^{-1}) = 0.003 54 g/mol
$\Delta E = \Delta mc^2$ = (0.003 54 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 3.2 x 10^{11} J/mol = 3.2 x 10^8 kJ/mol

Nuclear Transmutation

22.74 (a) $^{109}_{47}$Ag + $^4_2$He _ $^{113}_{49}$In (b) $^{10}_5$B + $^4_2$He _ $^{13}_7$N + $^1_0$n

22.75 (a) $^{235}_{92}U \_ ^{160}_{62}Sm + ^{72}_{30}Zn + 3\ ^{1}_{0}n$

(b) $^{235}_{92}U \_ ^{87}_{35}Br + ^{146}_{57}La + 2\ ^{1}_{0}n$

22.76 $^{209}_{83}Bi + ^{58}_{26}Fe \_ ^{266}_{109}Mt + ^{1}_{0}n$

22.77 $^{98}_{42}Mo + ^{1}_{0}n \_ ^{99}_{42}Mo$

22.78 $^{238}_{92}U + ^{12}_{6}C \_ ^{246}_{98}Cf + 4\ ^{1}_{0}n$

22.79 (a) $^{246}_{96}Cm + ^{12}_{6}C \_ ^{254}_{102}No + 4\ ^{1}_{0}n$

(b) $^{253}_{99}Es + ^{4}_{2}He \_ ^{256}_{101}Md + ^{1}_{0}n$

(c) $^{250}_{98}Cf + ^{11}_{5}B \_ ^{257}_{103}Lr + 4\ ^{1}_{0}n$

General Problems

22.80 $^{232}_{90}Th \_ ^{208}_{82}Pb + 6\ ^{4}_{2}He + 4\ ^{0}_{-1}e$

Reactant: $^{232}_{90}Th$ nucleus = $^{232}_{90}Th$ atom - 90 e^-

Product: $^{208}_{82}Pb$ nucleus + (6)($^{4}_{2}He$ nucleus) + 4 e^-

= ($^{208}_{82}Pb$ atom - 82 e^-) + (6)($^{4}_{2}He$ atom - 2 e^-) + 4 e^-

= $^{208}_{82}Pb$ atom + (6)($^{4}_{2}He$ atom) - 90 e^-

Change: ($^{232}_{90}Th$ atom - 90 e^-) - [$^{208}_{82}Pb$ atom + (6)($^{4}_{2}He$ atom) - 90 e^-]

= $^{232}_{90}Th$ atom - [$^{208}_{82}Pb$ atom + (6)($^{4}_{2}He$ atom)] (electrons cancel)

Mass change = 232.038 054 amu - [207.976 627 amu + (6)(4.002 603 amu)]

= 0.045 809 amu

(0.045 809 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.045 809 g/mol

$\Delta E = \Delta mc^2$ = (0.045 809 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2

ΔE = 4.12 x 10^{12} J/mol = 4.12 x 10^9 kJ/mol

22.81 Decay rate = kN

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.28 \times 10^9\ y} = 5.41 \times 10^{-10}\ y^{-1}$$

KCl, 74.55 amu

N = number of $^{40}K^+$ ions in a 1.00 g sample of KCl

$$N = (0.000\ 117)(1.00\ g)\left(\frac{1\ mol\ KCl}{74.55\ g}\right)\left(\frac{1\ mol\ K^+}{1\ mol\ KCl}\right)(6.022 \times 10^{23}\ mol^{-1})$$

$N = 9.45 \times 10^{17}\ ^{40}K^{+}$ ions

Decay rate = $kN = (5.41 \times 10^{-10}\ y^{-1})(9.45 \times 10^{17}) = 5.11 \times 10^{8}$/y

$$\text{Disintegration/s} = (5.11 \times 10^{8}/\text{y})\left(\frac{1\ \text{y}}{365\ \text{d}}\right)\left(\frac{1\ \text{d}}{24\ \text{h}}\right)\left(\frac{1\ \text{h}}{3600\ \text{s}}\right) = 16.2/\text{s}$$

22.82 $^{241}_{94}\text{Pu} \rightarrow {}^{233}_{92}\text{U} + 2\ {}^{4}_{2}\text{He} + 2\ {}^{0}_{-1}\text{e}$

Reactant: $^{241}_{94}\text{Pu}$ nucleus = $^{241}_{94}\text{Pu}$ atom - 94 e^-

Product: $^{233}_{92}\text{U}$ nucleus + (2)($^{4}_{2}\text{He}$ nucleus) + 2 e^-

= ($^{233}_{92}\text{U}$ atom - 92 e^-) + (2)($^{4}_{2}\text{He}$ atom - 2 e^-) + 2 e^-

= $^{233}_{92}\text{U}$ atom + (2)($^{4}_{2}\text{He}$ atom) - 94 e^-

Change: ($^{241}_{94}\text{Pu}$ atom - 94 e^-) - [$^{233}_{92}\text{U}$ atom + (2)($^{4}_{2}\text{He}$ atom) - 94 e^-]

= $^{241}_{94}\text{Pu}$ atom - [$^{233}_{92}\text{U}$ atom + (2)($^{4}_{2}\text{He}$ atom)]

Mass change = 241.056 845 amu - [233.039 628 amu + (2)(4.002 603 amu)]

= 0.012 011 amu

$(0.012\ 011\ \text{amu})(1.660\ 54 \times 10^{-24}\ \text{g/amu})(6.022 \times 10^{23}\ \text{mol}^{-1}) = 0.012\ 011$ g/mol

$\Delta E = \Delta mc^2 = (0.012\ 011\ \text{g/mol})(10^{-3}\ \text{kg/g})(3.00 \times 10^{8}\ \text{m/s})^2$

$\Delta E = 1.08 \times 10^{12}$ J/mol = 1.08×10^{9} kJ/mol

22.83 $^{293}_{118}\text{X}$, $^{289}_{116}\text{Y}$, and $^{285}_{114}\text{Z}$

22.84 $$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$$

$$\ln\left(\frac{100 - 99.99}{100}\right) = (-0.693)(\text{tover1.53 s}); \quad t = 20.3\ \text{s}$$

22.85 $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.063\ \text{s}^{-1}} = 11\ \text{s}$$

$$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$$

$$\ln\left(\frac{100 - 99.99}{100}\right) = (-0.693)\left(\frac{t}{11\ \text{s}}\right); \qquad t = 150\ \text{s}$$

22.86 (a) For $^{50}_{24}\text{Cr}$:

First, calculate the total mass of the nucleons (26 n + 24 p)

Mass of 26 neutrons = (26)(1.008 66 amu) = 26.225 16 amu

Mass of 24 protons = (24)(1.007 28 amu) = 24.174 72 amu

Mass of 26 n + 24 p = 50.399 88 amu

Next, calculate the mass of a ^{50}Cr nucleus by subtracting the mass of 24 electrons from

the mass of a ^{50}Cr atom.

Mass of ^{50}Cr atom	= 49.946 05 amu
-Mass of 24 electrons = -(24)(5.486 x 10^{-4} amu)	= -0.013 17 amu
Mass of ^{50}Cr nucleus	= 49.932 88 amu

Then subtract the mass of the ^{50}Cr nucleus from the mass of the nucleons to find the mass defect:

Mass defect = mass of nucleons - mass of nucleus

= (50.399 88 amu) - (49.932 88 amu) = 0.467 00 amu

Mass defect in g/mol:

(0.467 00 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.467 00 g/mol

Now, use the Einstein equation to convert the mass defect into the binding energy.

$\Delta E = \Delta mc^2 = (0.467\ 00\ g/mol)(10^{-3}\ kg/g)(3.00 \times 10^8\ m/s)^2$

$\Delta E = 4.203 \times 10^{13}\ J/mol = 4.203 \times 10^{10}\ kJ/mol$

$$\Delta E = \frac{4.203 \times 10^{13}\ J/mol}{6.022 \times 10^{23}\ nuclei/mol} \times \frac{1\ MeV}{1.60 \times 10^{-13}\ J} \times \frac{1\ nucleus}{50\ nucleons} = 8.72\ \frac{MeV}{nucleon}$$

(b) For $^{64}_{30}Zn$:

First, calculate the total mass of the nucleons (34 n + 30 p)

Mass of 34 neutrons = (34)(1.008 66 amu) = 34.294 44 amu

Mass of 30 protons = (30)(1.007 28 amu) = 30.218 40 amu

Mass of 34 n + 30 p = 64.512 84 amu

Next, calculate the mass of a ^{64}Zn nucleus by subtracting the mass of 30 electrons from the mass of a ^{64}Zn atom.

Mass of ^{64}Zn atom	= 63.929 15 amu
-Mass of 30 electrons = -(30)(5.486 x 10^{-4} amu)	= -0.016 46 amu
Mass of ^{64}Zn nucleus	= 63.912 69 amu

Then subtract the mass of the ^{64}Zn nucleus from the mass of the nucleons to find the mass defect:

Mass defect = mass of nucleons - mass of nucleus

= (64.512 84 amu) - (63.912 69 amu) = 0.600 15 amu

Mass defect in g/mol:

(0.600 15 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.600 15 g/mol

Now, use the Einstein equation to convert the mass defect into the binding energy.

$\Delta E = \Delta mc^2 = (0.600\ 15\ g/mol)(10^{-3}\ kg/g)(3.00 \times 10^8\ m/s)^2$

$\Delta E = 5.401 \times 10^{13}\ J/mol = 5.401 \times 10^{10}\ kJ/mol$

$$\Delta E = \frac{5.401 \times 10^{13}\ J/mol}{6.022 \times 10^{23}\ nuclei/mol} \times \frac{1\ MeV}{1.60 \times 10^{-13}\ J} \times \frac{1\ nucleus}{64\ nucleons} = 8.76\ \frac{MeV}{nucleon}$$

The ^{64}Zn is more stable.

22.87 $\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right)$; $\frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$

$\ln\left(\frac{2.9}{15.3}\right) = (-0.693)\left(\frac{t}{5730\ y}\right)$; $t = 1.38 \times 10^4$ y

22.88 ${}^{2}_{1}H + {}^{3}_{2}He \rightarrow {}^{4}_{2}He + {}^{1}_{1}H$

mass ${}^{2}_{1}H$	2.0141 amu
mass ${}^{3}_{2}He$	3.0160 amu
-mass ${}^{4}_{2}He$	- 4.0026 amu
-mass ${}^{1}_{1}H$	-1.0078 amu
mass change	0.0197 amu

(0.0197 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.0197 g/mol

$\Delta E = \Delta mc^2$ = (0.0197 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2

$\Delta E = 1.77 \times 10^{12}$ J/mol = 1.77×10^9 kJ/mol

22.89 $t_{1/2} = 1.1 \times 10^{20}$ y = (1.1×10^{20} y)(365 d/y) = 4.0×10^{22} d

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.0 \times 10^{22}\ d} = 1.7 \times 10^{-23}\ d^{-1}$

N = 6.02×10^{23} atoms

Decay rate = kN = (1.7×10^{-23} d^{-1})(6.02×10^{23} atoms) = 10/d

There are 10 disintegrations per day.

22.90 ${}^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{94}Pu + 2\ {}^{0}_{-1}e$

22.91 3.9×10^{23} kJ = 3.9×10^{26} J = 3.9×10^{26} kg · m^2/s^2

$\Delta E = \Delta mc^2$; $\Delta m = \frac{\Delta E}{c^2} = \frac{3.9 \times 10^{26}\ kg \bullet m^2/s^2}{(3.00 \times 10^8\ m/s)^2} = 4.3 \times 10^9$ kg

The sun loses mass at a rate of 4.3×10^9 kg/s.

22.92 ${}^{10}B + {}^{1}n \rightarrow {}^{4}He + {}^{7}Li + \gamma$

mass ${}^{10}B$	10.012 937 amu
mass ${}^{1}n$	1.008 665 amu
-mass ${}^{4}He$	- 4.002 603 amu
-mass ${}^{7}Li$	-7.016 004 amu
mass change	0.002 995 amu

(0.002 995 amu)(1.660 54 x 10^{-24} g/amu) = 4.973×10^{-27} g

$\Delta E = \Delta mc^2$ = (4.973×10^{-27} g)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2 = 4.476×10^{-13} J

Kinetic energy = 2.31 MeV x $\frac{1.60 \text{ x } 10^{-13} \text{ J}}{1 \text{ MeV}}$ = 3.696 x 10^{-13} J

γ photon energy = ΔE - KE = 4.476 x 10^{-13} J - 3.696 x 10^{-13} J = 7.80 x 10^{-14} J

22.93 Each alpha emission decreases the mass number by four and the atomic number by two. Each beta emission increases the atomic number by one.

$^{237}_{93}Np$ _ $^{209}_{83}Bi$

Number of α emissions = $\frac{\text{Np mass number \_ Bi mass number}}{4}$

$= \frac{237 \_ 209}{4}$ = 7 α emissions

The atomic number decreases by 14 as a result of 7 alpha emissions. The resulting atomic number is (93 - 14) = 79.

Number of β emissions = Bi atomic number - 79 = 83 - 79 = 4 β emissions

22.94 (a) $^{100}_{43}Tc$ _ $^{0}_{1}e$ + $^{100}_{42}Mo$ (positron emission)

$^{100}_{43}Tc$ + $^{0}_{-1}e$ _ $^{100}_{42}Mo$ (electron capture)

(b) Positron emission

Reactant: $^{100}_{43}Tc$ nucleus = $^{100}_{43}Tc$ atom - 43 e^-

Product: $^{100}_{42}Mo$ nucleus + e^+ = $^{100}_{42}Mo$ atom - 42 e^- + 1 e^+

Change: ($^{100}_{43}Tc$ atom - 43 e^-) - ($^{100}_{42}Mo$ atom - 42 e^- + 1 e^+)

= $^{100}_{43}Tc$ atom - $^{100}_{42}Mo$ atom - 2 e^-

Mass change = 99.907 657 amu - 99.907 48 amu - (2)(0.000 5486 amu)

= -0.000 92 amu

(-0.000 92 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = -0.000 92 g/mol

$\Delta E = \Delta mc^2$ = (-0.000 92 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2

ΔE = -8.3 x 10^{10} J/mol = -8.3 x 10^7 kJ/mol

Electron Capture

Reactant: $^{100}_{43}Tc$ nucleus + e^- = $^{100}_{43}Tc$ atom - 42 e^-

Product: $^{100}_{42}Mo$ nucleus = $^{100}_{42}Mo$ atom - 42 e^-

Change: ($^{100}_{43}Tc$ atom - 42 e^-) - ($^{100}_{42}Mo$ atom - 42 e^-)

= $^{100}_{43}Tc$ atom - $^{100}_{42}Mo$ atom (electrons cancel)

Mass change = 99.907 657 amu - 99.907 48 amu = 0.000 177 amu

(0.000 177 amu)(1.660 54 x 10^{-24} g/amu)(6.022 x 10^{23} mol^{-1}) = 0.000 177 g/mol
$\Delta E = \Delta mc^2$ = (0.000 177 g/mol)(10^{-3} kg/g)(3.00 x 10^8 m/s)^2
ΔE = 1.6 x 10^{10} J/mol = 1.6 x 10^7 kJ/mol

Only electron capture is observed because there is a mass decrease and a release of energy.

22.95 (a) α emission: $^{226}_{89}Ac \rightarrow {}^{222}_{87}Fr + {}^{4}_{2}He$

β emission: $^{226}_{89}Ac \rightarrow {}^{226}_{90}Th + {}^{0}_{-1}e$

electron capture: $^{226}_{89}Ac + {}^{0}_{-1}e \rightarrow {}^{226}_{88}Ra$

(b) $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{0.556\ d^{-1}} = 1.25\ d$

If 80% reacts, then 20% is left.

$$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \quad \ln\left(\frac{20}{100}\right) = (-0.693)\left(\frac{t}{1.25\ d}\right)$$

$$t = \frac{\ln\left(\frac{20}{100}\right)(1.25\ d)}{(-0.693)} = 2.90\ d$$

Multi-Concept Problems

22.96 $BaCO_3$, 197.34 amu

$$1.000\ g\ BaCO_3 \times \frac{1\ mol\ BaCO_3}{197.34\ g\ BaCO_3} \times \frac{1\ mol\ C}{1\ mol\ BaCO_3} \times \frac{12.011\ g\ C}{1\ mol\ C} = 0.060\ 86\ g\ C$$

4.0 x 10^{-3} Bq = 4.0 x 10^{-3} disintegrations/s
(4.0 x 10^{-3} Bq = 4.0 x 10^{-3} disintegrations/s)(60 s/min) = 0.24 disintegrations/min

$$\text{sample radioactivity} = \frac{0.24\ \text{disintegrations/min}}{0.060\ 86\ g\ C} = 3.94\ \text{disintegrations/min per gram of C}$$

$$\ln\left(\frac{N}{N_0}\right) = (-0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t = 0}}$$

$$\ln\left(\frac{3.94}{15.3}\right) = (-0.693)\left(\frac{t}{5730\ y}\right); \qquad t = 11{,}000\ y$$

22.97 $t_{1/2}$ = 138 d = 138 d x $\dfrac{1\ y}{365\ d}$ = 0.378 y

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{0.378\ y} = 1.83\ y^{-1}$$

$$0.700 \text{ mg} \times \frac{1 \times 10^{-3} \text{ g}}{1 \text{ mg}} = 7.00 \times 10^{-4} \text{ g}$$

$$N_o = (7.00 \times 10^{-4} \text{ g})\left(\frac{1 \text{ mol Po}}{210 \text{ g Po}}\right)(6.022 \times 10^{23} \text{ atoms/mol}) = 2.01 \times 10^{18} \text{ atoms}$$

$$\ln\left(\frac{N}{N_o}\right) = -kt = -(1.83 \text{ y}^{-1})(1 \text{ y}) = -1.83; \qquad \frac{N}{N_o} = e^{-1.83} = 0.160$$

$N = 0.160\ N_o = (0.160)(2.01 \times 10^{18} \text{ atoms}) = 0.322 \times 10^{18} \text{ atoms}$

atoms He = atoms Po decayed

atoms He = 2.01×10^{18} atoms - 0.322×10^{18} atoms = 1.688×10^{18} atoms

$$\text{mol He} = \frac{1.688 \times 10^{18} \text{ He atoms}}{6.022 \times 10^{23} \text{ atoms/mol}} = 2.80 \times 10^{-6} \text{ mol He}$$

$20^oC = 293$ K

$$P = \frac{nRT}{V} = \frac{(2.80 \times 10^{-6} \text{ mol})\left(0.082\,06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(293 \text{ K})}{0.2500 \text{ L}} = 2.69 \times 10^{-4} \text{ atm}$$

$$P = 2.69 \times 10^{-4} \text{ atm} \times \frac{760 \text{ mm Hg}}{1.00 \text{ atm}} = 2.05 \text{ mm Hg}$$

22.98 First find the activity of the ^{51}Cr after 17.0 days.

$$\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t} = 0}$$

$$\ln\left(\frac{N}{4.10}\right) = (\_\ 0.693)\left(\frac{17.0 \text{ d}}{27.7 \text{ d}}\right)$$

$\ln N - \ln(4.10) = -0.4253$

$\ln N = -0.4253 + \ln(4.10) = 0.9857$

$N = e^{0.9857} = 2.68\ \mu\text{Ci/mL}$

(20.0 mL)(2.68 μCi/mL) = (total blood volume)(0.009 35 μCi/mL)

total blood volume = 5732 mL = 5.73 L

22.99 First find the activity (N) that the ^{28}Mg would have after 2.4 hours assuming that none of it was removed by precipitation as $MgCO_3$.

$$\ln\left(\frac{N}{N_0}\right) = (\_\ 0.693)\left(\frac{t}{t_{1/2}}\right); \qquad \frac{N}{N_0} = \frac{\text{Decay rate at time t}}{\text{Decay rate at time t} = 0}$$

$$\ln\left(\frac{N}{0.112}\right) = (\_\ 0.693)\left(\frac{2.40 \text{ h}}{20.91 \text{ h}}\right)$$

$\ln N - \ln(0.112) = -0.0795$

ln N = - 0.0795 + ln(0.112) = -2.27
$N = e^{-2.27} = 0.103$ μCi/mL

20.00 mL = 0.020 00 L and 15.00 mL = 0.015 00 L
mol $MgCl_2$ = (0.007 50 mol/L)(0.020 00 L) = 1.50×10^{-4} mol $MgCl_2$
mol Na_2CO_3 = (0.012 50 mol/L)(0.015 00 L) = 1.87×10^{-4} mol Na_2CO_3
The mol of CO_3^{2-} are in excess, so assume that all of the Mg^{2+} precipitates as $MgCO_3$ according to the reaction:

	$Mg^{2+}(aq)$	+	$CO_3^{2-}(aq)$	→	$MgCO_3(s)$
initial (mol)	0.000 150		0.000 187		0
change (mol)	- 0.000 150		- 0.000 150		+ 0.000 150
final (mol)	0		0.000 037		0.000 150

$[CO_3^{2-}]$ = 0.000 037 mol/(0.020 00 L + 0.015 00 L) = 0.001 06 M

Now consider the dissolution of $MgCO_3$ in the presence of CO_3^{2-}.

	$MgCO_3(s)$	_	$Mg^{2+}(aq)$	+	$CO_3^{2-}(aq)$
initial (M)			0		0.001 06
change (M)			+x		+x
equil (M)			x		0.001 06 + x

The $[Mg^{2+}]$ in the filtrate is proportional to its activity after 2.40 h.

$$x = [Mg^{2+}] = 0.029\ \mu\text{Ci/mL} \times \frac{0.007\ 50\ \text{M}}{0.103\ \mu\text{Ci/mL}} = 0.002\ 11\ \text{M}$$

$[CO_3^{2-}]$ = 0.001 06 + x = 0.001 06 + 0.002 11 = 0.003 17 M
$K_{sp} = [Mg^{2+}][CO_3^{2-}] = (0.002\ 11)(0.003\ 17) = 6.7 \times 10^{-6}$

23 Organic Chemistry

23.1

23.2

23.3

23.4 C_7H_{16}

23.5 Structures (a) and (c) are identical. They both contain a chain of six carbons with two –CH_3 branches at the fourth carbon and one –CH_3 branch at the second carbon. Structure (b) is different, having a chain of seven carbons.

23.6 The two structures are identical. The compound is

23.7 (a) pentane

2-methylbutane

2,2-dimethylpropane

(b) 3,4-dimethylhexane
(c) 2,4-dimethylpentane
(d) 2,2,5-trimethylheptane

23.8 (a) (b)

(c) (d)

23.9 2,3-dimethylhexane

23.10 (a) 1,4-dimethylcyclohexane (b) 1-ethyl-3-methylcyclopentane
(c) isopropylcyclobutane

23.11 (a) (b) (c)

23.12

23.13 (a) (b)

23.14 (a) (b)

23.15 (a) 3-methyl-1-butene (b) 4-methyl-3-heptene (c) 3-ethyl-1-hexyne

23.16 (a) (b)

(c)

23.17 (a) (b) (c)

23.18

23.19

23.20 (a) (b) (c)

23.21 (a) (b) (c)

23.22

23.23 (a) (b)

23.24 (a) (b)

(c)

23.25 (a) (b)

23.26

23.27 (a) (b)

23.28

Understanding Key Concepts

23.29

23.30 (a) (b)

23.31 (a) (b)

23.32 (a) alkene, ketone, ether (b) alkene, amine, carboxylic acid

23.33 (a) 2,3-dimethylpentane (b) 2-methyl-2-hexene

23.34

23.35

23.36 There are many possibilities. Here are two:

23.37

Additional Problems
Functional Groups and Isomers

23.38 A functional group is a part of a larger molecule and is composed of an atom or group of atoms that has a characteristic chemical behavior. They are important because their chemistry controls the chemistry in molecules that contain them.

23.39 (a) (b) (c) (d)

23.40 (a) (b) (c)

23.41 (a) (b) (c) (d)

23.42

23.43 (a)

(b)

(c)
(d)

23.44 (a) alkene and aldehyde (b) aromatic ring, alcohol, and ketone

23.45 ester, aromatic ring, and amine

Alkanes

23.46 In a straight-chain alkane, all the carbons are connected in a row. In a branched-chain alkane, there are branching connections of carbons along the carbon chain.

23.47 An alkane is a compound that contains only carbon and hydrogen and has only single bonds. An alkyl group is the part of an alkane that remains when a hydrogen is removed.

23.48 In forming alkanes, carbon uses sp^3 hybrid orbitals.

23.49 Because each carbon is bonded to its maximum number of atoms and cannot bond to additional atoms, an alkane is said to be saturated.

23.50 C_3H_9 contains one more H than needed for an alkane.

23.51 (a) Underlined carbon has five bonds.

(b) Underlined carbon has five bonds.

(c) Underlined carbon has six bonds.

23.52 (a) 4-ethyl-3-methyloctane (b) 4-isopropyl-2-methylheptane
(c) 2,2,6-trimethylheptane (d) 4-ethyl-4-methyloctane

23.53 2,2,4-trimethylpentane

23.54 (a) (b)

(c) (d)

23.55 (a) (b) (c) (d)

23.56 (a) 1,1-dimethylcyclopentane (b) 1-isopropyl-2-methylcyclohexane
(c) 1,2,4-trimethylcyclooctane

23.57 (a) The longest chain contains six carbons and the molecule should be named from a hexane root; the correct name is 3,3-dimethylhexane.
(b) The longest chain contains seven carbons and the molecule should be named from a heptane root; the correct name is 3,5-dimethylheptane.
(c) The ring is a cycloheptane ring and the methyl groups are in the 1 and 3 position; the correct name is 1,3-dimethylcycloheptane.

23.58 The structures are shown in Problem 23.2.
hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane

23.59

heptane 2-methylhexane

3-methyhexane 2,2-dimethylpentane

3,3-dimethylpentane 2,3-dimethylpentane 2,4-dimethypentane

2,2,3-trimethylbutane 3-ethylpentane

23.60

(a)

(b)

(c)

23.61 Reaction (a) is likely to have a higher yield because there is only one possible monochlorinated substitution product. Reaction (b) has four possible monochlorinated substitution products, which would result in a lower yield of the one product shown.

Alkenes, Alkynes, and Aromatic Compounds

23.62 (a) sp^2 (b) sp (c) sp^2

23.63 Alkenes, alkynes, and aromatic compounds are said to be unsaturated because they do not contain as many hydrogens as their alkane analogs.

23.64 Today the term "aromatic" refers to the class of compounds containing a six-membered ring with three double bonds, not to the fragrance of a compound.

23.65 An addition reaction is the reaction of an XY molecule with an alkene or alkyne.

23.66 (a) (b) (c)

23.67

23.68 (a) 4-methyl-2-pentene (b) 3-methyl-1-pentene
(c) 1,2-dichlorobenzene, or o-dichlorobenzene
(d) 2-methyl-2-butene (e) 7-methyl-3-octyne

23.69 (a) (b) (c)

23.70

1-pentene 2-pentene

2-methyl-1-butene

Only 2-pentene can exist as cis-trans isomers.

2-methyl-2-butene 3-methyl-1-butene

23.71

1-pentyne 2-pentyne

3-methyl-1-butyne

23.72 (a) $CH_2=CHCH_2CH_2CH_2CH_3$ This compound cannot form cis-trans isomers.
(b) $CH_3CH=CHCH_2CH_2CH_3$ This compound can form cis-trans isomers because of the different groups on each double bond C.
(c) $CH_3CH_2CH=CHCH_2CH_3$ This compound can form cis-trans isomers because

of the different groups on each double bond C.

23.73 (a)
This compound can form cis-trans isomers because of the different groups on each double bond C.

(b) This compound cannot form cis-trans isomers.

(c)
This compound can form cis-trans isomers because of the different groups on each double bond C.

23.74 (a) (b)

(c)

23.75 (a)
5-methyl-2-hexene

(b)
2,2-dimethyl-3-hexyne

(c)
2-methyl-1-hexene

(d)
1,3-diethylbenzene

23.76 Cis-trans isomers are possible for substituted alkenes because of the lack of rotation about the carbon-carbon double bond. Alkanes and alkynes cannot form cis-trans isomers because alkanes have free rotation about carbon-carbon single bonds and alkynes are linear about the carbon-carbon triple bond.

23.77 Small-ring cycloalkenes don't exist as cis-trans isomers because the trans isomer could not close the carbon-carbon chain back on itself to form a ring.

23.78 (a)

(b)

(c)

23.79 (a)

(b)

(c)

23.80 (a)

(b)

(c)

(d)

23.81

cyclohexane

Alcohols, Amines, and Carbonyl Compounds

23.82 (a) (b)

(c) (d)

23.83 (a) $CH_3CH_2CH_2NH_2$ (b) $(CH_3CH_2)_2NH$ (c) $CH_3CH_2CH_2NHCH_3$

23.84 Quinine, a base will dissolve in aqueous acid, but menthol is insoluble.

23.85 Pentanoic acid will react with aqueous $NaHCO_3$ to yield CO_2, but methyl butanoate will not.

23.86 An aldehyde has a terminal carbonyl group. A ketone has the carbonyl group located between two carbon atoms.

23.87 In aldehydes and ketones, the carbonyl-group carbon is bonded to atoms (H and C) that don't attract electrons strongly. In carboxylic acids, esters, and amides, the carbonyl-group carbon is bonded to an atom (O or N) that does attract electrons strongly.

23.88 The industrial preparation of ketones and aldehydes involves the oxidation of the related alcohol.

23.89 Carboxylic acids, esters, and amides undergo carbonyl-group substitution reactions, in which a group –Y substitutes for the –OH, –OC, or –N group of the starting material.

23.90 (a) ketone (b) aldehyde (c) ketone (d) amide (e) ester

23.91 (a)

N,N-dimethylpropanamide pentanamide

N-methylbutanamide

(b)

methyl pentanoate ethyl butanoate

propyl propanoate

23.92

	$C_6H_5CO_2H(aq)$	+ $H_2O(l)$	⎯	$H_3O^+(aq)$	+ $C_6H_5CO_2^-(aq)$
initial (M)	1.0			~0	0
change (M)	-x			+x	+x
equil (M)	1.0 - x			x	x

$$K_a = \frac{[H_3O^+][C_6H_5CO_2^-]}{[C_6H_5CO_2H]} = 6.5 \times 10^{-5} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$x = [H_3O^+] = [C_6H_5CO_2H]_{diss} = 0.0081$ M

$$\% \text{ dissociation} = \frac{[C_6H_5CO_2H]_{diss}}{[C_6H_5CO_2H]_{initial}} \times 100\% = \frac{0.0081 \text{ M}}{1.0 \text{ M}} \times 100\% = 0.81\%$$

23.93 (a) (b) (c)

23.94 (a) methyl 4-methylpentanoate (b) 4,4-dimethylpentanoic acid
(c) 2-methylpentanamide

23.95 (a) N,N-dimethyl-4-methylhexanamide (b) isopropyl 2-methylpropanoate
(c) N-ethyl-p-chlorobenzamide

23.96 (a) (b)

(c)

23.97 (a) (b)

(c)

23.98 (a)

(b)

(c)

23.99 (a)

(b)

(c)

23.100 amine, aromatic ring, and ester

carboxylic acid alcohol

23.101

Polymers

23.102 Polymers are large molecules formed by the repetitive bonding together of many smaller molecules, called monomers.

23.103 Polyethylene results from the polymerization of a simple alkene by an addition reaction to the double bond. Nylon results from the sequential reaction of two difunctional molecules.

23.104

23.105 (a)

(b)

23.106 (a) (b) (c)

23.107

23.108

23.109

General Problems

23.110 (a) (b)

(c) (d)

(e) (f)

23.111 (a) 2,3-dimethylhexane (b) 4-isopropyloctane
(c) 4-ethyl-2,4-dimethylhexane (d) 3,3-diethylpentane

23.112 Cyclohexene will react with Br_2 and decolorize it. Cyclohexane will not react.

23.113 Cyclohexene will react with Br_2 and decolorize it. Benzene will not react with Br_2 without a catalyst.

23.114 (a) (b) (c)

23.115

Multi-Concept Problems

23.116 (a) Calculate the empirical formula. Assume a 100.0 g sample of fumaric acid.

$$41.4 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.45 \text{ mol C}; \qquad 3.5 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 3.47 \text{ mol H}$$

$$55.1 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.44 \text{ mol O}$$

Because the mol amounts for the three elements are essentially the same, the empirical formula is CHO (29 amu).

(b) Calculate the molar mass from the osmotic pressure.

$$\Pi = MRT; \quad M = \frac{\Pi}{RT} = \frac{\left(240.3 \text{ mm Hg} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}}\right)}{\left(0.082\ 06 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}}\right)(298 \text{ K})} = 0.0129 \text{ M}$$

$(0.1000 \text{ L})(0.0129 \text{ mol/L}) = 1.29 \times 10^{-3}$ mol fumaric acid

fumaric acid molar mass = $\frac{0.1500\ \text{g}}{1.29\ \text{x}\ 10^{-3}\ \text{mol}} = 116\ \text{g/mol}$

molecular mass = 116 amu

(c) Determine the molecular formula. $\frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{116}{29} = 4$

molecular formula = $C_{(1 \times 4)}H_{(1 \times 4)}O_{(1 \times 4)} = C_4H_4O_4$

From the titration, the number of carboxylic acid groups can be determined.

mol $C_4H_4O_4$ = 0.573 g x $\frac{1\ \text{mol}\ C_4H_4O_4}{116\ \text{g}}$ = 0.004 94 mol $C_4H_4O_4$

mol NaOH used = (0.0941 L)(0.105 mol/L) = 0.0099 mol NaOH

$\frac{\text{mol NaOH}}{\text{mol}\ C_4H_4O_4} = \frac{0.0099\ \text{mol}}{0.004\ 94\ \text{mol}} = 2$

Because 2 mol of NaOH are required to titrate 1 mol $C_4H_4O_4$, $C_4H_4O_4$ is a diprotic acid. Because $C_4H_4O_4$ gives an addition product with HCl and a reduction product with H_2, it contains a double bond.

(d) The correct structure is

23.117 (a) CO_2, 44.01 amu; H_2O, 18.02 amu

mol CO_2 = 0.1213 g CO_2 x $\frac{1\ \text{mol}\ CO_2}{44.01\ \text{g}\ CO_2}$ = 0.00276 mol CO_2

mol H_2O = 0.0661 g H_2O x $\frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O}$ = 0.00367 mol H_2O

mass C = 0.00276 mol CO_2 x $\frac{1\ \text{mol C}}{1\ \text{mol}\ CO_2}$ x $\frac{12.011\ \text{g C}}{1\ \text{mol C}}$ = 0.0332 g C

mass H = 0.00367 mol H_2O x $\frac{2\ \text{mol H}}{1\ \text{mol}\ H_2O}$ x $\frac{1.008\ \text{g H}}{1\ \text{mol H}}$ = 0.00740 g H

mass O = 0.0552 g sample - 0.0332 g C - 0.00740 g H = 0.0146 g O

mol C = 0.00276 mol CO_2 x $\frac{1\ \text{mol C}}{1\ \text{mol}\ CO_2}$ = 0.00276 mol C

mol H = 0.00367 mol H_2O x $\frac{2 \text{ mol H}}{1 \text{ mol } H_2O}$ = 0.00734 mol H

mol O = 0.0146 g O x $\frac{1 \text{ mol O}}{16.00 \text{ g O}}$ = 0.000913 mol O

$C_{0.00276}\ H_{0.00734}\ O_{0.000913}$ (divide each subscript by the smallest)

$C_{0.00276\ /\ 0.000913}\ H_{0.00734\ /\ 0.000913}\ O_{0.000913\ /\ 0.000913}$

$C_{3.023}\ H_{8.039}\ O$

C_3H_8O

$2\ C_3H_8O(l) + 9\ O_2(g) \rightarrow 6\ CO_2(g) + 8\ H_2O(l)$

(b) C_3H_8O is a molecular formula because a multiple such as $C_6H_{16}O_2$ is not possible.

(c)

(d) Acetone is . The most likely structure for C_3H_8O is .

(e) C_3H_8O, 60.10 amu

mol C_3H_8O = 5.000 g C_3H_8O x $\frac{1 \text{ mol } C_3H_8O}{60.10 \text{ g } C_3H_8O}$ = 0.08320 mol C_3H_8O

$\Delta H^o_{combustion} = \frac{-166.9 \text{ kJ}}{0.08320 \text{ mol}}$ = -2006 kJ/mol = -2006 kJ

$C_3H_8O(l) + 9/2\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

$\Delta H^o_{combustion} = [\ 3\ \Delta H^o_f(CO_2) + 4\ \Delta H^o_f(H_2O)] - \Delta H^o_f(C_3H_8O)$

$\Delta H^o_f(C_3H_8O) = [\ 3\ \Delta H^o_f(CO_2) + 4\ \Delta H^o_f(H_2O)] - \Delta H^o_{combustion}$

= [(3 mol)(-393.5 kJ/mol) + (4 mol)(-285.8 kJ/mol)] - (-2006 kJ)

= -317.7 kJ

ΔH^o_f = -317.7 kJ/mol

23.118 (a) propanamide

(b)

(c)

(d) An observed trigonal planar N does not agree with the VSEPR prediction. The second resonance structure is consistent with a trigonal planar N.

