# Equilibrium

**Objective 1**: Outline the characteristics of systems in dynamic equilibrium.

1. System must be reversible and a closed system.
2. The rate of the forward process is equal to the rate of the reverse.
3. The concentrations of the reactants and products are constant.
4. It appears that no further reaction is occurring.
5. Reactants AND Products are present at equilibrium.

**Objective 2:** Deduce the equilibrium constant expression from the equation for a homogenous (same phase) or heterogenous (mixed phase) reaction

- $K_c$ K=Equilibrium Constant C=Concentration
- Example Reaction: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$
    - $K_c = \frac{(NH_3)^2}{(N_2)(H_2)^3}$ PRODUCTS ALWAYS ON TOP
- Equilibrium Expression = Law of Mass Action
- $K_c$ for a given system depends only on Temp
- $C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g)$
    - When phases are mixed, Solids, and Liquids don't appear in the $K_c$ Expression
    - $K_c = \frac{(CO)(H_2)}{(H_2O)}$ PRODUCTS ALWAYS ON TOP

**Objective 3:** Deduce the extent of a reaction from the magnitude of the $K_c$

- $K_c \gg 1$: Products highly favored at equilibrium
- $K_c \ll 1$: Reactants highly favored at equilibrium

**Objective 4:** Apply LeChatliers' Principle to predict the qualitative effects of certain stimulation on a system at equilibrium.

- LeChatliers' Principle: When a stress acts on a system at equilibrium, the system shifts to counteract the stress and returns to Equilibrium.
- Concentration:

- Increase in (reactant) causes the system to shift toward the right
- Decrease in (reactant) causes the system to shift to the left
- Pressure changes cause shifts only if there are different numbers of moles on the left and right
- If pressure increases due to a decrease in volume, the system will shift toward the side with fewer gas moles
- If the pressure decreases due to an increase in volume, the system will shift toward the side with more gas moles.
- *If pressure increases due to the addition of a nonreactive gas, it has no effect. Look for Noble Gases but any Gas that does not react fits.

- Temperature:
  - When a reaction is endothermic, heat energy is a reactant. When a reaction is exothermic, heat energy is a product.
  - An increase in temp on an endothermic reaction shifts the system to the right while an increase in temperature on an exothermic system shifts the system to the left.
  - Endothermic: Energy + A + B ↔ C + D   $K_c$ ↑ as Temp ↑
  - Exothermic: A + B ↔ C + D + energy   $K_c$ ↓ as Temp ↓

**Objective 5:** State and explain the effect of a catalyst on an equilibrium system.

- The catalyst has no effect on the equilibrium position of the equilibrium constant since it increases the rates of both the forward and reverse reactions

**Objective 6:** Relate $K_c$ values for closely related systems.

- Ex: $N_2$ (g) + $3H_2$ (g) ↔ $2NH_3$ (g)
  - $K_c = \frac{(NH_3)^2}{(N_2)(H_2)^3}$
  - So for $NH_3$ ↔ $N_2$ (g) + $3H_2$ (g)   $K_2 = \frac{1}{K_1}$
  - If $2N_2 + 6H_2 \leftrightarrow 4NH_3$   $K_3 = \frac{(NH_3)^4}{(N_2)^2(H_2)^6}$

- $K_c$ for a reaction that is the sum of several elementary steps is the product of the $K_c$ values for the steps
- For Example: $Cu(OH)_2$ (s) ↔ $Cu2^+$ (aq)     is defined as $K_1$
  - $Cu^{2+}$ (aq) + $4NH_3$ ↔ $Cu(NH_3)^{2+}$ (aq)     is defined as $K_2$
  - Adds together to: $Cu(OH)_2$ (s) + $4NH_3$ ↔ $2OH^-$ (aq) + $Cu(NH_3)_4^{2+}$
  - $K_c = K_1 \cdot K_2$
- Example 2:
  - $SO_2$ (g) $\frac{1}{2}O_2$ (g) ↔ $SO_3$     is defined as $K_1$
  - 2SO3 (g) ↔ 2SO2 (g) + O2(g)     is defined as $K_2$
  - How is $K_1$ related to $K_2$?

    a) $K_2 = (K_1)^2$

    b) $(K_2)^2 = K_1$

    c) $K_2 = K_1$

    d) $K_2 = \frac{1}{K_1}$

    e) $K_2 = \frac{1}{(K_1)^2}$

**Objective 7:** Define Q (reaction quotient) and use its value to determine what a system must do to reach equilibrium.

- Q = $K_c$ expression filled with nonequilibrium concentrations
- 3 possibilities for Q
  - $Q = K_c$ System is at equilibrium
  - $Q > K_c$ System must proceed left
  - $Q < K_c$ System must proceed right
- Example: A mixture at 500 K contains $I_2$ at a concentration of 0.020 M and I at a concentration of $2x10^{-9}$. Is the reaction at equilibrium? If not, which direction must the reaction proceed? Given $I_2$ ↔ 2I  and $K_c$=$5.6x10^{-12}$

- $Q = \frac{(I)^2}{(I_2)} = \frac{(2x10^9)^2}{(0.020)} = 1x10^{-16}$ $Q<K_c$ system must proceed to the right