Chapter 15

Section 15.1 Students should know that physical or **chemical equilibrium** can be approached from either reaction direction and is achieved when the forward and reverse reaction rates are the same. It is important to understand that chemical equilibria may correspond to comparable amounts of reactants and products or lie to the left (reactant favored) or the right (product favored).

Section 15.2 Students should know that the **mass action expression** or the expression for the **equilibrium constant, K_c**, for a chemical reaction is the ratio of the equilibrium molar concentrations of the products divided by the equilibrium molar concentrations of the reactants, each raised to the respective stoichiometric coefficient in the balanced equilibrium equation. The **equilibrium constant, K_p**, for equilibria involving gases uses the equilibrium partial pressure of products and reactants in place of molar concentrations. The equilibrium constant for a specific chemical equilibrium varies only with the temperature.

$$\text{for the reaction: } aA + bB \Leftrightarrow cC + dD$$

$$\text{if the reactants and products are in solution, then } K_C = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

$$\text{or if reactants and products are in the gas phase, then } K_P = \frac{(P_C)^c \cdot (P_D)^d}{(P_A)^a \cdot (P_B)^b}$$

$$\text{where } [X] = \text{molarity of X; and } P_X = \text{partial pressure of X}$$

Section 15.3 Students should know that the reverse of a reaction has an equilibrium constant that is the reciprocal of the *K* of the forward reaction. You should know that if reactions are summed to give an overall reaction, their equilibrium constants are multiplied together to obtain an overall equilibrium constant. Doubling the coefficients of a reaction equation means that the value of the equilibrium constant is squared.

Section 15.4 Students should know that the **reaction quotient (Q)** is the value of the mass action expression for concentration (or partial pressures) of reactants and products that may or may not be at equilibrium. If $Q < K$, the reaction proceeds in the forward direction. If $Q > K$, it runs in reverse. At equilibrium, Q = K. The equilibrium constant is a thermodynamic property of a chemical reaction: the greater the decrease in standard free energy, the larger the value of the equilibrium constant.

Section 15.5 Students should know that the free-energy change ΔG of a reversible reaction and its reaction quotient Q are related: **$\Delta G = \Delta G^o + RT \ln Q$**, where ΔG^o is the standard free-energy change. At equilibrium, ΔG is zero and Q = K. This leads to **$\Delta G^o = -RT \ln K$**, which can be used with a known value of ΔG^o to calculate the equilibrium constant K at any temperature. A negative value of ΔG^o corresponds to K > 1 and a positive ΔG^o corresponds to K < 1.

Section 15.6 Students should know that **heterogeneous equilibria** involve more than one phase (for example, gas and solid). The concentrations of **pure liquid and solids** do not change during a reaction and so are omitted from equilibrium constant expressions.

Section 15.7 Students should know that according to **Le Châtelier's principle,** systems (including chemical reactions) at equilibrium respond to stress by shifting position to relieve the stress. Adding or removing a reactant or product, or applying pressure to a reaction mixture that includes gases, creates stress that shifts the position of a chemical equilibrium. <u>A catalyst decreases the time it takes a system to achieve equilibrium, but it does not change the value of the equilibrium constant.</u>

Section 15.8 Students should know that equilibrium constants K_c or K_p can be calculated from known equilibrium concentrations or equilibrium partial pressures. Also, be aware that the equilibrium concentrations or pressures of reactants and products can be calculated from initial concentrations or pressures, the reaction stoichiometry, and the value of the equilibrium constant.

Section 15.9 Students should know that higher reaction temperatures increase the equilibrium constant of an endothermic reaction but decrease the equilibrium constant of an exothermic reaction. You need to understand how the slope and intercept of a plot of ln K versus 1/T for an equilibrium system can be used to determine the standard enthalpy and standard entropy changes for the equilibrium, respectively.