Chapter 17
Chemical Equilibrium – The Extent of Chemical Reactions

**Equilibrium**

**At Equilibrium:**
- the rate at which products are consumed equals the rate at which products are produced.
- concentration of reactants and products remain constant with time (steady state)

**Viewed at a submicroscopic level:**
- both reactions (forward and reverse reactions) are still going on like crazy, just occurring at the same rate!!

**Viewed at the human level**
- No changes in concentration with time i.e. a steady state situation.
Equilibrium

For the general elementary step:

\[ aA + bB \overset{K_f}{\rightleftharpoons} cC + dD \]

Write the rate laws for the forward and reverse reactions.

Rate for forward reaction = 

Rate for reverse reaction = 

At equilibrium... rate of forward reaction = rate of reverse reaction.

Rearrangement leads to the **Equilibrium Constant** and the **Equilibrium Constant Expression**.

On what does the value of the Equilibrium Constant depend?

Sample Questions

1. What does the value of \( K_c \) tell you about the concentrations of the products relative to the concentration of the reactants at equilibrium for the following reactions.
   a. \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \); \( K_c = 1.7 \times 10^3 \) at 500 K.
   b. \( N_2O_4(g) \rightleftharpoons 2 NO_2(g) \); \( K_c = 4.64 \times 10^{-3} \) at 25 °C.

2. In general if \( K_c \gg 10^3 \), what does this tell you about the concentrations of reactants and products at equilibrium? if \( K_c \ll 10^{-5} \)? if \( 10^{-5} < K_c < 10^3 \)?

3. For each of the following reactions, write the equilibrium constant expression.
   a. \( 4 NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6 H_2O(g) \)
   b. \( 3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4 H_2(g) \)
   c. \( 2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g) \)
   d. \( SiCl_4(g) + 2H_2(g) \rightleftharpoons Si(s) + 4HCl(g) \)
   e. \( 2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \)
   f. \( Hg^{2+}(aq) + 2 Cl^-(aq) \rightleftharpoons HgCl_2(s) \)
   g. \( 2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(l) + CO_2(g) \)

4. An equilibrium mixture of \( N_2 \), \( H_2 \), and \( NH_3 \) at 700 K contains 0.036 M \( N_2 \) and 0.15 M \( H_2 \). At this temperature, \( K_c = 0.29 \), for the reaction

\[ N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \]

What is the concentration of \( NH_3 \)? (5.9 x 10^{-3} M)
Mathematical Manipulation of Kc

Calculate the numerical value of the equilibrium constant for each reaction below given the following: \( \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \) \( K_c = 4.1 \times 10^8 \) at 25 °C

a. \( 2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g) \) \( K_c = ? \)

What happens to the value of \( K_c \) when the reaction is reversed?

b. \( 3 \text{N}_2(g) + 9 \text{H}_2(g) \rightleftharpoons 6 \text{NH}_3(g) \) \( K_c = ? \)

What happens to the value of \( K_c \) when the coefficients are multiplied?

c. \( \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightleftharpoons \text{NH}_3(g) \) \( K_c = ? \)

d. \( \text{NH}_3(g) \rightleftharpoons \frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \) \( K_c = ? \)

For Gas Phase Reactions...

One can write the equilibrium constant (Kp) in terms of partial pressure

\[ \text{aA(g) + bB(g) } \rightleftharpoons \text{cC(g) + dD(g)} \]

\[ K_p = ?? \]

\[ P_{total} = \sum P_i = P_a + P_b + P_c + P_d \]

Write the equilibrium constant expression in terms of partial pressures (K_p) for the following reactions:

1. \( \text{CH}_4(g) + 2 \text{H}_2(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{H}_2(g) \)
2. \( 2 \text{NO(g) + O}_2(g) \rightleftharpoons 2 \text{NO}_2(g) \)
3. \( 4 \text{NH}_3(g) + 5 \text{O}_2(g) \rightleftharpoons 4 \text{NO}(g) + 6\text{H}_2\text{O(g)} \)
4. \( 3 \text{F}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ClF}_3(g) \)
5. \( \text{CH}_4(g) + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g) + 3 H}_2(g) \)
Relationship between $K_c$ and $K_p$

The pressure of each component in a mixture of ideal gases is directly proportional to its molar concentration

1. Use the equilibrium shown below to derive an equation relating $K_c$ to $K_p$.
   \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad K_c = 2.8 \times 10^2 \text{ at } 727 \text{ °C} \]
   For this reaction, what is the numerical value of $K_p$ at 727°C?

2. What is the general form of the equation relating $K_p$ to $K_c$?

Sample Questions

1. Hydrogen is produced industrially by the steam-hydrocarbon re-forming process. The reaction that takes place in the first step of this process is:
   \[ \text{H}_2\text{O}(g) + \text{CH}_4(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \]
   a. If $K_c = 3.8 \times 10^{-3}$ at 1000 K, what is the value of $K_p$ at the same temperature?
   b. If $K_p = 6.1 \times 10^4$ at 1125 °C, what is the value of $K_c$ at the same temperature?

2. In the industrial synthesis of hydrogen, mixtures of CO and H$_2$ are enriched in H$_2$ by allowing the CO to react with steam. The chemical equation for this so-called water-gas shift reaction is
   \[ \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \]
   What is the value of $K_c$ at 700 K if the partial pressures in an equilibrium mixture at 700 K are 1.31 atm of CO, 10.0 atm of H$_2$O, 6.12 atm of CO$_2$, and 20.3 atm of H$_2$? (9.48)

3. Nitric oxide reacts with oxygen to give nitrogen dioxide, an important reaction in the Ostwald process for the industrial synthesis of nitric acid:
   \[ 2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \]
   If $K_c = 6.9 \times 10^3$ at 227 °C, what is the value of $K_p$ at this temperature? If $K_p = 1.3 \times 10^3$ at 1000 K, what is the value of $K_c$ at 1000K? (at 500 K: $K_p = 1.7 \times 10^2$; at 1000 K: $K_c = 1.1$)