Chemical Equilibrium

Equilibrium - The forward and reverse reactions occur at equal rates; the concentrations of the reactants and products remain constant.

The Equilibrium Expression:

- For the reaction **$aA + bB \Leftrightarrow cC + dD$**

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- For solutions, concentrations are expressed as molarities.
- Called the Law of Mass Action.
- If the direction of the reaction is reversed, the new value of K is the reciprocal of the original value (1/K).
- If two reactions are added, the new value of K is the product of the two individual values.

Equilibria for Gases:

- It is more convenient to measure partial pressures of gases, rather than molarities.
- For the reaction **$aA_{(g)} + bB_{(g)} + \ldots \Leftrightarrow gG_{(g)} + hH_{(g)}$**

$$K_p = \frac{(P_H)^h (P_G)^g}{(P_A)^a (P_B)^b}$$

- The relationship between the partial pressure equilibrium constant and the concentration equilibrium constant is:

$$\mathbf{K_p = K(RT)^{\Delta n(gas)}}$$

$\Delta n_{(gas)}$ is the change in the number of moles of gas as the reaction proceeds in the forward direction.

Equilibria for Solids and Liquids:

- Solids and liquids are not included in the equilibrium expression since their concentrations do not change during the reaction - they are pure.

Interpreting Different Values for K:

- When K > 1, the reaction is favored.

- A very large value for K means that the reaction goes to completion (it is not reversible).
- A very small value for K means that the forward reaction, as written, does not occur significantly.

The Reaction Quotient (Q):

- Has the same form as the equilibrium constant but uses initial concentrations, not the concentrations at equilibrium.

$$Q = \frac{[C]_0^c \, [D]_0^d}{[A]_0^a \, [B]_0^b}$$

- Is used to show the shift from initial concentrations to equilibrium concentrations.
- Allows us to predict the direction in which the net reaction must occur in order to establish equilibrium.

If Q is greater than K:

- The ratio of initial concentrations of products to reactants is too large. To reach equilibrium products must be changed to reactants. The system proceeds to the left.

If Q is less than K:

- The system must proceed to the right in order to create more products.

If Q is equal to K:

- The initial concentrations are the equilibrium concentrations. No shift will occur.

LeChatelier's Principle:

- If a stress is applied to a system at equilibrium, the position of the equilibrium will shift in the direction which reduces the stress.

1. Adding or removing reactants and products:

- Changing the concentration of a reactant or product will cause a shift to reestablish equilibrium. For example: if a reactant's concentration is increased, the equilibrium position will shift to the right, giving more products.
- If the component removed or added is a pure solid or liquid in a heterogeneous equilibrium mixture, there will be no change in the equilibrium position.

2. Changing Pressure or Volume in Gaseous Equilibria:

- Adding or removing one of the gaseous components will cause an increase or decrease in that gases partial pressure, causing a shift in the equilibrium position to compensate.
- Increasing the external pressure will increase the partial pressures of all the components by reducing the volume. The equilibrium will shift in the direction which gives the lowest number of moles of gas.
- Decreasing the external pressure will increase the volume. The equilibrium will shift in the direction which gives the largest number of moles of gas.
- If there is no difference in the number of moles of gas on the reactants side and the products side, a change in external pressure will not change the equilibrium position.
- If an inert gas is added to a system at constant external pressure, the volume of the gas mixture increases, giving the same effect as increasing the volume.
- If an inert gas is added to the system at constant volume, the equilibrium position stays the same.

3. Changing the Equilibrium Temperature:

- Changes the value of K.
- For an exothermic reaction, raising the temperature favors the reactants.
- For an endothermic reaction, raising the temperature favors the products.
- Remember - most solid solutes increase their solubility with increases in temperature (more of the solute will dissolve before equilibrium is reached).

4. Adding a Catalyst:

- A catalyst does not shift the equilibrium position, it just lowers the activation energy (allows the reaction to proceed at a faster rate).

Equilibrium Calculations:

The notes for this section will be given in class. Please read through the sample textbook problems and try working them for yourself. REVIEW QUADRATIC EQUATIONS !!!!!!!