# Lecture 2, Class 2 (Lecture Notes):
## Free Energy and Chemical Equilibria (Chapter 1)

**Chemical Transformation**

- Reaction of chemical agents in the environment is usually (but not always) going to represent a net sink for contaminants; *i.e.* a negative component of the term *r* in the advection-dispersion-reaction equation.
- Together with biological transformations, which can be expected to have a similar net effect, the presence of such processes is straightforward to detect from mass balance considerations, but the underlying mechanisms can be complicated.
- To understand the nature of a chemical sink (or source) we need to consider both why chemical changes occur (reactants → products) and the rate(s) at which these reactions take place.

**The Gibbs Function**

- Like physical examples, change in a chemical system (or control volume) is driven by the tendency of the system to move towards a condition of minimum potential energy, or where the Gibbs “free” energy ($G$) is lowest.
- Gibbs free energy is given by $G = H - TS$ (or $\Delta G = \Delta H - T\Delta S$) where $H$ is the enthalpy, $S$ the entropy and $T$ (in kelvin) the absolute temperature of the system.
- Enthalpy (units of energy) is a measure of the net intra- and intermolecular forces (*i.e.* bonding interactions) of a system.
- Entropy (units of energy) is often suggested to correspond to “disorder,” but it is better considered a measure of the number of energy states available to a system.
- Regardless of the exact nature of the chemistry involved, a system spontaneously undergoes a chemical change in the direction leading to $\Delta G$ being negative.

For a general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

Let $Q$, the reaction quotient, be given by:

$$Q = [C]^c[D]^d / [A]^a[B]^b$$

Then $\Delta G$ for a particular reaction is:

$$\boldsymbol{\Delta G = \Delta G^0 + RT \ln Q}$$

where $\Delta G^0$ is the standard free energy change and $R$ is the gas constant.

Scheme 2.1 The reaction quotient and free energy changes.

- If a valid chemical equation can be written and the concentrations of the various species determined, $\Delta G$ can be calculated as $\Delta G^0$ is a constant for any given reaction and many values have been tabulated ($R$ is the gas constant and $T$ the absolute temperature) ⇒ whether A and B are formed, or consumed.

**Chemical Equilibria**

- In addition to directions of chemical change, the Gibbs function also provides information concerning the equilibrium composition of reaction mixtures.
- At equilibrium, there is no net change in the concentrations of reactants and products, so $\Delta G$ must be a minimum.

For the general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G = \Delta G^0 + RT \ln Q = 0 \text{ at equilibrium}$$

$$\mathbf{\Delta G^0 = -RT \ln Q \text{ at equilibrium}}$$

Substituting for $Q$ and rearranging, we define an equilibrium constant ($K$):

$$K = [C]^c[D]^d / [A]^a[B]^b = \exp(-\Delta G^0/RT)$$

Scheme 2.2 Equilibrium and the law of mass action.

- In the case of dilute solutions the concentration terms are molar (M). Strictly, these should be activities ($\{a_i\} = \gamma_i[c_i]$) not concentrations, but this is usually only important under conditions of high ionic strength, *e.g.* in seawater. By convention, gas concentrations are represented as pressures, while solids (and most pure substances) are entered as unity.
- Again, many equilibrium constants are tabulated under standard conditions and some are available over a range of temperatures and pressures. There are a few special cases, *e.g.* the ionic product of water ($K_w$).

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = [H^+][OH^-]/ [H_2O] = 1.8 \times 10^{-16} \text{ mol/ liter}$$

Multiplying both sides by the concentration of water, 55.4 M:

$$K_W = [H^+][OH^-] = 10^{-14} \text{ mol}^2/\text{ liter}^2$$

$$-\log_{10} K_W = p[H^+] + p[OH^-] = 7 + 7 = 14$$

Therefore, neutrality = pH 7.0

Scheme 2.3 The ionic product of water and the pH scale.

- Under dilute acidic/basic aqueous conditions, like in aquatic environments, where the water concentration is essentially constant at 55.4 M, water ionization actually contributes very little to the net pH; *e.g.* Ex. 1-6:

$^1/_3$ of 6% $\approx$ $^1/_3$ 60 g/liter = 20 g/liter $\Rightarrow$ (20 g/liter)/(46 g/mol) = 0.43 M

$$K_a = 1.75 \times 10^{-5} \text{ mol/liter} \approx [H^+][A^-]/0.43 \approx [H^+]^2/0.43$$

$[H^+] \approx \sqrt{(0.43\ M \times 1.75 \times 10^{-5}\ mol/liter)} = 2.8 \times 10^{-3}\ M \Rightarrow pH = -\log(2.8 \times 10^{-3}) = 2.6$

- Other physical constraints, such as the conservation of mass and the principle of electroneutrality, can sometimes be a great help in solving equilibrium problems; *e.g.* Ex. 1-7:

a) Balancing the opposite ionic charges in the stream, we may write

$$2[Ca^{2+}] + [H^+] = 2[SO_4^{2-}] + [OH^-] + [Cl^-]$$

$$[Ca^{2+}] = \{2(6 \times 10^{-3}) + 10^{-10} + (3 \times 10^{-4}) - 10^{-4}\}/2 = 6.1 \times 10^{-3}\ M$$

b) Now, remembering that the concentration of a solid is unity

$$[CaSO_4]/([Ca^{2+}][SO_4^{2-}]) = 1/\{(6.1 \times 10^{-3})(6 \times 10^{-3})\} = 2.7 \times 10^4$$

Since $K = 4.17 \times 10^4$ precipitation of $CaSO_4$ will occur.

**Sections in Text:** 1.6 - 1.65

**Next Time:** 1.66

**Problems:** p. 59, no.'s 8 & 9; p. 60, no. 10