

• **Chapter 18 Review:**

- **Multiple Choice Questions** (18-20 are challenge questions)
- **In Textbook:** Problems pg. 792 #28, 38(a & b), 52, 54, 56, 57, 61, 62, 64, 66, 68
- **In Study Guide:** pp. 379-381 #2, 6, 7, 9, 12, 13; pp 385-386 #3, 6, 8, 10, 12, 13  
\*\* Underlined questions should be done b/c these types of questions were not in text book review.

**Topics:**

- 1) Spontaneity (thermodynamic feasibility): A reaction is spontaneous (thermodynamically feasible) if it occurs under specified conditions. (In other words, the net reaction is in the forward direction.) Spontaneity depends on both changes in enthalpy ( $\Delta H$ ) and changes in entropy ( $\Delta S$ ).
- 2) Entropy: measurement of disorder. The greater the disorder, the greater the entropy. An increase in entropy corresponds to an increase in microstates (more ways to arrange molecules).
  - a) Be able to determine whether entropy is increasing or decreasing for a particular process.
  - b) Be able to calculate the change in entropy of a reaction given the standard entropy values for each substance.
$$\Delta S_{\text{sys}}^{\circ} = \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants})$$

*Remember: You are plugging in absolute entropy values. The entropy of a perfect crystalline substance is zero at a temperature of absolute zero. (In contrast,  $\Delta H_f^{\circ}$  and  $\Delta G^{\circ}$  values are arbitrarily set.)*
- 3) Second Law of Thermodynamics: For all spontaneous processes, the entropy of the universe must increase.  $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surroundings}} > 0$ 
  - a) Thus, spontaneous processes are favored by  $+\Delta S_{\text{sys}}$  and by  $+\Delta S_{\text{surroundings}}$ .
  - b)  $\Delta S_{\text{surroundings}}$  is determined by the change in temperature of the surroundings. If the system releases heat to the surroundings (exothermic reaction), the entropy of the surroundings increases because the molecules move faster.
  - c) Thus, the enthalpy of a reaction affects the spontaneity of a reaction because it affects the entropy of the surroundings.  $-\Delta H$  is the favored change. Thus, exothermic reactions are often spontaneous.
- 4) Gibbs Free Energy: energy available to do work
  - a)  $\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_f^{\circ}(\text{products}) - \sum \Delta G_f^{\circ}(\text{reactants})$  (Note: All values are at standard conditions.)
  - b) Be able to use  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$  (when standard conditions) or  $\Delta G = \Delta H - T\Delta S$  (nonstandard)
  - c) When  $-\Delta G$ , the reaction is spontaneous. (*The net reaction proceeds in the forward direction.*)  
When  $+\Delta G$ , the reaction is not spontaneous. (*The net reaction proceeds in the reverse direction.*)
    - i) If have  $+\Delta S$ , increasing the temperature will increase the tendency of the rxn to occur spontaneously.
    - ii) If have  $-\Delta S$ , increasing the temperature will decrease the tendency of the rxn to occur spontaneously.
  - d) When  $\Delta G = 0$ , the system is at equilibrium. (Forward and reverse rxn's occur with equal preference.)
    - i) One can calculate the temperature at which the sign of  $\Delta G$  changes by setting  $\Delta G = 0 = \Delta H - T\Delta S$  and solving for T. (One could also use standard state values.)
    - ii) Since systems are at equilibrium during phase transitions (bp, mp, fp...etc.), one can calculate the change in entropy during a phase transition by setting  $\Delta G = 0 = \Delta H - T\Delta S$ . For example, to determine the  $\Delta S$  for vaporization of water, one would plug in  $\Delta H_{\text{vap}}$  of water and BP of water.

## 5) Gibb's Free Energy and Chemical Equilibrium

a)  $\Delta G = \Delta G^\circ + RT \ln Q$  (Equation will be given on test.) Remember:  $\Delta G^\circ$  is a constant, but  $\Delta G$  changes with changing  $Q$  values (not at standard state conditions).

i) For a spontaneous reaction, as the net reaction proceeds towards products,  $Q$  increases. This reduces the spontaneity of the reaction and eventually, equilibrium will be reached.

ii) For a non-spontaneous reaction, as the net reaction proceeds towards the reactants,  $Q$  decreases. This increases the spontaneity of the reaction and eventually equilibrium will be reached.

b) Eventually all reversible reactions must reach equilibrium where  $\Delta G = 0$ . Thus, at equilibrium,

$$\boxed{\Delta G^\circ = -RT \ln K}$$
  $K_p$  is used for gases and  $K_c$  (or specifically  $K_{sp}$ ,  $K_a$ ,  $K_b$ ) is used for solutions.

*\*This equation is very important because it relates  $\Delta G^\circ$  to  $K$ . Thus,  $\Delta G^\circ$  tells you the relative amounts of reactants and products at equilibrium. In contrast,  $\Delta G$  tells you the direction of the net reaction at one set of conditions.*

c) Point of emphasis:  $\Delta G$  informs you of the spontaneity of a reaction. It does not inform you at all about the rate of the reaction—that is kinetics. It is quite common to have a spontaneous reaction that does not occur at any appreciable rate—usually because the activation energy is very high.