GENERAL CHEMISTRY REVIEW

Review Topics Include:

- Naming Simple Compounds
- Rules for Reporting Significant Figures
- Units of Concentration
- Review of the Equilibrium Expression
- Review of Simple Acid/Base Properties
- Rules for Predicting pH of Solution
- Solubility
- Rules for Assigning Oxidation States
- Review of Thermodynamics
- Review of Electrochemistry

Naming Simple Compounds

Binary Ionic Compounds, where the metal ion has only one oxidation state
(Group 1A, alkali metals and group 2A, alkali earth metals)

1. the cation (positive ion) named first using the element name
2. monatomic cations take name from the corresponding element (i.e., cesium)
3. monatomic anions (negitive ions) named from the element root and adding *-ide* suffix (i.e., bromide)

For example, CsBr is named cesium bromide.

Binary Ionic Compounds, where the metal ion has variable oxidation state (Transition elements)

1. the oxidation state on the metal ion is specified by Roman Numeral in brackets
2. monoatomic anions are named as before

For example, CuCl and $CuCl_2$ are named as copper (I) chloride and copper (II) chloride, respectively. The older method of using the suffix *-ous* and *-ic* to indicate low and high oxidation states respectively is still encountered. Thus, the above compounds could appear as cuprous chloride and cupric chloride.

Binary Compounds involving only non-metals (Group 4A - 8A)

1. first element in the formula is named using element name (i.e., nitrogen)
2. second element named as if it were an anion (i.e., oxide)
3. prefixes (*mono, di, tri, tetra, penta, hexa* etc.) used to denote number of atoms
4. prefix *mono-* never used for naming the first element (i.e., nitrogen dioxide as opposed to mononitrogen dioxide)

For example, NO_2 is named nitrogen dioxide and P_2O_7 is named diphosphorous heptaoxide.

For compounds involving **polyatomic ions**, similar rules apply. The names of the following common polyatomic ions must be committed to memory.

CO_3^{2-} (carbonate) **HCO_3^-** (hydrogen carbonate; aka bicarbonate)

NH_4^+ (ammonium) **NO_2^-** (nitrite) **NO_3^-** (nitrate)

S^{2-} (sulfide) **SO_3^{2-}** (sulfite) **SO_4^{2-}** (sulfate) **HSO_4^-** (hydrogen sulfate)

PO_4^{3-} (phosphate) **HPO_4^{2-}** (hydrogen phosphate) **$H_2PO_4^-$** (dihydrogen phosphate)

CN^- (cyanide) **ClO^-** (hypochlorite) **$CH_3CO_2^-$** (ethanoate; aka acetate)

MnO_4^- (permanganate) **CrO_4^{2-}** (chromate)

Sample Exercises:

1. Name each of the following.
a) $Ca_3(PO_4)_2$
b) Cr_2O_3
c) ClO_2

2. Give the molecular formula for each of the following.
a) sodium hypochlorite
b) mercury (II) sulfate

Rules for Reporting Significant Figures

1. Nonzero digits always count as significant figures

2. Zeros are what mix people up. There are three situations in which they can occur.

leading zeros precede all nonzero digits and are **never** significant (i.e., 0.000182 has three sign. figs.)

captive zeros are between nonzero digits and are **always** significant (i.e., 1008.02 has six sign. figs.)

trailing zeros are significant **only if** a number contains a decimal point (i.e., 1200 has two sign. figs.; 1200.00 has six sign. figs., 1.200×10^3 has four sign. figs.)

*** Note here the advantage of using exponential notation to clear up these ambiguities!**

3. Exact numbers have no bearing on the number of significant figures in a calculated result. Examples of these are the following;

conversion factors such as 1 L = 1000 mL
numbers reflecting an exact count such as 8 stones or 16 people
stoichiometry in chemical reactions involves exact numbers

Operations

Rules for multiplication/division

The answer to contain the same **number of sign. figs.** as the least precise measurement used in the calculation.

72.5674	*six sign. figs*
x 3.34	*three sign. figs (limiting term)*
242.3751160	*initial answer (must be rounded off to three sign. figs.)*
	Final Answer = 2.42×10^2

Rules for addition/subtraction

The answer to contain the same **number of decimal places** as the least precise measurement used in the calculation.

456.367963	
- 452.1	*least number of decimal places (limiting term)*
4.267963	*initial answer (must be rounded off to one decimal place)*
	Final Answer = 4.3 !

Rules for logarithms

In logarithmic values, only those numbers to the right of the decimal place count as significant.
For example,

pH = 10.26 has only two significant figures and corresponds to a $[H^+] = 5.5 \times 10^{-11}$ **M**
$pK_a = 4.730$ has three significant figures and corresponds to $K_a = 1.86 \times 10^{-5}$

Sample Exercises:

3. What is the pH if the concentration of H^+ is measured to be 1.25×10^{-6} **M** ?

4. What is the pK_{sp} if the solubility product has been determined to be 2×10^{-30} ?

UNITS OF CONCENTRATION

Several different units are used to express the concentration of species in solution. You are familiar with the concept of molarity (**M**) and it's usefulness in chemical calculations since it reflects actual numbers of particles in a system. (Recall: moles of solute = mass of solute/MW solute)

$$Molarity(M) = \frac{moles\ of\ solute}{litres\ of\ solution}$$

Two common units that you have not used as frequently are ppm (parts per million), and **N** (normality).

PART PER MILLION (mass ratio analogous to wt%)

The unit of ppm is the number of milligrams of solute per kg of solvent. For example, a solution that has 1.0 mg of Cl^- in 1.0 kg of water contains 1.0 mg of Cl^- in 1000 g of water. As there are 1000 mg in 1 g the concentration is

$$\frac{1.0\text{ mg Cl}^-}{1\text{ kg solvent}} = \frac{1.0\text{ mg Cl}^-}{1000\text{ g solvent}} = \frac{1.0\text{ mg Cl}^-}{1000000\text{ mg solvent}}$$

i.e. from this last expression there is 1 mg of Cl^- in 1 million mg of water, hence the term parts per million or ppm. This solution has a Cl^- concentration of 1.0 ppm.

Assuming the density of water to be 1.0 g/mL the above solution contains 1.0 mg of Cl^- in 1000 mL (1 L) of water so 1 ppm = 1 mg/L (or 1 μg/mL). The above assumption about the density of water becomes less valid at high temperatures or in highly concentrated solutions such as effluents or in seawater where the density is greater than 1.0 g/mL (density seawater = 1.04 g/mL). **Thus, 1 ppm ≠ 1 mg/L for seawater!**

Parts per billion: 1 ppb = 1000 x ppm = 1μg/L (or ng/mL)
The above solution has a Cl^- concentration of 1 ppm or 1000 ppb

Confusion can be encountered when reporting the concentration of elements that are present in polyatomic species, such as the nitrogen in nitrate form or the phosphorous in phosphates. for example, 1 mg/L of **N** (nitrogen) corresponds to 4.4 mg/L of $\mathbf{NO_3}^-$ (nitrate) since a nitrate has 4.4 times the mass of a nitrogen (62 g/mol versus 14 g/mol). To clarify what species is being referred to, you may see units reported as mg/L $\mathbf{N\text{-}NO_3}^-$ or mg/L $\mathbf{NO_3}^-$ **- N**. This indicates that it is the mass (in mg) of nitrogen (present in the chemical form of nitrate) per liter of water.

For air samples, ppm means parts per million by volume rather than by mass and this is often denoted by ppmv. The concentration of CO_2 in air is about 325 ppm or 325 mL of CO_2 in 1 million mL (1000 L) of air.

Sample Exercises:

5. Convert the following to freshwater concentrations.
a) 3.2 mmol/L of P to ppm of PO_4^{3-}
b) 1.9 x 10^{-6} **M** of copper to ppb Cu

6. Convert the following concentrations to molarity.
a) 9.8 mg/L of O_2
b) 150 ppb Arsenic in seawater

NORMALITY

Normality is defined as the number of *equivalents* per liter. An *equivalent* is a multiple of the number of moles of a substance and depends on the context of the reaction (e.g., *equivalents* of acid, *equivalents* of electrons or *equivalents* of charge). Normality units have been retained in water analysis and in industrial analysis because of their advantage is in carrying out titration calculations. Its disadvantage is that it's definition depends on the type of reaction involved. There are three broad classifications (i) acid/base reactions, (ii) oxidation/reduction reactions and (iii) precipitation or complexation reactions.

$$Normality(N) \; = \; \frac{equivalents\ of\ solute}{litres\ of\ solution}$$

The equivalent referred to in this equation is defined as follows:

$$\text{number of equivalents} = \frac{\text{weight of solute (grams)}}{\text{equivalent weight of solute (grams/equivalent)}}$$

The tricky part is determining the equivalent weight of the solute.

The equivalent weight, $EW = \frac{\text{Molecular Weight, MW}}{\text{constant, } K}$ (or $= \frac{\text{Molar Mass)}}{\text{constant, } K}$

K is an integer constant ($K \geq 1$), and is equal to the number of moles of active species (protons, electrons etc) per mole of substance. For example, for H_2SO_4 each mole of sulfuric acid yields two moles of protons, so $K = 2$ and the EW = ½ MW.

In general: **Normality = *K* x Molarity**

Sample Exercises:

7. A solution contains the following ions. Calculate the number of milliequivalents of positive and negative charge, respectively.

80 mg/L Ca^{2+}	100 mg/L HCO_3^-
22 mg/L Na^+	25 mg/L Cl^-
12 mg/L Mg^{2+}	12 mg/L SO_4^{2-}
1.2 mg/L Al^{3+}	

8. A 1.00 L sample reacted with 22.62 mL of 0.1034 **M** H_2SO_4. How many equivalents of acid were neutralized?

Review of the **Equilibrium Expression**, K_{eq}

The equilibrium expression for the generalized reaction is determined experimentally by measuring concentrations for solutions (K_c) or partial pressures for gases (K_p). It can also be calculated from thermodynamic information, such as ΔG^o or E^o.

$$a\,\mathbf{A} \;+\; b\,\mathbf{B} \;\;==========\;\; c\,\mathbf{C} \;+\; d\,\mathbf{D}$$

$$K_{eq} = \frac{[C\,]^c\,[D\,]^d}{[A\,]^a\,[B\,]^b}$$

Experimental equilibrium constants are obtained from measured concentrations or pressures and has units of concentration raised to the appropriate power. However, the Equilibrium Expression is actually defined thermodynamically as a quotient of chemical *activities* rather than concentrations. Activities are numerically similar to concentrations (particularly at low concentrations) but are unitless expressions, thus equilibrium constants often appear without units.

The numerical value of the Equilibrium constant (**K**$_{eq}$);

- is constant at a given temperature
- is independent of initial concentrations
- depends on the form of the balanced equation

The position of heterogeneous equilibria does not depend on the concentrations of solids and pure liquids (i.e., the chemical *activity* of solids and pure liquids = 1). Therefore, these concentration terms do not appear in the equilibrium expression. For example:

$$CaCO_3(s) \;+\; H_2O(l) \;+\; CO_2(g) \;\;==========\;\; Ca^{2+}(aq) \;+\; 2\,HCO_3^-(aq)$$

$$K_{eq} = [Ca^{2+}][HCO_3^-]^2 / P_{CO2}$$

Combining chemical reactions and equilibrium constants:

Equilbrium constants for unknown reactions can be derived from the combination known chemical equilibria.

The equilibrium constant for a reaction that is equivalent to the sum of several other reactions is the product of the equilibrium constants of the constituent reactions.

$$\begin{array}{ll} A + B \;======== \; C + D & K_1 \\ A + C \;======== \; E & K_2 \\ \hline 2\,A + B \;======== \; D + E & K_{eq} = K_1\,K_2 \end{array}$$

If a reaction is reversed, the equilibrium constant is the inverse of the original constant (1/K)

$$NH_3 \;+\; H_3O^+ \;\;========\;\; NH_4^+ \;+\; H_2O \qquad K_{eq} = 1/K_a(NH_4^+)$$

Predicting the direction of a reaction using Q, the reaction quotient:

The reaction quotient, **Q** has the same form as the equilibrium expression, but involves any set of reactant and product concentrations, not necessarily those at equilibrium. The value of **Q** can be compared to that of **K** to predict which way an equilibrium will shift given a set of initial concentrations.
For instance, if **Q > K** the reaction will shift to the left
if **Q < K** the reaction will shift to the right
if **Q = K** the reaction is at equilibrium

Calculating equilibrium concentrations/pressures given initial conditions:

Using the balanced chemical equation and the initial concentrations, set up an expression for the equilibrium concentration of reactants and products in terms of *x*, the extent of reaction. Substitute these equilibrium concentrations into the expression for the equilibrium constant and solve for *x*. Once *x* is known it can be substituted into the earlier equations to give the equilibrium concentrations. These types of equilibrium problems are often complicated by cumbersome polynomial equations. Here are several short cuts;

- To solve a quadratic equation of the form $ax^2 + bx + c = 0$, use the quadratic formula.

- Under certain circumstances simplifications are possible which greatly reduce the mathematical difficulty of the problem. Such a situation arises when treating a system with a very small equilibrium constant (see examples). After solving for *x*, check to see if the approximation was a valid one!

Samples Exercises:

9. Write an expression for the equilibrium constant for the dissolution of calcium carbonate in the presence of carbon dioxide gas (see rxn above) from the following information.

$CaCO_3(s)$ ========== $Ca^{2+}(aq)$ + $CO_3^{2-}(aq)$	K_{sp}
$HCO_3^-(aq)$ + H_2O ========= $CO_3^{2-}(aq)$ + H_3O^+	$K_{a2}(H_2CO_3)$
$CO_2(g)$ ======== $CO_2(aq)$	K_H
$CO_2(aq)$ + H_2O ======= $HCO_3^-(aq)$ + $H_3O^+(aq)$	$K_{a1}(H_2CO_3)$

10. Consider the following reaction between the powerful disinfectant hypochlorous acid (HOCl) and water to form a weaker disinfectant hypochlorite ion (OCl^-).

$HOCl$ + H_2O ======== H_3O^+ + OCl^- $K_{eq} = 2.5 \times 10^{-8}$

a) Compute the equilibrium ratio of HOCl to OCl^- and the percent of the total 'OCl' present as HOCl at pH 8.0.
b) At a particular instant, the activities (concentrations) of H_3O^+ , HOCl and OCl^- in solution are 10^{-7}, 10^{-3} and 10^{-4}, respectively. Determine whether the reaction above is at equilibrium and if not, predict wheter the concentration of HOCl will increase or decrease as the reaction proceeds.

Review of Simple Acid/Base Properties

Where HA is used to represent any generic Bronsted acid:

$$HA(aq) \quad + \quad H_2O(l) \quad ========== \quad H_3O^+(aq) \quad + \quad A^-(aq)$$

$$K_a = \{[H_3O^+][A^-]/[HA]\}$$

STRONG ACIDS completely dissociate and therefore have very large values of K_a. Examples include HCl, HNO_3, $HClO_4$ and H_2SO_4. The conjugate base of strong acids are very weak bases. Therefore, Cl^-, NO_3^-, ClO_4^- and SO_4^{2-} are examples of weak bases and are said to be neutral anions.

WEAK ACIDS remain largely undissociated and have relatively small values of K_a. Examples include HF, HNO_2, HOCl and H_2S. The conjugate bases of weak acids are relatively strong bases. Therefore, F^-, NO_2^-, OCl^- and S^{2-} are examples of basic anions.

STRONG BASES are quantitatively converted into hydroxide ion in aqueous solution.
NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$ are examples of strong bases, although the latter two have limited solubility in water.

WEAK BASES partially react with water to produce hydroxide ions.

$$NH_3(aq) \quad + \quad H_2O(l) \quad ========== \quad NH_4^+(aq) \quad + \quad OH^-(aq)$$

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

Water is amphoteric . It can both donate and accept a proton, thus it has the ability to act either as an acid or a base.

$$H_2O \quad + \quad H_2O \quad ======== \quad H_3O^+ \quad + \quad OH^-$$

$$K_w = [H_3O^+][OH^-] \qquad K_w = 1.0 \text{ x } 10^{-14} \text{ at } 25^oC$$

In general: K_b (base) = K_w/K_a(conjugate acid) and K_a(acid) = K_w/ K_b(conjugate base)

Thus, K_a (NH_4^+) = $K_w/K_b(NH_3)$

$pH = -\log a_{H+} \approx -\log [H^+]$

In general: $pH + pOH = pK_w$
In pure water at 25^oC; $pH = pOH = 7.0$

Rules for Predicting the pH of Aqueous Solutions

In general:	Aqueous solutions of covalent oxides are acidic (i.e., CO_2, SO_2, SO_3 and NO_2) Note: rainwater is naturally acidic (pH ~ 5.8 - 6.2) due to the presence of atmospheric CO_2 Aqueous solutions of ionic oxides are basic (i.e., CaO, MgO and K_2O)
Neutral ions:	All Group 1A and 2A cations (e.g., Na^+, Ca^{2+} etc) Anions which are conjugates of strong acids (Cl^-, NO_3^- etc)
Acids:	Uncharged strong or weak acids (e.g., HCl, H_2CO_3 etc.) Metal cations other than those of Groups 1A and 2A Cationic conjugates of nitrogen bases (e.g., NH_4^+, C_5H_5NH+ etc) The two anions HSO_4^- and $H_2PO_4^-$
Bases:	All anions not listed above Uncharged nitrogen bases, such as NH_3, C_5H_5N etc

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Sample Exercises:

11. State whether the following aqueous solutions are expected to be acidic, basic or neutral
a) $CuCl_2$
b) Na_3PO_4
c) NH_4Br
d) MgS

12. Calculate the concentration of ammonium chloride in a solution whose pH is measured as 5.13, given that the K_a for the ammonium ion is 5.6×10^{-10} **M**.

13. Calculate the value of K_b for cyanide ion, given that a 1.6×10^{-2} **M** solution of potassium cyanide has a pH of 10.76. (Compare your answer with that obtained using the K_a for HCN).

14. Commercial bleach is a 5% (wt/wt) solution of sodium hypochlorite. The value of K_a for hypochlorous acid (HOCl) is 2.8×10^{-8}.
a) Do you expect bleach to be acidic or basic?
b) Calculate the K_b of hypochlorite ion.
c) Calculate the pH of a 5% bleach solution.

Solubility (Dissolution and Precipitation)

You are expected to be able to:

- use the *solubility rules* to predict solubility behaviour of binary compounds.
- calculate the *solubility product*, K_{sp}, given the solubilities and vice versa.
- explain the effect of pH and a common ion on solubility.

Solubility rules for ionic compounds

1. Almost all salts of the Group 1A (alkali metals) and of NH_4^+ are soluble in water
2. All nitrates are soluble in water
3. Most chlorides, bromides and iodides are soluble, the exceptions are those of Ag^+ and Hg_2^{2+}
4. Most sulfates are soluble, the major exceptions being those of barium, lead, mercury, bismith and tin. Calcium sulfate is sparingly soluble.
5. Most carbonates, oxides, hydroxides, phosphates and sulfides are insoluble. Exceptions are the alkali metals (rule 1). Calcium and barium hydroxides are fairly soluble.

For the general case where MX(s) represents an ionic compound;

$$MX(s) \quad ========== \quad M^+(aq) \quad + \quad X^-(aq)$$

$$K_{sp} = [M^+][X^-]$$

And solubility (s) is equal to the number of moles of solid dissolved per liter of solution.

In general, ionic compounds are less soluble in a solution that contains either ion from another source. Thus calcium sulfate is less soluble in a solution that contains calcium from another source, such as calcium carbonate.

In general, ionic compounds that contain a basic anion become more soluble in acidic solution as the protons present will associate with the basic anion thus effectively lowering their concentration. Thus, hydroxides, sulfides, carbonates, fluorides and phosphates all become more soluble at low pH.

Sample Exercises:

15. In which of the following cases would you expect precipitation to occur when equal volumes 0.1 **M** solutions are mixed?

a) calcium chloride and silver nitrate
b) potassium sulfide and cadmium chloride
c) barium hydroxide and copper (II) sulfate

16. Given that the K_{sp} of CaF_2 is 5.3 x 10^{-9} $\mathbf{M}^3$

a) Calculate the solubility of CaF_2
b) Is calcium floride more or less soluble in basic solution?
c) Is calcium fluoride more or less soluble in ‘hard’ water?

Rules For Assigning Oxidation States

1. For free elements the oxidation state is zero.
   e.g. Fe(s), O_2(g), O_3(g), H_2(g), Hg(l), Hg(g), S(s) etc.

2. For monoatomic ions, the oxidation state is given by the charge on the ion.
   e.g. Cl^- (**-1**), Fe^{2+} (**+2**), Fe^{3+} (**+3**), S^{2-} (**-2**), Ca^{2+} (**+2**), H^+ (**+1**) etc

3. Certain elements when present in compounds have common oxidation states.

   a) alkali metals (Li^+, Na^+, K^+) are always **+1**

   b) alkali earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) are always **+2**

   c) hydrogen is **+1** (except in metal hydride compounds such as LiH)

   d) oxygen is **-2** (except in peroxides such as H_2O_2)

   e) halogens (F^-, Cl^-, Br^-, I^-) are usually **-1** (exceptions include interhalogen compounds e.g., in Cl_2F_7, chlorine is **+7** and fluorine is **-1** and oxyanions e.g., in ClO_3^- chlorine is **+5**)

4. The sum of the oxidation states in a molecule is zero.
   e.g. H_2O (**+1**) + (**+1**) + (**-2**) = 0 $Fe(OH)_2$ (**+2**) + 2(**-2**) + 2(**+1**) = 0

5. The sum of the oxidation states in an ion is equal to the charge on the ion.
   e.g. OH^- (**-2**) + (**+1**) = -1 SO_4^{2-} (**+6**) + 4(**-2**) = -2

Note: Oxidation corresponds to an increase in the oxidation state and reduction corresponds to a a decrease in the oxidation state.

Sample Exercises:

17. Determine the oxidation states for all of the atoms in each of the following:
a) NO_3^-, NH_3, NH_4^+, N_2
b) Na_2S, Na_2SO_3, $Na_2S_2O_3$, Na_2SO_4
c) ClO_4^-, ClO_3^-, ClO_2^-, ClO^-
d) CO_2, H_2CO_3, C_2H_5OH, CH_3CHO

18. Indicate whether the following processes involve oxidation or reduction
a) SO_4^{2-} ---> H_2S
b) NH_4^+ ---> NO_3
c) NaClO -----> Cl^-
d) 2 Cu^+ -----> Cu^{2+} + Cu

19. In the following reactions identify the species that is oxidised and that being reduced.
a) IO_4^- + I^- + H^+ ---> I_2 + H_2O
b) NO_3^- + H^+ + Cl^- ---> NO + Cl_2 + H_2O
c) NO_3^- + Cu + H^+ ---> NO_2 + Cu^{2+} + H_2O

Thermodynamics Review

Gibbs free energy changes: ΔG

Reactions spontaneously proceed in a direction to lower free energy.

In general:
If $\Delta G < 0$*, then the reaction is spontaneous in the direction written*
If $\Delta G > 0$*, then the reaction is spontaneous in the opposite direction*
If $\Delta G = 0$*, then the reaction is at equilibrium*

When all species are present at their standard state (1 atm for gases and 1 **M** for species in solution), free energy changes are denoted as ΔG^o_{rxn} for any given reaction. Standard free energy changes can be determined by any one of four different approaches depending on the type of experimental data available.

1. From standard enthalpies of formation (ΔH^o_f) and entropy changes (ΔS^o)

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

2. From standard free energies of formation, (ΔG^o_f)of reactants and products

$$\Delta G^o_{rxn} = \Sigma\Delta G^o_f \text{ (products)} - \Sigma\Delta G^o_f\text{(reactants)}$$

3. From equilibrium constants (K).

$$\Delta G^o_{rxn} = - RT \ln K_{eq}$$ note: $K_{eq} = \exp\{-\Delta G^o/RT\}$

where R is the universal gas constant ($R= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the Kelvin temperature

4. From electrochemical data (E^o)

$$\Delta G^o_{rxn} = -nFE^o$$ note: $E^o = -\Delta G^o/nF$

where n is the number of moles of e^- transferred and F is Faraday's constant ($F=96,485 \text{ C mol}^{-1}$)

To calculate free energy changes for systems not at standard state conditions (ΔG), several approaches can be taken.

1. Using the reaction quotient (experimental species concentrations, i.e., non-standard state)

$$\Delta G = \Delta G^o + RT \ln Q$$

where Q is the reaction quotient

2. Using the experimental (non-standard state) electochemical cell potential

$$\Delta G = -nFE$$

Review of Electrochemistry

Summary of definitions of electrochemical terms.

Oxidiation: a chemical process in which the reactant loses electrons (involves an increase in oxidation state)

Reduction: a chemical process in which the reactant gains electrons (involves a decrease in oxidation state)

Anode: the electrode at which oxidation occurs

Cathode: the electrode at which reduction occurs

Galvanic Cell: an electrochemical cell which produces electricity, such as a flashlight battery

Electrolytic Cell: an electrochemical cell which is driven by the input of electricity, such as in the chlor-alkali process

Standard reduction potentials are thermodynamic parameters related to the driving force (ΔG) for the reaction to proceed. They are tabulated for a great many half-reactions (written as reductions) in standard reference sources. These half-reactions are listed in order of decreasing values of E^o (i.e., decreasing driving force to occur as reductions). Therefore, the most powerful oxidizers are those species at the top of standard reduction tables. Remember, large E^o the greater the driving force to occur in the direction written. Hence species such as F_2, O_3, H_2O_2 and Cl_2 are strong oxidizing agents. At the other extreme, metals such as Li, Na and Mg are powerful reducing agents.

The potential for the complete cell is calculated from the individual half-reactions.

$$E^o_{cell} = E^o_{cathode} \quad + \quad E^o_{anode}$$

where E^o_{anode} has the sign of the standard reduction potential <u>reversed</u>.

The greater the value of the cell potential, the greater the driving force for the reaction to proceed in the direction written. A more positive E corresponds to a more negative ΔG, the Gibbs free energy, since

$$\Delta G = -nFE$$

where, n = number of electrons involved in a redox process
F = Faraday constant (96,487 Coulombs/mol)
E = cell potential

Recall, spontaneous reactions have negative ΔG, but positive E

ΔG^o, E^o the values of ΔG or E when all reactants and products are at unit activity (in practice these are the values found in tables or calculated form tabulated data).

Nernst Equation:

$$E = E^o - (RT/nF) \ln Q$$

where, n, F, E and E^o defined as before.
R = universal gas constant (8.314 J mol^{-1} K^{-1})
T = temperature (Kelvin)
Q = reaction quotient

Since (RT/F) = 0.0257 at 25°C, the Nernst equation can be written as at this temperature.

$$E = E^o - (0.0257/n) \ln Q$$

At equilibrium, $\Delta G = 0$ and therefore $E = 0$

Hence, $E^o = (0.0257/n) \ln K$
where K replaces Q at the equilibrium condition.

This can be rearranged such that; $K = \exp \{nE^o/0.0257\}$

Sample exercises:

20. In each of the following, state whether oxidation or reduction is occurring.
a) CH_4 ------> CO_2 + other products
b) $Cl_2(g)$ + $2e^-$ ------> $2\ Cl^-(aq)$
c) ClO_2^- ------> ClO_2 + e^-

21. Using the standard reduction potentials, list the following species in order of increasing oxidizing ability. ClO_2 Cl_2 O_3 O_2

22. Use the standard reduction potentials to predict if a reaction will occur if copper metal will react with a solution containing silver ions, Ag^+. Calculate the E^o for the complete electrochemical cell.

23. Identify the half-reactions (neglecting spectator ions) and calculate the equilibrium constant, K_{eq}.

$$Br_2(l) + 2\ FeBr_2(aq) \;=\!=\!=\!=\!=\!=\; 2\ FeBr_3(aq)$$