Chapter 15: Chemical Equilibrium

- chemical equilibrium – condition where the concentration of products and reactants do not change with time

15.1 The concept of Equilibrium

- at equilibrium $k_f[A] = k_r[B]$
- $\frac{[B]}{[A]} = \frac{k_f}{k_r} = \text{cons tan t}$

15.2 The Equilibrium Constant

- equilibrium condition can be reached from either forward or reverse direction
- Cato Maximillian Galdberg (1836-1902), and Peter Wauge (1833-1900)
  - Law of mass action – relationship between concentrations of reactions and products at equilibrium
  - If $aA + bB \leftrightarrow pP + qQ$:
  - $k_c = \frac{[P]^p[Q]^q}{[A]^a[B]^b}$ (equilibrium expression)
  - equilibrium expression depends only on stoichiometry of reaction and not mechanisms
  - equilibrium constant:
    - does not depend on initial concentrations
    - does not matter if other substances present as long as they do not react with reactants or products
    - varies with temperatures
    - no units

15.2.1 Expressing Equilibrium Constants in Terms of Pressure, k_p

  - $k_p = \frac{(P_P)^p (P_Q)^q}{(P_A)^a (P_B)^b}$

15.2.2 The Magnitude of Equilibrium Constants

  - k>>1; equilibrium lies to the right; products favored
  - k<<1; equilibrium lies to the left; reactants favored

15.2.3 The Direction of the Chemical Equation and K

  - equilibrium expression written in one direction is the reciprocal of the one in the other direction

15.3 Heterogeneous Equilibria

- homogeneous equilibria – substances in the same phase
- heterogeneous equilibria – substances in different phases
- concentration of pure liquid or solid
- $\frac{\text{Density}}{M} = \frac{\text{mol}}{\text{cm}^3}$
- density of pure liquid or solid is constant at any temperature
- if pure solid or liquid is involved in a reaction, its concentration is excluded from equilibrium expression
- pure solids must be present for equilibrium to be reached even through they are excluded from equilibrium expression

15.4 Calculating Equilibrium Constants

- determining unknown equilibrium concentrations
  - 1) tabulate known initial and equilibrium concentrations

- 2) calculate change in concentration that occurs as system reaches equilibrium
- 3) use stoichiometry to determine change in concentration of unknown species
- 4) from initial concentrations and changes in concentrations, calculate equilibrium concentrations

15.4.1 Relating k_c and k_p

- PV = nRT; P = (n/V)RT = MRT
- P_A = [A](RT)
- $K_p = k_c(RT)^{\Delta n}$
    - Δn = change in moles from reactants to products

15.5 Applications of Equilibrium Constants

- equilibrium constant:
    - 1) product direction reaction mixture will proceed
    - 2) calculate concentrations of reactants and products once equilibrium is reached

15.5.1 Predicting the Direction of Reaction

- reaction quotient
    - at equilibrium Q=k
    - $Q>k$; reaction moves right to left
    - $Q<k$; reaction moves left to right

15.5.2 Calculating of Equilibrium Concentrations

15.6 Le Châtelier's Principle

- if system at equilibrium is disturbed by change in temperature, pressure or concentration then system will shift equilibrium position

15.6.1 Change in Reactant or Product Concentration

- addition of substance will result in consummation of part of added substance
- if substance removed, reaction will move to produce more of the substance

15.6.2 Effects of Volume and Pressure Changes

- reducing volume, reaction shifts to reduce number of gas molecules
- increase volume, reaction shifts to produce more gas molecules
- increase pressure, decrease volume reduces total number of moles
- pressure volume changes do not affect k as long as temperature is constant
    - changes concentrations of gaseous substances

15.6.3 Effect on Temperature Change

- endothermic: reactants + heat ↔ products
- exothermic: reactants ↔ products + heat
- increase temperature, equilibrium shifts in direction that absorbs heat
- endothermic: increase T, increase k
- exothermic: increase T, decrease k
- cooling shifts equilibrium to produce heat

15.6.4 The Effect of Catalysts

- catalysts increase rate at which equilibrium is obtained
- does not change composition of equilibrium mixture