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,

$aA + bB \longrightarrow cC + dD$

The reaction stops when the reactants are used up.

However, for a reversible reaction like this

$aA + bB \rightleftharpoons cC + dD$

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, $R_f \; \alpha \; [A]^a [B]^b$

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

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

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

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,

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A^a, P_B^b, P_C^c **and** P_D^d **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

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)},$$

the equilibrium constant in term of pressure is expressed as

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A^a, P_B^b, P_C^c **and** P_D^d **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,

$$PV = nRT$$

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

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

$$\therefore \quad P = CRT$$

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

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

Recall that

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

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

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** $K_p \succ K_c$

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** $K_p \prec K_c$

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

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

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

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

where Δn **=** $(c+d)-(a+b)$

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

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

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

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H^o}{2.303R}\left[\frac{T_2 - T_1}{T \times_1 T_2}\right]$$

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^o), the equation becomes

$$\log\frac{K_{p_2}}{K_{p_1}} = \frac{\Delta E^o}{2.303R}\left[\frac{T_2 - T_1}{T \times_1 T_2}\right]$$