

CHM 101 LECTURE NOTE

COURSE TITLE: INTRODUCTORY PHYSICAL CHEMISTRY

CREDIT UNIT: 03

PART TITLE: CHEMICAL EQUILIBRIUM

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COURSE SYNOPSIS

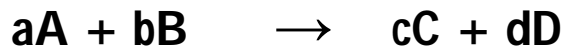
- **The concept of equilibrium**
- **Equilibrium Law (Law of Mass action)**
- **Relationship between K_p and K_c**
- **Relationship between ΔG and K**
- **Effect of temperature on the equilibrium constant.**
- **Homogenous chemical equilibria**
- **Heterogeneous equilibria system**
- **Factors affecting equilibrium constants**
- **Chemical equilibrium in solution**
 - **water dissociation constant**
 - **hydrolysis and hydrolysis constant**
- **Solubility equilibria**
- **Common-ion effects**

RECOMMENDED TEXTBOOKS/ REFERENCES

- 1. Principle of physical chemistry by J.M. Gross**
- 2. Physical chemistry by Atkins**
- 3. Essentials of physical chemistry by Bahl and Bahl**
- 4. Chemistry: The central science by Brown, Lemay,
Bursten and Murphy.**
- 5. Physical chemistry by K.K. Sharma and L.K. Sharma**

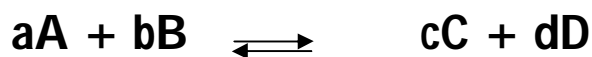
Concept of Equilibrium

Consider this direct reaction,



The reaction stops when the reactants are used up.

However, for a reversible reaction like this



the equilibrium is attained when the rate of forward reaction is equal to the rate of backward reaction.

Chemical equilibrium is the state of a reversible reaction when the two opposing reactions occur simultaneously.

At equilibrium, the concentrations of reactants and products do not change with time.

The Equilibrium Law (Law of Mass action)

The law states that "at constant temperature, the rate at which a substance reacts is directly proportional to the active masses of the reactant"

Active mass is a thermodynamic quantity and it is expressed $a = fc$, where a - active mass, f - activity co-efficient (fugacity), c - molar concentration.

For ideal gaseous and solution reaction, $f = 1$.

Therefore, the active mass is equal to molar concentration.

According to the law, $R_f \propto [A]^a [B]^b$

$$\Rightarrow R_f = K_f [A]^a [B]^b$$

Also, $R_b \propto [C]^c [D]^d$

$$\Rightarrow R_b = K_b [C]^c [D]^d$$

At equilibrium, $K_f [A]^a [B]^b = K_b [C]^c [D]^d$

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

K_c is the equilibrium constant in term of concentration,

In term of activities,

$$K_A = \left\{ \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} \right\},$$

The concept of activity addresses the deviation from ideal behaviour. Therefore, it can be defined as an idealized concentration. K_A is exact and does not depend on pressure.

In term of pressure,

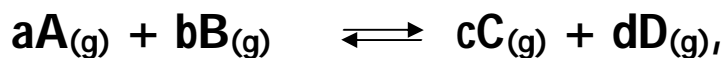
$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad \text{where } P_A^a, P_B^b, P_C^c \text{ and } P_D^d \text{ are the}$$

partial pressure of various gaseous species at equilibrium.

Relationship between K_p and K_c

In a gaseous reaction, the concentration of the gases at any given temp is expressed in term of their partial pressures.

Consider this gaseous reaction



the equilibrium constant in term of pressure is expressed as

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad \text{where } P_A^a, P_B^b, P_C^c \text{ and } P_D^d \text{ are the}$$

partial pressure of various gaseous species at equilibrium.

However, K_p and K_c are not numerically equal, the relationship can be derived as follow

For an ideal gases,

$$PV = nRT$$

$$\Rightarrow P = \frac{n}{V} RT$$

$$\text{But } \frac{n}{V} = C$$

$$\therefore P = CRT$$

$$K_p = \frac{C_C^c (RT)^c C_D^d (RT)^d}{C_A^a (RT)^a C_B^b (RT)^b}$$

$$= \frac{C_C^c C_D^d (RT)^{(c+d)}}{C_A^a C_B^b (RT)^{(a+b)}}$$

Recall that

$$K_c = \frac{C_C^c D_D^d}{A_A^a B_B^b}$$

$$\therefore K_p = K_c (RT)^{\Delta n}$$

Where $\Delta n = (c+d) - (a+b)$ i.e change in the amount of gaseous reagents

When Δn is positive, \Rightarrow the number of molecules of products are larger than those of the reactants i.e $K_p > K_c$

When Δn is zero, \Rightarrow the number of molecules of products = the number of molecules of the reactants i.e $K_p = K_c$

When Δn is negative, \Rightarrow the number of molecules of products are smaller than those of the reactants i.e $K_p < K_c$

If the equilibrium constant is expressed in term of mole fractions, X it is related to K_p by

$$K_p = \frac{(X_C P)^c (X_D P)^d}{(X_A P)^a (X_B P)^b}$$

$$K_p = \left(\frac{(X_C)(X_D)}{(X_A)(X_B)} \right) \times P^{(c+d)-(a+b)}$$

$$\therefore K_p = K_x P^{\Delta n}$$

where $\Delta n = (c+d) - (a+b)$

Relationship between ΔG and the equilibrium constant

The change in free energy of a reaction and the equilibrium constant K are related to each other by the expressions

$$\Delta G^\circ = -RT \ln K$$

Temperature dependence on the equilibrium constant

The value of equilibrium constant varies with temperature change. The relationship between the equilibrium constants at two different temperatures and the enthalpy change is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 \times T_2} \right]$$

Where K_{p_2} and K_{p_1} are the equilibrium constants at temperature T_2 and T_1 respectively.

In terms of change in internal energy (ΔE°), the equation becomes

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta E^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$