Chem1 Problems

Calculations involving units; density 1

1-1 **Extraction of gold from seawater**
The ocean contains about 4×10^{-6} mg of gold per litre.

a) Express the concentration of gold in seawater in *parts per million* (by weight); assume that the density of seawater is 1.0 g/ml.

b) What mass of gold would be contained in one cubic kilometre of seawater?

1-2 **Density-volume relation** Ordinary commercial nitric acid is a liquid having a density of 1.42 g/ml, and containing 69.8% HNO_3 by weight.

a) Calculate the mass of HNO_3 contained in 800 ml of nitric acid.

b) What volume of acid will contain 100 g of HNO_3?

1-3 **Buoyancy and displacement** A 1.00-cm cube of wood whose density is 0.85 g/ml is floating in a container of water. To what depth will the cube be submerged?

1-4 **Density and buoyancy** A piece of metal weighs 9.25 g in air, 8.20 g in water, and 8.36 g when immersed in gasoline. What is the density of the metal? What is the density of the gasoline?

1-5 **Heat of reaction** A flask contains 100 g of water at 18.0 °C, together with a small amount of dissolved hydrochloric acid (HCl). Into this flask was poured 100 g of water, also at 18.0 °C, containing a small amount of sodium hydroxide. The temperature of the mixed solution increased to 24.5 °C. Neglecting the effect of the substances dissolved in the water and the loss of heat to the container, calculate the energy (in joules) released by the reaction of HCl with NaOH.

1-6 **Specific heat of zinc** A piece of zinc weighing 2.40 g is heated to 200 °C, and is then dropped into 10.0 ml of water at 15.0 °C. The temperature of the zinc falls and that of the water rises until thermal equilibrium is reached and both are at 18.0 °C. What is the specific heat capacity of zinc metal?

Data: density of water = 1.00 $\mathrm{g\,ml^{-1}}$; 1 ml = 1 cc;
specific heat capacity of water = 4.184 $\mathrm{J\,g^{-1}\,K^{-1}}$.

Basic atomic theory 2

I. Atoms, moles, and equations.

2-1 Weight of an atom, atomic weight, and the mole
The atomic weight of calcium is 40.08.

a) Calculate the mass, in kg, of a single atom of Ca.

b) Calculate the number of moles in 10^{12} atoms of Ca, and in one atom of Ca.

c) How many moles of Ca are there in 10.0 g of calcium metal?

2-2 Average atomic weight of an isotopic mixture The three stable isotopes of neon are found in nature in the following ratios: $^{20}Ne/^{21}Ne = 350$; $^{22}Ne/^{21}Ne = 34.0$. Use this information to determine the atomic weight of natural neon.

2-3 Atomic weight from mass spectrum The mass spectrum of Cl_2 shows peaks at masses 70, 72, and 74, with heights in the ratio of 9 to 6 to 1. Explain these observations; how many isotopes of chlorine are observed here, and what are their mass numbers?

2-4 Balancing equations Balance the following equations:

a) $NiS + O_2 \longrightarrow NiO + SO_2$

b) $HBrO_3 + HBr \longrightarrow Br_2 + H_2O$

c) $Al + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + H_2$

d) $Ba_3N_2 + H_2O \longrightarrow Ba(OH)_2 + NH_3$

e) $C_2H_2 + O_2 \longrightarrow CO_2 + H_2O$

II. Quantum theory of the atom

2-5 **Photoelectric effect** When light of 400 nm wavelength strikes the surface of calcium metal, electrons having a kinetic energy of 6.3E-20 J are emitted. Calculate the binding energy of the electrons in calcium, and the minimum frequency of light required to elicit this photoelectric effect.

2-6 **Smog formation** The first step in the formation of photochemical smog is the photodissociation of nitrogen dioxide into reactive intermediates: $NO_2 + h\nu \longrightarrow NO + O$ This reaction requires light of wavelength shorter than 430 nm. Use this information to estimate the energy, in kJ/mol, of the bond between the nitrogen and oxygen atom in O-N-O.

2-7 **Particle wavelength** Calculate the De Broglie wavelength of *a*) an electron moving at 100 km/sec; *b*) a 10-g hummingbird moving at 100 cm/sec.

2-8 **Emission spectrum of hydrogen** A well-known feature of the hydrogen emission spectrum is the Balmer line that arises from the transition between states $n_2 = 3$ and $n_1 = 2$. Calculate the frequency of this spectral line, and find the energy difference between these two states in kJ/mol.

velocity of light	$c = 3.00\text{E}8\ m\ s^{-1}$
Planck's constant	$h = 6.626\text{E-}34$ J s
electron rest mass	$m_e = 9.11\text{E-}31$ kg
electron-volt	1 ev = 1.602E-19 J
joule	1 J = 1 kg $\text{m}^{-2}\,\text{s}^{-2}$
Rydberg constant	$\mathcal{R} = 1.097\text{E}5\ \text{cm}^{-1}$

Chem1 Problems

Calculations based on formulas and equations 3

3-1 **Boron content of borax** *Borax* is the common name of sodium tetraborate, $Na_2B_4O_7$. How many *moles* of boron and how many *grams* of boron are contained in 20 g of borax?

3-2 **Magnesium in chlorophyll** Chlorophyll contains 2.68% magnesium by weight. How many *atoms* of Mg will there be in 1.00 g of chlorophyll?

3-3 **Law of Multiple Proportions** In the early 19th Century, when the formulas of many substances were unknown, the Law of Multiple Proportions served as a useful means of estimating the atomic weight of an element. All that was needed was a list of "combining weights" of the element in question, in a sufficiently representative variety of compounds that at least one compound would likely contain only one atom of the element per molecule of the compound.

Use the following data to estimate the molar mass (atomic weight) of bromine:

compound	*molar mass*	*mass-% Br in cmpd*
hydrogen bromide	81	98.7
aluminum bromide	267	89.8
sulfur bromide	224	71.4
phosphorus bromide	431	92.9
methylene bromide	174	91.9
bromobenzene	159	50.3

3-4 **Analysis by combustion** The combustion of a *hydrocarbon* (a compound containing only hydrogen and carbon) produces water and carbon dioxide. A weighed quantity of a hydrocarbon, 2.240 g, on complete combustion, yields 4.532 g of carbon dioxide and a quantity of water containing 1.010 g of hydrogen. Use this information to determine

a) The weight of carbon in the hydrocarbon;

b) The weight of carbon in the carbon dioxide produced;

c) The weight of oxygen in the carbon dioxide;

d) The weight of carbon (*not* hydrocarbon) that combines with 16.0 g of oxygen.

3-5 **Nitrogen content of a fertilizer** The high nitrogen content of ammonium sulfate makes this substance commercially important as a fertilizer. Calculate the percent by weight of nitrogen in this substance, whose formula is $(NH_4)_2SO_4$.

3-6 **Formula from percent composition** The molar mass of nicotine, a colorless oil, is 162.1; its weight-composition is 74.0% carbon, 8.7% hydrogen, and the remainder in nitrogen. Use this information to determine both the simplest formula and the actual formula of nicotine.

3-7 **Amount of raw material required** In the contact process for the commercial production of the important industrial chemical sulfuric acid, the sulfur present in FeS_2 is eventually converted into H_2SO_4. Assuming that the conversion is complete, how many litres of sulfuric acid (specific gravity 1.86) can be made from 4000 pounds of ore?

3-8 **Limiting reactant stoichiometry** Sulfur and copper, when heated together, react to form cuprous sulfide, Cu_2S.

a) How many grams of sulfur will combine with 12.7 g of copper in this reaction?

b) How many grams of Cu_2S can be made from 12.7 g of Cu and 2.50 g of S?

3-9 **Composition of a hydrate** Barium chloride forms a crystalline *hydrate*, $BaCl_2 \cdot xH_2O$, in which x molecules of water are incorporated into the crystal lattice for every unit of $BaCl_2$. This water can be driven off by heat; if 1.10 g of barium chloride hydrate is heated and reweighed several times until no further loss of weight (i.e., loss of water) occurs, the final weight of the sample is 0.937 g. What is the value of x in the formula of the hydrate?

3-10 **Formula from combustion analysis** An 11.00-mg sample of an organic compound containing carbon, hydrogen, and oxygen was burned in an excess of oxygen: 26.4 mg of CO_2 and 5.40 mg of H_2O were obtained. Calculate the *weight-percent composition* of the compound, and its *molecular formula*.

3-11 **Heat content of a fuel** The heat of combustion of methane, the principal constituent of natural gas, is 891 kJ/mol. What weight of methane must be burnt in order to liberate 300,000 kJ of heat?

Gases 4

4-1 **The atmospheric ozone layer** Ozone (O_3) molecules in the stratosphere absorb much of the harmful ultraviolet radiation from the sun. Typical values of pressure and temperature for the stratosphere are 250 K and 0.001 atm. If 5% of the molecules consist of O_3, how many O_3 molecules are present in each cubic cm of the air in this region?

4-2 **Vaporization of Dry Ice** Dry Ice is solid CO_2 which, upon absorbing heat, sublimes directly to the gas. 1.00 g of Dry Ice is placed in a 1.0-litre evacuated container, which is then placed in a 23 °C room. Calculate the pressure inside the container after thermal equilibrium has been reached.

4-3 **Molecular weight of a gas** A certain gas was found to have a density of 2.94 g/l at 150 °C and a pressure of 720 torr. What is the molar mass of this gas?

4-4 **Ideal gas law** If 300 ml of argon gas at 20 °C has a mass of 0.26 g and exerts a pressure of 400 torr,

a) what would be the *volume* of 0.13 g of the same gas at 30 °C and 900 torr pressure?

b) at what *temperature* would 0.52 g of the same gas exert a pressure of 500 torr in a volume of 250 ml?

c) what *weight* of the gas in a volume of 250 ml would be required to produce a pressure of 2.0 atm at a temperature of 25 °C?

4-5 **Dalton's law of partial pressures** Calculate the mass of each component present in a mixture of fluorine and xenon contained in a 2.0-litre flask. The partial pressure of Xe was 350 torr and the total pressure was 724 torr at 25 °C.

4-6 **Baking powder biscuits** A biscuit made with baking powder has a volume of 20 ml, of which one-fourth consists of empty space created by gas bubbles produced when the baking powder decomposed to CO_2. What weight of $NaHCO_3$ was present in the baking powder in the biscuit? (Assume that the gas reached its final volume during the baking process when the temperature was 400 °C).

4-7 **Reaction stoichiometry** Copper oxide (CuO) can be treated with ammonia gas (NH_3) to produce metallic copper, nitrogen gas, and water vapor. Starting with 10.0 g of CuO and 10.0 l of ammonia at STP, find the total volume of gas after the reaction is complete, measured at 1 atm and 200 °C. What will be the partial pressures of each gaseous product?

Atomic structure and the periodic table 5

5-1 **Electron configurations** Without consulting any tables, give plausible electron configurations of the following species:

a) $_{6}C$ $_{7}N$ $_{15}P$ $_{21}Sc$ $_{24}Cr$ $_{28}Ni$ $_{30}Zn$ $_{31}Ga$ $_{52}Te$ $_{79}Au$

b) $_{23}V^{3+}$ $_{24}Cr^{3+}$ $_{26}Fe^{2+}$ $_{26}Fe^{3+}$

5-2 **Isoelectronic species** Separate the following into groups of isoelectronic species:

a) Li^{+} NH_4^{+} Ca^{2+} Cl^{-} CH_4 Ne He

b) Li^{+} NH_3 H_3O^{+} S^{2-} Na^{+} H^{-} K^{+}

5-3 **Ionization energies** The energy needed to remove one electron from a gaseous potassium atom is only about two-thirds as much as that needed to remove one electron from a gaseous calcium atom, yet nearly three times as much energy is needed to remove one electron from K^{+} as from Ca^{+}.

Give a plausible explanation of this contrast, and predict how the ionization energy of Ca^{+} would compare with that of neutral K.

5-4 **Periodicity** Arrange the following substances in the order specified, and explain the reasons for your choices:

a) Mg^{2+}, Ar, Br^{-}, Ca^{2+} in order of increasing *radius* ;

b) Na, Na^{+}, O, Ne in order of increasing *ionization energy* ;

c) H, F, Al, O in order of increasing *electronegativity.*

5-5 **Comparison of properties** Among the elements with atomic numbers 14-24, identify the element that has:

a) The highest first ionization energy;

b) the highest *third* ionization energy;

c) the lowest electronegativity;

d) the most basic oxide;

e) the most acidic oxide;

f) metalloid properties.

States of matter 6

6-1 **Boiling points**
Which member of each of the following pairs has the higher boiling point?

(*a*) CO_2 or SiO_2; (*b*) Ne or Xe; (*c*) CH_4 or CH_3OH; (*d*) CH_4 or CCl_4.

6-2 **Melting points** Which member of each pair has the higher melting point?

(*a*) $AlCl_3$ or CCl_4; (*b*) NaCl or MgO; (*c*) K or Ca.

6-3 **Hydrogen bonding** Which of the following liquids would be expected to exhibit hydrogen bonding?

(*a*) CH_3OH; (*b*) CH_3OCH_3; (*c*) H_2S; (*d*) CH_3NH_2.

6-4 **Relative humidity**

a) What mass of water is present in 1 m^3 of air at atmospheric pressure if the relative humidity is 80% at 25 °C and 760 torr?

b) Outside air at 0 °C and 80% relative humidity passes into a house, where it is heated to 22 °C with no change in pressure. What will be the relative humidity of the air inside the house if no other sources of moisture are present?

6-5 **Phase diagram of carbon dioxide** Refer to the CO_2 phase diagram in your text. Suppose that a sample of carbon dioxide at −80 °C and 1 atm is (1) compressed at constant temperature to a pressure of 7 atm, then (2) heated at constant pressure to a temperature of −50 °C, and then (3) held at constant temperature while the pressure is reduced to 3 atm.

Describe any phase changes that will occur during each of the stages 1, 2, and 3.

6-6 **Kinetic molecular model** In terms of the kinetic molecular model of matter, explain why

a) a liquid in an open container will eventually vaporize, even if the temperature is below the boiling point;

b) the boiling point of a liquid will be lower at higher altitudes;

c) the temperature of a pure, boiling liquid substance does not change even though heat is continually flowing into the container.

Vapor pressure of water

T, °C	0	5	10	20	22	25	30	100
P, torr	4.6	6.5	9.2	17.5	19.8	23.8	31.8	760

Solutions and their physical properties 7

7-1 **Preparation of a solution** What weight of barium nitrate hydrate, $Ba(NO_3)_2{\cdot}H_2O$, is required to prepare 600 ml of a solution that is 0.040 *M* in nitrate ion?

7-2 **Preparation of a solution** What volume of .04 *M* nitrate ion solution can be prepared from

a) 2.0 g of solid $Sr(NO_3)_2$;

b) 32 ml of 0.10 *M* $Sr(NO_3)_2$ solution?

7-3 **Density of ethanol solution** A 9.9 *M* solution of ethanol (C_2H_5OH) in water contains 50.0 % ethanol by weight. What is the density of this solution?

7-4 **Concentration units** A 40.0 weight-% solution of sugar ($C_6H_{12}O_6$) in water has a density of 1.180 g/ml at 20 °C . Find the *molarity* and the *molality* of sugar in the solution, and the *mole fraction* of water in the solution.

7-5 **Lattice and hydration energies** When one mole of $CuSO_4{\cdot}5H_2O$ is dissolved in water, 11.9 kJ of heat is absorbed, whereas the dissolution of one mole of the anhydrous salt is accompanied by the *liberation* of 66.5 kJ. Account for this difference in the heats of solution in terms of lattice and hydration energies.

7-6 **Antifreeze solution**

Glycerol, ($HOCH_2CHOHCH_2OH$, MW = 92.0) is a commonly used antifreeze agent. For a 22 weight-% solution of this substance in water, calculate

a) the vapor pressure at 25 °C and at 100 °C;

b) the normal boiling point of the solution;

c) the freezing point of the solution.

(the vapor pressure of water at 25 °C is 23.8 torr)

7-7 **Dissociation of nitrous acid** An aqueous solution of nitrous acid (HNO_2) freezes at −0.198 °C .

a) How many moles of dissolved particles are present per kilogram of water?

b) If the solution was prepared by adding 0.100 mole of HNO_2 to 1000 g of water, what is the percentage dissociation of nitrous acid in this solution?

7-8 **Vapor pressure of a solution** Benzene and toluene form a nearly ideal solution. At 80 °C, the vapor pressure of pure benzene (FW=78.1) is 753 torr, and that of pure toluene (FW=92.1) is 290 torr. The following questions refer to a solution containing equal masses of benzene and toluene.

a) Calculate the partial pressure of each substance in the vapor that would be in equilibrium with the above solution at 80 °C;

b) At what atmospheric pressure will this solution boil at 80 °C?

c) Suppose that some of the vapor from this solution is collected and condensed. What will be the composition of the resulting liquid?

7-9 **Solution of a volatile solute** At 25 °C, solid iodine has a vapor pressure of 0.31 torr. Chloroform, a liquid, has a vapor pressure of 199.1 torr. In a saturated solution of iodine in chloroform, the mole fraction of iodine is 0.0147.

a) What is the partial pressure of iodine vapor in equilibrium with this solution?

b) Assuming ideal behavior, what is the total vapor pressure of this solution?

Acids and bases I: fundamental concepts 8

8-1 Acid-base theory Write equations showing how the Bronsted-Lowry concept of acids and bases would explain what happens when the following substances are dissolved in water:

(a) $HCl(g)$ (b) $NH_3(g)$ (c) $SO_2(g)$

8-2 Conjugate species

a) Write the formulas of the conjugate *acids* of

H_2O Cl^- SO_4^{2-} NH_3 $Al(H_2O)_5(OH)^{+2}$

b) Write the formulas of the conjugate *bases* of

H_2O HBr NH_3 CH_3COOH CH_3CH_2OH

8-3 Reaction with water Show by means of balanced net equations, how the following ions can behave as acids or bases in aqueous solution:

(a) CN^- (b) NH_4^+ (c) $Fe(H_2O)_6^{3+}$ (d) NH_2^-

8-4 Acid - base reactions Complete the following equations; all reactions except the last are presumed to take place in aqueous solution.

a) $HCl + Ca(OH)_2 \longrightarrow$

b) $HCN + NaOH \longrightarrow$

c) $HCN + NH_3 \longrightarrow$

d) $NH_4Cl + NaNH_2 \longrightarrow$ (in liquid NH_3)

8-5 Autoprotolysis Write equations illustrating autoprotolysis in the following pure liquids:

(a) H_2O (b) NH_3

8-6 Acid-base titration Vinegar consists essentially of a solution of acetic acid in water. It was found that 22.3 ml of 0.240 M NaOH will neutralize a 50.0-ml sample of vinegar. What is the concentration of acetic acid in this vinegar?

8-7 pH and pOH Calculate the pH and pOH of a solution that is:

a) 10^{-3} M in HCl;

b) 3.2E-5 M in $Sr(OH)_2$

8-8 pH of the blood The pH of the blood is normally around 7.4. What is the hydrogen ion concentration?

Oxidation-reduction reactions 9

9-1 **Oxidation numbers** Determine the oxidation number of the underlined element in each of the following species:

$\underline{Fe}O$ $\underline{Fe}_2O_3$ $\underline{Fe}O_4^{2+}$ $\underline{Fe}_3O_4$ $H_2\underline{S}$ $H_2\underline{S}O_4$ $\underline{S}O_2$ $\underline{S}O_3$
$H\underline{S}O_3^-$ $\underline{N}O$ $\underline{N}_2O_3$ $\underline{N}H_2OH$ $H_2\underline{P}O_2^-$ $H_2\underline{P}_4O_7$ $H_4\underline{I}O_6$
$H_3\underline{P}O_4$ $\underline{I}O_3^-$

9-2 **Oxidizing and reducing agents** For each of the following electron-transfer reactions, identify the *oxidizing agent* , the *reducing agent* , the subtance *oxidized* , and the substance *reduced* :

a) $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

b) $2Fe(s) + O_2(g) \longrightarrow 2FeO(s)$

c) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

d) $2H^+(aq) + Fe(s) \longrightarrow Fe^{2+}(aq) + H_2(g)$

9-3 **Balancing redox equations** Complete and balance the following equations, bearing in mind that this may involve the addition of H^+ or OH^- ions to one side of the equation, and H_2O to the other. All reactions are assumed to take place in acidic solution unless otherwise indicated.

a) $Fe + Cl_2 \longrightarrow FeCl_3$

b) $Cr_2O_7^{2-} + H_2SO_3 \longrightarrow Cr^{3+} + HSO_4^-$

c) $CrO_4^{2-} + HSO_3^- \longrightarrow Cr(OH)_4^- + SO_4^{2-}$ (*alkaline solution*)

d) $H_2O_2 + Br_2 \longrightarrow BrO_3^- + H_2O$

e) $U_3O_8(s) \longrightarrow UO_2^{2+}(aq) + U^{2+}(aq)$

f) $CH_3OH + NaClO_3 + H_2SO_4 \longrightarrow CO_2 + ClO_2 + Na_2SO_4$

g) $KClO_3 + HCl \longrightarrow KCl + ClO_2 + Cl_2 + H_2O$

h) $H_4IO_6^- + PI_3 \longrightarrow H_3PO_4 + IO_3^-$

Chemical Bonding I 10

10-1 **Bond energies** Use bond energies (consult the table in your textbook) to compute approximate values for the energy changes associated with the following gas-phase reactions:

a) $H_2 + Cl_2 \longrightarrow 2HCl$

b) $H_2CCH_2 + H_2 \longrightarrow H_3CCH_3$

10-2 **Ionic character** Arrange the following compounds in order of increasing ionic character:

CF_4 SF_2 NH_3 BeF_2 BF_3 ClF_3

10-3 **Bond type** Indicate the type of bond– electrovalent (ionic), polar covalent, or nonpolar covalent– which is expected to exist in each of the following compounds:

ICl K_2S PCl_3 PF_3 $MgCl_2$

S_8 NF_3 CCl_4 CS_2

10-4 **Lewis structures** Write Lewis electron-dot structures for the following species:

NH_3 NH_4^+ NH_2^- SCN^- SO_4^{2-}

10-5 **Octet rule** Which of the following species do *not* obey the octet rule?

BF_4^- CN SF_4 SiF_4 XeF_4 SF_6 I_3^-

10-6 **Resonance** The carbonate ion, CO_3^{2-}, has a planar structure with three equal bond angles and three equal carbon-oxygen distances.

a) Draw three equivalent Lewis formulas for this ion.

b) Draw two structures for the bicarbonate ion, $HOCO^{2-}$, and predict which of the carbon-oxygen bonds in these two ions would be the shortest and which would be the longest.

c) Would you expect the bonds in CO_2 to be similar in length to any of the carbon-oxygen bonds in these ions, or shorter, or longer? Explain.

10-7 **Lewis acid-base reactions** Indentify the Lewis acids and Lewis bases in the following reactions, and use structural formulas to illustrate the Lewis acid-base character of these reactions:

a) $BaO(s) + SO_2(g) \longrightarrow BaSO_4(s)$

b) $Ag^+(aq) + 2NH_3(aq) \longrightarrow Ag(NH_3)_2^+(aq)$

c) $Cl_3Al + O(CH_3)_2 \longrightarrow$ (*complete the reaction*)

d) $H_3C\text{-}CH_2^+ + Br^- \longrightarrow H_3C\text{-}CH_2Br$

10-8 **Molecular geometry** Predict the shapes of the following molecules, using the VSEPR (valence shell electron pair repulsion) model:

CS_2 $SiCl_4$ SCN^- PH_3 SF_6 NO_3^-

NO_2^- SO_4^{2-} ICl_2^- BrF_3 O_3 XeF_4

Chemical Bonding II 11

11-1 **Hybrid orbitals** Indicate the hybridization of the orbitals on the central atom of:

BeH_2 $AlCl_3$ SiH_4 PBr_5 SiF_6^{2-}

NH_3 NH_2^- NH_4^+ SO_3^{2-} CNO^-

11-2 **Multiple bonds** For each of the following molecules

H_3CCH_3 $H_2C{=}CH_2$ $HC{\equiv}CH$ C_6H_6 OCO

a) Construct Lewis electron dot structures;

b) Indicate the hybridization of the bonding orbitals on each non-hydrogen atom;

c) Sketch a diagram showing how the various orbitals overlap between atoms, and label the σ and π orbitals;

c) Indicate the C-C-H bond angle in each molecule as 45°, 90°, 105°, 109°, 120°, 135°, or 180°.

11-3 **Dipole Moments** Indicate which of the following molecules and ions would possess a permanent dipole moment:

$CHCl_3$ CH_2F_2 $H_3C\text{-}O\text{-}CH_3$ $N(CH_3)_3$ $N(CH_4)_4^+$

$Cl_3Si\text{-}SiCl_3$ H_2S CO_2 F_2O $SnCl_2$

11-4 **Transition metal complexes** Indicate the shape and hybridization in the following transition metal complexes:

$Ni(CO)_4$ (diamagnetic) $PtCl_2(NH_3)_2$

$[PtCl_2(NH_3)_4]^{+2}$ $Fe(CN)_6^{3-}$ (low-spin)

11-5 **Molecular orbitals** Give the molecular orbital configurations, and indicate the bond orders in the following species:

O_2^{2-} O_2^+ OF^- NO^- NO^+ C_2

11-6 **Acetylides** Acetylene, C_2H_2, forms ionic compounds such as CaC_2 and Na_2C_2 which contain the *acetylide* ion C_2^{2-}. Show whether molecular orbital theory would predict the stable existence of such an ion, and whether its bond distance and bond energy should be similar to, greater than, or less than those of C_2.

11-7 **Metallic valence** Consider the electrons available for bonding, and predict the relative melting points and hardnesses of the metals Rb, Sr, and Y.

Nuclear Chemistry 12

12-1 Nuclide notation Write the symbols, showing charge and mass number, for each of the following species:

(*a*) Helium with 2 neutrons; (*b*) Uranium with 142 neutrons;
(*c*) the nucleus containing 7 neutrons and 9 protons; (*d*) the neutron;
(*e*) the electron; (*f*) the proton.

12-2 Nuclear reactions Complete the following nuclear reaction equations:

a) ${}_3\text{Li}^7 + \boxed{} \longrightarrow 2\,{}_2\text{He}^4$

b) ${}_7\text{N}^{14} + {}_0\text{n}^1 \longrightarrow \boxed{} + {}_1\text{H}^1$

c) ${}_6\text{C}^{14} \longrightarrow {}_7\text{N}^{14} + \boxed{}$

d) ${}_4\text{Be}^9 + {}_0\gamma^0 \longrightarrow \boxed{} + {}_0\text{n}^1$

e) ${}_{98}\text{Cf}^{244} + \boxed{} \longrightarrow {}_{103}\text{Lr}^{255}$

f) ${}_{41}\text{Nb}^{93} + {}_6\text{C}^{12} \longrightarrow \boxed{}* \longrightarrow \boxed{} + 2{}_0\text{n}^1$

g) $\boxed{} + {}_1\text{H}^2 \longrightarrow [\text{Al}^{27}]* \longrightarrow \boxed{} + {}_1\text{H}^1$

12-3 Binding energy Find the binding energy per nucleon for the nuclides ${}_{20}\text{Ca}^{40}$ (mass 39.962589) and ${}_{90}\text{Th}^{232}$ (mass 232.03821).

12-4 Fusion reactions Among the various nuclear reactions that have been proposed as sources of controlled fusion power are:

$$\text{H}^3 + \text{H}^3 \longrightarrow \text{He}^4 + {}_0\text{n}^1 \qquad (1)$$

$$\text{H}^2 + \text{H}^2 \longrightarrow \text{He}^3 + {}_0\text{n}^1 \qquad (2)$$

$$\text{H}^2 + \text{H}^2 \longrightarrow \text{H}^3 + \text{H}^1 \qquad (3)$$

Which of these reactions would release the largest amount of energy? Nuclear masses in units of 10^{-27} kg: n^1, 1.6750; H^1, 1.6727; H^2, 3.3435; H^3, 5.0075; He^3, 5.0065; He^4, 6.6446.

12-5 Natural radioactivity Ordinary vanadium contains about 0.25 mole-% V^{50}, which has a half life of 4E14 year. What will be the average number of disintegrations per minute in a 1.0-g sample of vanadium that contains no other radioactive material?

12-6 Carbon-14 dating The half life of C^{14} is 5580 years, and its concentration in the atmosphere (and in all living organisims) is sufficient to produce 15.3 disintegrations per minute per gram of carbon. Charcoal removed from the door frame of a house built in the time of Hammurabi of Babylon has an activity of 9.3 disintegrations per minute per gram of carbon. About how long ago does this suggest that Hammurabi lived?

12-7 The curie The activity of a radioactive sample is often expressed in curies: 1 curie is 3.700E10 disintegrations per second. A sample containing P^{32}, a β-emitter with a half-life of 14.2 d, has an activity of 1 microcurie. What weight of P^{32} is in the sample?

Chemical Equilibrium 13

13-1 **Combined equilibrium constant** At 1000 °C, the following reactions take place with the equilibrium constants shown:

$$C(s) + 2H_2O(g) \longrightarrow CO_2(g) + 2H_2(g) \qquad K_1 = 3.85$$

$$H_2(g) + CO_2(g) \longrightarrow H_2O(g) + CO(g) \qquad K_2 = 0.71$$

Use this information to calculate the equilibrium constant for the reaction

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

13-2 **Equilibrium condition** Write an expression for the equilibrium quotient for each of the following reactions:

a) $3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$

b) $3CO(g) + 7H_2(g) \longrightarrow C_3H_8(g) + 3H_2O(g)$

c) $I_2(s) \longrightarrow I_2(g)$

d) $Fe_3O_4(s) + 4H_2(g) \longrightarrow 4H_2O(\ell) + 3Fe(s)$

e) $Na_2CO_3 \cdot 10H_2O(s) \longrightarrow Na_2CO_3(s) + 10H_2O(g)$

f) $CN^-(aq) + H_2O(\ell) \longrightarrow HCN(aq) + OH^-(aq)$

g) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$

13-3 **Combined equilibrium constant** Sulfide ion (S^{2-}) in alkaline solution reacts with solid sulfur to form a series of polysulfide ions having the formulas S_2^{2-}, S_3^{2-}, S_4^{2-}, and so on. The equilibrium constant for the formation of the disulfide ion S_2^{2-} is 1.7, and that for S_3^{2-} is 5.3, starting in each case from elemental sulfur and S^{2-}.

What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

13-4 **Equilibrium constant from experimental data** Nitrosyl chloride is an orange gas that dissociates at high temperatures into chlorine and nitrogen oxide:

$$2ClNO(g) \longrightarrow 2NO(g) + Cl_2(g)$$

In a certain experiment, 3.00 moles of NO, 2.00 moles of Cl_2, and 5.00 moles of ClNO were introduced into a 25.0-litre container.

a) Find the numerical value of the reaction quotient Q_n under these conditions.

b) After the reaction was allowed to come to equilibrium at the temperature of the experiment, there were 6.12 moles of ClNO in the container. Use this information to evaluate the equilibrium constant K_c.

13-5 **Degree of dissociation of HI** The equilibrium constant for the reaction

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

has the value 0.0156 at a certain temperature. If 2 moles of HI are placed in a 1-litre vessel and brought to this temperature, what would be the equilibrium concentrations of all three molecules, and what percent of the HI molecules would be dissociated?

13-6 **Solid-gas equilibrium** Ammonium hydrosulfide is a crystalline solid that decomposes according to the following reaction:

$$NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$$

At 25 °C, the equilibrium vapor pressure of NH_4HS is 500 torr. A sample of NH_4HS is allowed to come to equilibrium with its decomposition products in a closed container at 25 °C, and then sufficient ammonia is added to the system to bring the partial pressure of this gas to 800 torr.

What will be the partial pressure of NH_3, and the total pressure in the container, once equilibrium has been re-established?

13-7 **Formation of an ester** Alcohols react with organic acids to form esters plus water. When 1.00 mole of pure ethanol reacts with 1 mole of acetic acid at room temperature, the equilibrium mixture contains $\frac{2}{3}$ mole each of water and the ester, ethyl acetate. All substances are liquids at room temperature.

$$C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O$$

a) Evaluate the equilibrium constant for this reaction.

b) Find the equilibrium composition of the system after 3 moles of alcohol have been mixed with 1 mole of acetic acid.

13-8 **Equilibrium composition from percent dissociation** Phosphorus pentachloride is known to dissociate according to

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

The equilibrium constant K_p is 3.60 at 540 °K.

If 0.200 mol of PCl_5 and 3.00 mol of PCl_3 are placed in a container and heated to 540 °K at a total pressure of 1.00 atm, what will be the partial pressures of all substances present at equilibrium?

13-9 **Distribution equilibrium** The distribution coefficient of iodine between carbon tetrachloride and water is 85.4 at 25 °C. A solution of iodine in water is skaken with an equal volume of CCl_4 in a separatory funnel, thus removing most of the iodine from the aqueous phase.

a) What is the concentration of iodine in the aqueous phase that will be in equilibrium with a .0220 *M* solution of iodine in carbon tetrachloride?

b) What percentage of the iodine can be removed from a 0.001 *M* aqueous solution by extraction with an equal volume of CCl_4?

13-10 **Le Châtelier Principle** Assume that the reaction

$$2Cl_2(g) + 2H_2O(g) \longrightarrow 4HCl(g) + O_2(g)$$

is at equilibrium. State the effect (*increase, decrease*, or *no change*) of each of the changes listed in the left column below, on (*a*) the equilibrium quotient and (*b*) the quantity listed in the right column. Temperature and volume are constant unless otherwise indicated.

a)	volume of container is increased	number of moles of H_2O
b)	more oxygen is added	number of moles of H_2O
c)	more oxygen is added	number of moles of HCl
d)	volume of container is decreased	number of moles of HCl
e)	volume of container is decreased	number of molecules
f)	helium gas is added	number of moles of HCl

Acids and bases: quantitative calculations 14

14-1 **Brønsted-Lowry concept** Write balanced net equations illustrating what happens when the following substances are added to pure water. In each case, label the acid, base, conjugate acid, and conjugate base, and state whether the resulting solution will be acidic, alkaline, or about neutral.

(*a*) HBr (*b*) NH_3 (*c*) $Ca(OH)_2$ (*d*) HSO_4^-
(*e*) Na_2O (*f*) NaCN (*g*) $SO_2(g)$

14-2 **Water autoprotolysis** At 0 °C, K_w= 1.14E15. Is a solution at this temperature whose pH is 7.0 *neutral, acidic*, or *basic*? What is the ratio of [H^+] to [OH^-]?

14-3 **Acid dissociation constant** The pH of a 0.072 *M* solution of benzoic acid is found to be 2.68.

a) What is the value of K_a for benzoic acid?

b) What is the value of K_b for the benzoate anion?

14-4 **Solution of ammonia** Electrical conductivity measurements reveal that a 0.010 *M* solution of ammonia is 4.3% ionized at 25 °C. Find the pH of this solution, and evaluate K_b for NH_3.

14-5 **pH of a weak acid solution** Find the hydronium ion concentration in a 0.100 *M* solution of hydrofluoric acid, HF, for which K_a = 7.0E-4.

14-6 **Acidity of hexaaquoiron(III)** The pH of a 0.100 *M* solution of $FeCl_3$ is found to be 2.00. Assuming that the only significant proton transfer is from $Fe(H_2O)_6^{3+}$, calculate the acidity constant K_a of this species, and the percent of the Fe(III) that is in the form of $Fe(H_2O)_5^{2+}$ under these conditions.

14-7 **Dilute solution of a strong acid** What are the concentrations of all ionic species present in a 5E-7 *M* solution of hydrochloric acid? Answer this question by writing out the three equations required to specify the unknowns [H_3O^+], [Cl^-], and [OH^-]. (We take [HCl] to be zero, thus eliminating a fourth unknown and the need to employ a fourth equation). These equations represent water autoprotolysis, chloride ion mass balance, and charge balance. Show how these equations can be combined into one of the form

$$[H^+] = C_a + \frac{K_a}{[H^+]}$$

and that this is a quadratic equation of the form

$$ax^2 + bx + c = 0$$

Then solve the latter equation numerically for [H^+].

Acid-base mixtures; buffer solutions 15

15-1 **Buffer action** A solution contains 0.200 mol/l of acetic acid, pK_a= 4.7.

a) Find the pH of this solution.

b) What would be the pH if 0.200 mol/l of NaOH were added to the solution?

c) Find the pH if only 0.100 mol/l of NaOH were added to the original acetic acid solution.

d) What would be the new pH, and the percent change in pH, if 0.005 mol/l of HCl were added to the acetic acid - NaOH solution in (*c*)?

15-2 **Blood carbonate** Carbon dioxide, produced by oxidation of glucose in the tissues, is carried by the blood to the lungs. Part of it is in solution as carbonic acid, and nearly all the remainder is present as hydrogen carbonate ion, HCO_3^-. If the pH of the blood is 7.4, find what fraction of the carbon dioxide is carried by the ion. (Use $K_1 = 4.47 \times 10^{-7}$)

15-3 **Acid-base indicator** An acid-base indicator has a pK_a of 4.52. The acid form of the indicator is red and the basic form is blue. Over what range of pH will the color of this indicator change? Assume that a definite color change occurs when the relative concentrations of the two forms change from 75% of one form to 75% of the other.

15-4 **Buffer solution**

a) How would you prepare one litre of buffer solution having a pH of 8.50, starting with 0.100 *M* KCN and the usual substances available in the laboratory? (For HCN, $K_a = 4.8 \times 10^{-10}$).

b) How much would the pH of this buffer solution change if 5.00×10^{-4} mol of $HClO_4$ is added to 100 ml of the solution? What would be the effect of adding the same quantity of NaOH to 100 ml of the buffer?

15-5 **Dilute monoprotic acid** The exact equation relating the concentrations of the species in a solution of a monoprotic acid can be written as

$$[\mathrm{H}^+]^3 + K_a[\mathrm{H}^+]^2 - (K_w + C_aK_a)[H^+] - C_aK_a = 0$$

a) Use a simpler (quadratic) relation to estimate the pH of a 0.10 *M* solution of HF (pK_a= 3.17), and use this value as the beginning point of a trial-and-error solution of the cubic equation. What is the percent error in using the quadratic instead of the cubic equation?

b) Try the same thing for a 10^{-5} *M* solution of hydrofluoric acid.

15-6 **Polyprotic acid** A 0.100 *M* solution of phosphoric acid, H_3PO_4, is treated with sufficient sodium hydroxide to raise the pH to 8.0. What would be the concentrations of all species present in the resulting solution? (Use the following K_a's for the three successive ionization steps of phosphoric acid: 7.5E−3, 6.2E−8, 4.8E−13)

15-7 **Sulfuric acid solutions** What are the relative concentrations of hydrogen sulfate and of sulfate ion in solutions of sulfuric acid, H_2SO_4, that are 0.01 M and 10^{-4} M ?
$K_1 = 1000$, $K_2 = 0.010$.

15-8 **Weak diprotic acid** Oxalic acid, HOOC-COOH is a weak acid found in rhubarb and certain other plants; its acid constants are $K_1 = .054$ and $K_2 = 5.4 \times 10^{-5}$.

a) Write charge balance and mass balance equations for aqueous solutions of oxalic acid.

b) Find the concentrations of all species in a 0.100 M solution of oxalic acid.

(*Suggestion:* Start by solving for the $[H_3O^+]$, using the quadratic formula. Then substitute this value into the charge balance expression to obtain $[Ox^{2-}]$.)

Chem1 Problems

Solubility equilibria 16

16-1 **Solubility product of calcium fluoride** A saturated solution of CaF_2 in water at 18 °C contains 0.00160 g of solute per 100 ml of solution. Evaluate K_{sp} for this substance.

16-2 **Solubility of silver sulfate** The solubility product constant for Ag_2SO_4 is 1.7×10^{-5}. Calculate the molar solubility of Ag_2SO_4 in (*a*) pure water, and (*b*) in 1.0 M Na_2SO_4 solution.

16-3 **Precipitation of a hydroxide** A solution contains Mg^{2+} at a concentration of 0.00100 M. How high must the pH be raised in order to bring about the precipitation of $Mg(OH)_2$, $K_{sp} = 1.1\text{E}{-11}$?

16-4 **Selective precipitation** A solution contains Cl^- at a concentration of 0.10 M , and CrO_4^{2-} (chromate) ions at 0.30 M .

a) If $AgNO_3$ is slowly added to this solution (assume no volume change), which substance will precipitate *first* : AgCl ($K_{sp} = 1.8\text{E}{-10}$), or Ag_2CrO_4 ($K_{sp} = 9\text{E}{-12}$)?

b) What will be the value of $[Cl^-]$ when the *second* substance begins to precipitate?

c) At this point, what percentage of the Cl^- originally present still remains in solution?

16-5 **Simultaneous solubility** The solubility product constants of CaF_2 and SrF_2 are 4.0E−11 and 2.8E-9, respectively. Calculate the concentrations of Ca^{2+} and Sr^{2+} in a solution that is in equilibrium with both of these solid fluoride salts.

16-6 **Carbonates in natural waters** Natural waters, being in equilibrium with the atmosphere, contain carbon dioxide at a concentration of about 10^{-5} M. The slightly acidic solution of carbonic acid that results can attack limestone ($CaCO_3$, $K_{sp} = 4.8\text{E}{-9}$) according to the net reaction

$$H_2CO_3 + CaCO_3(s) \longrightarrow Ca^{2+} + 2HCO_3^-$$

a) Find the equilibrium constant for this reaction. For carbonic acid, $K_1 = 4.4\text{E}{-7}$, $K_2 = 4.8\text{E}{-11}$.

b) Calculate the concentration of calcium ion in natural water that is in equilibrium with limestone, and find the number of litres that would be required to dissolve one mole of $CaCO_3$.

16-7 **Precipitation of sulfide from acidic solution** A solution contains 0.10 M Co^{2+} at a pH of around 7. The solution is saturated with H_2S gas at 1 atm pressure, so that $[H_2S]$ = 0.1 mol/l. To what value must the pH be reduced in order to just prevent the precipitation of cobalt sulfide?

(For CoS, $K_{sp} = 8.0\text{E-}23$; for H_2S, $K_1 = 9.1\text{E}{-8}$, $K_2 = 1.2\text{E}{-15}$)

16-8 **Solubility in presence of complexing agent** The dissociation constant of the diamminesilver complex $Ag(NH_3)_2^+$ is 5.9E−8. Calculate the solubility of silver thiocyanate (AgSCN, $K_{sp} = 1.0\text{E}{-12}$) in a 0.05 M solution of ammonia.

Thermochemistry and the First Law 17

17-1 Isothermal expansion of a gas Three moles of an ideal gas at 300K is allowed to expand against a constant external pressure of 2.0 atm, while absorbing heat from the surroundings at a rate sufficient to maintain a constant temperature. The initial pressure is 8.0 atm and the final volume is four times the initial volume.

a) Calculate the work done, the heat absorbed, ΔU and ΔH.

b) Calculate the work done if the same process is carried out in two steps, first to twice the initial volume, and then doubling the volume again.

c) Calculate the work done if the same process is carried out in an infinite number of steps.

17-2 Iced drink Ice cubes at 0 °C are used to cool 250 ml of water from 30.0 to 0 °C. How much of the ice will melt, assuming no heat transfer between the water and the surroundings?

Data: The enthalpy of fusion of ice is 6.02 kJ/mol, the constant-pressure heat capacity of liquid water is 75.3 kJ/mol-K, and the density of liquid water is 1.00 g/ml.

17-3 Vaporization of ice Suppose that 13.5 g of ice at 0 °C is converted to steam at 110 °C. Calculate q, w, ΔH° and ΔU° for this process.

Data : The densities of ice and water are 0.92 and 1.00 g/ml. The heat capacities in J/mol-K are: ice = 38, water = 75.3, steam = 33.3. The enthalpy of fusion of water is 6.02 kJ/mol, and the enthalpy of vaporization of water at 100 °C is 44.0 kJ/mol.

17-4 Rocket fuel An important consideration in the selection of a rocket fuel is the amount of energy available from a given weight of fuel plus oxidant. Use the following standard enthalpies of combustion to show whether *hydrogen* or *pentaborane* would be the better fuel according to this criterion.

$H_2(g)$, $\Delta H^\circ = -286$ kJ/mol; $B_5H_9(g)$, $\Delta H^\circ = -4380$ kJ/mol

17-5 Heat of combustion by bomb calorimetry A 0.600-g sample of solid naphthalene, $C_{10}H_8$, is burned in excess O_2 in a constant-volume calorimeter which contains 2500 ml of water. The observed temperature rise of the calorimeter and its contents was 2.225 °C.

a) Use this information to calculate ΔU° for the combustion of 1 mole of naphthalene.

b) Estimate the standard enthalpy of combustion of naphthalene. Assume that all gaseous substances behave ideally.

17-6 Reaction enthalpy Find the standard enthlapy change for the hydration reaction

$$SrO(s) + H_2O(\ell) \longrightarrow Sr(OH)_2(s)$$

Data: Standard enthalpies of formation in kJ/mol: $Sr(OH)_2(s) = -959$, $SrO(s) = -590$, $H_2O(\ell) - 286$.

17-7 Hess' law of heat summation Determine the standard enthalpy of formation of ozone from the following information:

$$F_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow OF_2(g) \qquad \Delta H^\circ = +21.8 \text{ kJ/mol}$$
$$F_2(g) + O_3(g) \longrightarrow OF_2(g) + O_2(g) \qquad \Delta H^\circ = -120.5 \text{ kJ/mol}$$

Thermodynamics of equilibrium 18

18-1 **Estimating entropy changes**

For each of the following processes, predict whether the entropy of the system will increase, decrease, or remain approximately constant:

a) $H_2O(s, 0\,°C) \longrightarrow H_2O(\ell, 0\,°C)$

b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

c) $Pb(s) \longrightarrow Pb(\ell)$

d) $C(\textit{graphite}) \longrightarrow C(\textit{diamond})$

e) $CdCl_2(s) \longrightarrow Cd^{2+}(aq) + 2Cl^-(aq)$

f) $6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$ (photosynthesis)

18-2 **Entropy of vaporization**

The normal boiling point of methanol is 65.0 °C, and its enthalpy of vaporization is 35.3 $kJ\,mol^{-1}$. Calculate the entropy change of the *system*, the *surroundings*, and the *universe* when one mole of methanol vaporizes at its normal boiling point.

18-3 **Isomerization equilibrium**

There are two isomeric hydrocarbons with the formula C_4H_{10}, known as *normal* butane and *iso*butane.

isomer	$\Delta H°_f$, $kJ\,mol^{-1}$	$\Delta G°_f$, $kJ\,mol^{-1}$
n-butane	−124.7	−15.9
iso-butane	−131.3	−18.0

a) Calculate the composition of the equilibrium mixture of *n*-butane and *iso*-butane at 298 K.

b) Is the conversion of normal butane to its isomer a spontaneous process at this temperature? At what temperature could an equimolar mixture of the two isomers coexist indefinitely without any net reaction?

18-4 **Evaporation of water**

At 25 °C the molar entropies of liquid and gaseous water at 1 atm pressure are 70.0 and 189 J/K-mol, respectively, and the heat of vaporization is 44.0 $kJ\,mol^{-1}$.

a) Show whether or not the following change can occur spontaneously at 25 °C.

$$H_2O(\ell) \longrightarrow H_2O(g,\ \textit{1atm})$$

b) Calculate the vapor pressure of water at 25 °C.

c) Calculate the temperature at which $\Delta G° = 0$

18-5 Properties of bromine from thermodynamic data Given the following data for bromine:

substance	ΔH°(kJ mol^{-1})	ΔG°(kJ mol^{-1})	S° (J/K-mol)
Br_2 (ℓ)	0	0	152.23
Br(g)	111.9	82.43	144.91
Br_2(g)	30.90	3.14	245.25

a) What is the enthalpy of the Br-Br bond?

b) What is the heat of vaporization of liquid bromine?

c) Calculate the vapor pressure of liquid bromine at 298 K.

d) Estimate the normal boiling point of liquid bromine.

e) Estimate the temperature at which the dissociation of bromine vapor into its atoms becomes spontaneous.

18-6 Cellular synthesis of sucrose The double sugar *sucrose* is composed of the two monosaccharides *glucose* and *fructose*:

$$\text{glucose} + \text{fructose} \longrightarrow \text{sucrose} \qquad \Delta G^\circ = +21.0 \text{kJ mol}^{-1}$$

In living cells, this reaction is driven by the enzyme-catalyzed hydrolysis of ATP (adenosine triphosphate) to ADP:

$$\text{ATP} \longrightarrow \text{ADP} + \text{P} \qquad \Delta G^\circ = -530.6 \text{kJ mol}^{-1}$$

(P here represents inorganic phosphate, not elemental phosphorus). The mechanism of this coupling involves the phosphorylation of glucose to glucose-6-phosphate, and the subsequent replacement of the phosphate group by fructose:

$$\text{ATP} + \text{glucose} \longrightarrow \text{glucose-6-P} + \text{ADP}$$

$$\text{glucose-6-P} + \text{fructose} \longrightarrow \text{sucrose} + \text{P}$$

Calculate the equilibrium constant for the cellular synthesis of sucrose. What would it be in the absence of ATP?

18-7 Precipitation of calcite In the operation of municipal waterworks, it is desirable that the water be slightly supersaturated with respect to $CaCO_3$ so that a small amount of this solid will precipitate out on the interior surfaces of the steel distribution pipes and help protect them from corrosion.

Determine whether or not this condition will be met for a water having the following composition: $[Ca^{2+}]$=0.001 M, $[HCO_3^-]$=.002 M, pH=8.7.

Data (ΔG°in kJ mol^{-1}): Ca^{2+}, −553; $CaCO_3(s)$, −1129; HCO_3^-, −587.

Electrochemistry 19

19-1 **Electroplating of copper** During the electroplating of copper from a $CuSO_4$ solution, a current of 0.50 A passes through the cell for one hour. How many electrons pass through the cell? How many grams of copper will be deposited?

19-2 **Fuel cell** A current of 7.50 A is produced in a fuel cell when CO is oxidized to CO_2 at the anode while oxygen is reduced at the cathode. How many grams of CO and of O_2 does the cell consume per hour?

19-3 **Electrolysis of salt solutions** Predict the main product at each electrode when each of the following 1 *M* solutions is subjected to electrolysis:

a) $NiBr_2$ with inert electrodes;

b) $NiSO_4$ with gold electrodes;

c) Na_2SO_4 with copper electrodes.

19-4 **Prediction of redox reactions** Predict whether the following reactions would tend to occur to a significant extent in aqueous solution. Assume that the effective concentrations of all species are 1 *M*.

a) $Sn + Cd^{2+} \longrightarrow Cd + Sn^{2+}$

b) $2I^- + Sn^{4+} \longrightarrow I_2(s) + Sn^{2+}$

c) $2Fe^{2+} + Br_2(\ell) \longrightarrow 2Fe^{3+} + 2Br^-$

d) $Cl_2(g) + 2H_2O \longrightarrow O_2 + 4H^+ + 2Cl^-$

19-5 **Disproportionation of Cu(I)** Use standard cell potentials to predict whether Cu^+ will be stable with respect to disproportionation to Cu(*s*) and Cu^{2+}. Calculate the equilibrium constant for this process.

19-6 **Cell reactions** Write the cell reaction corresponding to each of the following cells, and predict the reversible potential between the electrodes. Indicate whether this reaction will proceed to the right, and state the direction of electron flow through the external circuit when the two electrodes are connected.

a) $Fe(s) \mid Fe^{2+}(1.0\,M) \parallel H^+(1.0\,M) \mid H_2(1.0\text{ atm}) \mid Pt(s)$

b) $Pt(s) \mid Cl_2(g, 10^{-4}\text{ atm}) \mid Cl^-\ (.01\,M) \parallel Cl^-\ (.01\,M) \mid AgCl(s) \mid Ag(s)$

c) $Cu(s) \mid Cu(NO_3)_2(0.01\,M) \parallel Cu(NO_3)_2(.10\,M) \mid Cu(s)$

19-7 **Equilibrium compositions** An electrochemical cell consists of a silver electrode dipping into 0.10 *M* $AgNO_3$ and a nickel electrode dipping into 0.10 *M* $Ni(NO_3)_2$.

a) Write the net reaction that occurs as this cell generates electric current, and show the reaction that occurs at each electrode. Indicate the EMF and free energy contributed by each half cell, and then calculate the same quantities for the net cell reaction.

b) If a steady current of 0.10 A is supplied by this cell for 1.0 hour, what will be the change in mass of the nickel electrode?

c) If the volumes of the Ni^{2+} and Ag^{+} solutions are equal and the reaction is allowed to proceed until no more current flows, what will be the approximate final concentrations of these two ionic species?

19-8 **Solubility product** The standard half-cell potential for the electrode

$$Cu^{2+} + I^{-} + e^{-} \longrightarrow CuI$$

is +.860 volt. Use this value, together with any other required EMF values, to calculate the solubility product constant for CuI(s).

Kinetics and mechanisms of reactions 20

20-1 Interpretation of rate data For the reaction $2A + B \longrightarrow C + 3D$, the following data were obtained from five experiments:

experiment	[A]	[B]	rate = $d[A]/dt$
1	.23 *M*	.23 *M*	0.25 mol ℓ^{-1} h^{-1}
2	.46 *M*	.46 *M*	2.0 mol ℓ^{-1} h^{-1}
3	.23 *M*	.46 *M*	1.0 mol ℓ^{-1} h^{-1}
4	.46 *M*	.92 *M*	8.0 mol ℓ^{-1} h^{-1}
5	.92 *M*	.46 *M*	4.0 mol ℓ^{-1} h^{-1}

a) Write the rate law for this reaction;

b) Evaluate the rate constant;

c) Calculate the rate of formation of D at the moment at which [A] = [B] = .23 *M*.

20-2 Determination of reaction order A certain compound A decomposes in solution to form two other substances, B and C, under conditions such that the reverse reaction and competing reactions can be neglected. The following kinetic data were collected:

time, min	0	10	20	36	58	92	140
[A], mol/l	.100	.084	.071	.054	.037	.020	.009

State the order of this reaction, and evaluate the rate constant.

20-3 Propane isomerization kinetics

$$(CH_2)_3 \longrightarrow H_3C\text{–}CH{=}CH_2$$

The thermal isomerization of cyclopropane to propene has a first-order specific rate constant of 5.95E-4 sec^{-1} at 500 °C.

a) Calculate the *half-time* of the reaction;

b) What fraction of the cyclopropane will remain after 1.0 hour at this temperature?

20-4 First-order reaction Peroxydisulfate ion decomposes by a first-order reaction when heated in aqueous solution:

$$S_2O_8^{2-} + H_2O \longrightarrow 2HSO_4^- + \tfrac{1}{2}O_2$$

The half-time at 70 °C is 7.2 h; at 90 °C it is 0.72 h;

a) Evaluate the rate constant for this reaction at 70 °C and 90 °C.

b) What is the activation energy of the reaction?

c) If a 0.50 *M* solution of $K_2S_2O_8$ (a strong electrolyte) is heated at 70 °C for 25 hours, what will be the concentrations of $S_2O_8^{2-}$ and HSO_4^- ions at the end of this time?

20-5 Decomposition of ozone Ozone, which is formed in the upper atmosphere by the reaction of O_2 with oxygen atoms, has a positive free energy of formation and decomposes back into dioxygen:

$$2O_3 \longrightarrow 3O_2$$

The experimentally determined rate law for this decomposition is

$$\text{rate} = -d[O_3]dt = k[O_3]^2[O_2]^{-1}$$

The following two-step mechanism has been proposed for the decomposition of ozone:

(1) $O_3 \longrightarrow O_2 + O$ (Forward rate constant k_1, reverse rate constant k_2)

(2) $O + O_3 \longrightarrow 2\,O_2$ (rate constant k_3)

The first step is a rapidly established equilibrium (for which an equilibrium constant may be derived), and the slower second step is rate determining.

Show how the suggested mechanism is consistent with the observed rate law.

20-6 Hydrogenation of ethylene

The enthalpy of hydrogenation of ethylene is -125 kJ mol^{-1}.

a) If the temperature is increased, which of the rate constants (forward or reverse) will undergo the greater relative increase?

b) If the activation energy for the forward reaction is 117 kJ, what is the activation energy for the reverse reaction?

c) Addition of a certain catalyst causes the activation energy for the forward reaction to drop by 46 kJ. What is the activation energy for the reverse catalyzed reaction?

d) The use of this catalyst speeds up the forward reaction by a factor of ten million. By what factor does the reverse rate increase?