

Lecture 2 - August 27, 2009

I. chemical equilibrium

A. mass action law

1. for the reaction: $aA + bB \rightleftharpoons cC + dD$

- a.
$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = K = \text{an equilibrium constant}$$

2. concentrations are actually divided by their standard states
 - a. equilibrium constants are unitless
 - b. concentration of solutes in moles/L
 - c. concentrations of gases in bars
 - d. concentrations of pure solids, liquids, and solvents are = 1
3. K is dependent on T and I

B. K and ΔG

1. recall: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 - a. if $\Delta G^\circ < 0$, the reaction is spontaneous at T
 - b. if $\Delta G^\circ > 0$, the reaction is not spontaneous at T
2. can be related to ΔG° :

- a.
$$K = e^{-\Delta G^\circ/RT}$$

3. if $\Delta G^\circ < 0$, $K > 1$
4. if $\Delta G^\circ > 0$, $K < 1$

C. Le Châtelier's Principle

1. If equilibrium is disturbed by changes in concentrations, temperature, or pressure, the reaction will shift concentrations to return to equilibrium
2. Example: $\text{Co}(\text{H}_2\text{O})_6^{2+} + 4\text{Cl}^- \rightleftharpoons \text{CoCl}_4^{2-} + 6\text{H}_2\text{O}$ $\Delta H > 0$
 - a. $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is pink and CoCl_4^{2-} is blue
 - b. because $\Delta H > 0$, reaction is endothermic, uses heat as it proceeds
 - c. Heat + reactants \rightleftharpoons products
 - d. add heat, and reaction shift to the right, turns blue
3. temperature affects K

- a.
$$K = e^{-\Delta G^\circ/RT}$$

- b.
$$K = e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R}$$

- i. 1st term increases with increasing T
- ii. 2nd term is T independent
- c. If $\Delta H > 0$, K increases with increasing T
- d. If $\Delta H < 0$, K decreases with increasing T

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4. pressure and volume affects equilibrium, if gases are present
 - a. Example: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \quad \Delta H > 0$
 - i. 1 mole of gas converted to 2 moles of gas
 - ii. sudden increase in P
 - increases T, reaction shifts to the right
 - as it cools, shifts to the left, farther than starting position
 - b. P and V do not change K, simply shift the equilibrium position of the reaction
- D. Equilibrium and Rate
1. equilibrium can be defined as the point in a reaction where the forward and reverse rates of reaction are equal
 2. K only tells you the thermodynamically-predicted position of the reaction
 3. many reactions are slow to reach equilibrium, some never do
 4. catalysts
 - a. a catalyst increases the rate of a reaction
 - b. provides an alternative, faster pathway from reactants to products
 - c. does not change the energy difference between the two
 - d. does not change K or the ΔG° for the reaction, only the rate at which equilibrium is reached
- E. Solubility product
1. K_{sp}
 2. the equilibrium constant for a reaction in which a solid is in equilibrium with its dissolved ions
 3. Example mercurous chloride: $\text{Hg}_2\text{Cl}_2(\text{s})$, $K_{sp} = 1.2 \times 10^{-18}$
 - a. $\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$
 - b.
$$K_{sp} = \frac{[\text{Hg}_2^{2+}(\text{aq})][\text{Cl}^-(\text{aq})]^2}{[\text{Hg}_2\text{Cl}_2(\text{s})]} = [\text{Hg}_2^{2+}(\text{aq})][\text{Cl}^-(\text{aq})]^2 = 1.2 \times 10^{-18}$$
- F. Complex formation
1. Many cations and anions react form complex ions
 2. The formation of these ions has an equilibrium constant
 3. Multiple complexes often form in stepwise fashion
 4. Example: Pb^{2+} and Cl^-
 - a. $\text{Pb}^{2+}(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{PbI}^+(\text{aq}) \quad K_1$
 - b. $\text{PbI}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{PbI}_2(\text{aq}) \quad K_2$
 - c. $\text{PbI}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{PbI}_3^-(\text{aq}) \quad K_3$
 - d. can also be written in a cumulative manner
 - e. $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightleftharpoons \text{PbI}_2(\text{aq}) \quad \beta_2$
 - f. $\text{Pb}^{2+}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightleftharpoons \text{PbI}_3^-(\text{aq}) \quad \beta_3$
 - g. $\beta_n = K_1 K_2 K_3 \dots K_n$
 5. Often exists in equilibrium with a solid
 - a. $\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \quad K_{sp}$
 - b. all of the equilibria must be satisfied simultaneously

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G. Acids and bases

1. Many compounds can exchange a proton (H^+)
2. acids increase the $[H^+]$ in solution
3. bases decrease the $[H^+]$ in solution, increase the $[OH^-]$ in solution
4. acids are proton donors, bases are proton acceptors
5. water undergoes autoprotolysis:
 - a. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ or $H_2O \rightleftharpoons H^+ + OH^-$
 - b. $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
 - c. this equilibrium occurs in all aqueous solutions!
 - d. acidity
 - e. $pH = -\log[H^+]$
 - f. $pOH = -\log[OH^-]$
 - g. $pH + pOH = 14$
 - h. strong acids and bases - dissociate completely, no K
6. weak acids
 - a. only partially dissociate
 - b. Example: acetic acid, CH_3COOH
 - c. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad K_a$
 - d. $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.75 \times 10^{-5}$ (*just an equil. constant*)
 - e. $-\log K_a = pK_a$
 - f. $pH = pK_a + \log \frac{[A^-]}{[HA]}$ (*can you derive this?*)
 - g. pH vs. pK_a
 - i. $pH < pK_a, [HA] > [A^-]$
 - ii. $pH > pK_a, [HA] < [A^-]$
 - iii. $pH = pK_a, [HA] = [A^-]$