CHAPTER 5

CHEMICAL EQUILIBRIUM

5.1 CHARACTERISTICS OF EQUILIBRIUM STATE

Chemical equilibrium: Chemical equilibrium is the most important characteristic property of a reversible reaction. At equilibrium state, concentration of all reactants and all products do not change with time chemical equilibrium is attained only when rate of forward reaction becomes equal to the rate of backward reactions. Chemical equilibrium is dynamic in nature. Therefore, it is also called pseudo steady state.

Considering a simple reversible reaction $A + B \longrightarrow C + D$

For forward reaction, i.e., $A + B \xrightarrow{K_f} C + D$

For backward reaction, i.e., $C + D \xrightarrow{K_b} A + B$

If we plot a curve between rate of reaction versus time, we get



5.1.1 Characteristics of Equilibrium State

- (i) Equilibrium state can be achieved if a reversible reaction is carried out in closed space. However, this condition holds only for gaseous phase reaction.
- (ii) Chemical equilibrium is attained from either side, i.e.,

 $2SO_3 \Longrightarrow 2SO_2 + O_2;$ $2SO_3 + O_2 \Longrightarrow 2SO_3$

- (iii) Chemical equilibrium is attained earlier by using a catalyst; however, the presence of the catalyst does not alter the equilibrium state.
- (iv) It is dynamic in nature, i.e., reaction does not stop but both forward and backward reactions take place at equal rate.
- (v) Change of pressure, concentration or temperature favours one of the reaction (forward or backward) resulting in shift of equilibrium point in one direction. If we plot a curve between concentration versus time, there are three possibilities.

5.2 LAW OF MASS ACTION

This law was proposed by Guldberg and Wage: According to this law, the rate of chemical reaction is directly proportional to the product of the active masses of the reacting substances.

For a general reversible reaction, $aA + bB \implies mM + nN$

According to law of mass action

Rate of the forward reaction, $r_f \alpha [A]^a [B]^b$ or $r_f = K_f [A]^a [B]^b$ Rate of the reverse reaction, $r_b \alpha [M]^m [N]^n$ or $r_b = K_b [M]^m [N]^n$ At equilibrium, rate of forward reaction = rate of backward reaction i.e., $k_f [A]^a [B]^b = K_b [M]^m [N]^n$

$$\Rightarrow \frac{k_f}{k_b} = k_{eq} = k_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} = \text{equilibrium constant}$$

where k_c is equilibrium constant in terms of concentration.

5.3 RELATIONSHIP BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

Relationship between K_p and K_c:

 $K_p = k_c RT^{\Delta n}$, where $\Delta n = n_p - n_R$ = number of mole of gaseous product – number of mole of gaseous reactant

- $K_p = Equilibrium$ constant in terms of prassure
- $K_c =$ Equibrium constant in terms of conscentration
- $K_x =$ Equilibrium constant in terms of mole fraction
- $K_n =$ Equilibrium constant in terms of moles

Relationship between K_p and K_x:

$$k_p = k_x (P_t)^{\Delta r}$$

Relationship between K_p and K_n : $k_p = k_n \left(\frac{P_t}{\Sigma n}\right)^{\Delta n}$

a α [M] or a = $\gamma \times$ [M]

 \therefore [M] = molar concentration

 α = active mass

 γ = activity coefficient

Activity coefficient for dilute solution $\gamma = 1$.

- Thus if rate µ active mass
- \Rightarrow Rate μ molar concentration.

5.4 EFFECT OF ALGEBRAIC OPERATION ON EQUILIBRIUM CONSTANT

 The equilibrium constant of a forward reaction and that of its backward reaction are reciprocal of each other.

E.g.,
$$2SO_3 \rightleftharpoons 2SO_2 + O_2; k_f = \frac{|SO_2|^2|O_2|}{|SO_3|^2}$$

 $2SO_2 + O_2 \rightleftharpoons 2SO_3; k_b = \frac{|SO_3|^2}{|SO_2|^2|O_2|} \implies k_f = \frac{1}{k_b}$

(ii) If a chemical reaction is multiplied by a certain factor, its equilibrium constant must be raised to a power equal to that factor in order to obtain the equilibrium constant for the new reaction.

E.g., for NO +
$$\frac{1}{2}O_2 \rightleftharpoons NO_2$$
; $k_{c_1} = \frac{[NO_2]}{[O_2]^{1/2}[NO]}$; 2NO + $O_2 \rightleftharpoons 2NO_2$; $k_{c_2} = \frac{[NO_2]^2}{[NO]^2[O_2]}$

 $\Rightarrow k_{c_1} = (k_{c_2})^2$

(iii) If two or more reversible reactions are added to give a net reversible reaction, then the equilibrium constant of net reaction is product of equilibrium constant of individual reversible step added.

Example:
$$\frac{S + O_2 \rightleftharpoons SO_2, K_1}{S + \frac{1}{2}O_2 \rightleftharpoons SO_3, K_2}$$
$$\frac{SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3, K_2}{S + \frac{3}{2}O_2 \rightleftharpoons SO_3, k_3 = k_1.k_2}$$

Note:

- (i) If number of moles of product is equal to number of moles of a reactant, i.e., $\Delta n = 0$ $\Rightarrow k_p = K_c = k_r = k_n$
- (ii) For a mixture of real gases, $\gamma_i = \frac{f_i}{P_i} \implies f_i = \gamma_i P_i$, where f_i is fugacity of i^{th} component.

5.5 MASS ACTION RATIO, I.E., REACTION QUOTIENT

Reaction Quotient: At any point in a reversible reaction, ratio of the concentration terms in the same form as in the equilibrium constant expression can be formulated. This ratio is referred to as reaction quotient or mass action ratio (Q_c).



5.6 SPONTANEITY OF A REACTION

If the free energy change of a chemical reaction is negative, the reaction can take place spontaneously, i.e., it is feasible. If the free energy change is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed. For a reaction to be spontaneous, ΔG must have a negative value.

 $\Delta G = \Delta H - T\Delta S$ for which ΔH should be negative and T ΔS should be positive.

Role of temperature: Temperature being a multiplying parameter for entropy factor ($T\Delta S$) of a system, plays an important role in controlling the spontaneity of a reaction.

- (a) At high temperature, the entropy factor predominates: In the case of an endothermic reaction, Δ H is always positive. Thus, the energy factor does not favour the reaction. But if the reaction is accompanied by even a small increase of entropy, the high temperature will increase the entropy factor T Δ S by a large extent. Hence, Δ G may become negative at a sufficiently high temperature. This explains that endothermic reactions become feasible at increasing temperatures.
- (b) At low temperature, energy factor predominates: In the case of an exothermic reaction, ΔH is always negative. Thus, the energy factor always tends to favour the reaction. If such a reaction takes place at a low temperature, then even if it is accompained by decrease of entropy, the opposing factor T ΔS may remain very small and therefore the value of ΔG may still have a large negative value. This points explain why exothermic reactions in many cases remain feasible at decreasing temperatures.

Standard free energy of formation of a compound: Standard free energy of formation of a compound is defined as free energy change involved in the formation of a compound in standard state (25°C and 1 atm) from its elements in their standard states. This is denoted by ΔG_F° .

$$\Delta G_{F}^{o} = \Delta H_{F}^{o} - T\Delta S_{F}^{o}$$

Standard free energy change of a reaction may be calculated with the help of standard free energy change of formation of compounds involved in the reaction, $\Delta G^{\circ} = [\Delta G_{F}^{\circ}]_{\text{products}} - [\Delta G_{F}^{\circ}]_{\text{reactants}}$.

5.7 HETEROGENEOUS EQUILIBRIA

When reactants and products present in an equilibrium have more than one phase in such a case pure solids and pure liquids have essentially constant concentrations. Thus, we ignore pure solids and pure liquids in writing equilibrium constant expression.

e.g., (i)
$$CaCO_{3}(s) \rightleftharpoons CaO(s) + CO_{2}(g)$$

 $K_{p} = p_{CO_{2}} = n_{CO_{2}} \times \frac{P}{\Sigma n}$
(ii) $3Fe(s) + 4H_{2}O(g) \rightleftharpoons Fe_{3}O_{4}(s) + 4H_{2}(g)$
 $K_{p} = \frac{(P_{H_{2}})^{4}}{(p_{H_{2}O})^{4}} = \frac{(n_{H_{2}})^{4}}{(n_{H_{2}O})^{4}} \times \left(\frac{P}{\Sigma n}\right)^{0}$

As a general rule, the concentrations of pure solids and pure liquids are not included when writing an equilibrium equation because their concentrations are constants that are incorporated into the value of the equilibrium constant. We include only the concentrations of gases and the concentrations of solutes in solutions because only those concentrations can be varied.

The equilibrium constant K_p is related to standard free energy change (ΔG°) by the relation $\Delta G^\circ = -2.303 \text{ RT} \log_{10} K_p$ at standard state, T = 25°C; P = 1 atm.

When $\Delta G^{\circ} = -ve$, forward reaction is thermodynamically feasible (K > 1)

 ΔG° = +ve or K < 1, reverse reaction is feasible.

 $\Delta G^{\circ} = 0$, then k = 1, i.e., equilibrium condition.

5.8 DEGREE OF DISSOCIATION

Degree of dissociation is defined as the fraction of one mole of a molecule dissociated. It is denoted by α . Its value is always less than 1. When the value becomes equal to 1, it is said that the substance is completely dissociated.

Experimental determination of degree of dissociation, is determined by measuring vapour density of a reaction mixture at equilibrium. Considering a general reversible reaction

	А		nB
Initial number of moles	1		0
Number of mole at equilibrium	$(1 - \alpha)$		nα
Total number of moles at equilibrium = (1	$(1 - \alpha) + n\alpha =$	= 1 + (n –	1)α.

5.8.1 Determination of Degree of Dissociation by Measurement of Vapour Denisty

If d be the observed vapour density at a particular temperature when degree of dissociation is α and D be

the vapour density when there is no dissociation, then $\alpha = \frac{D-d}{(n-1)d}$

In terms of molecular mass, $\alpha = \frac{M-m}{(n-1)m}$, where M = initial molecular mass

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m = molecular mass at equilibrium

e.g., (i)
$$PCl_5 \implies PCl_3 + Cl_2$$
, here n =
 $x = \frac{D-d}{(2-1)d} = \frac{D-d}{d}$

Degree of dissociation by using pressure-temperature determination: Consider the following gaseous reaction.

$$\begin{array}{cccc} \operatorname{PCL}_{3}(g) & \longrightarrow & \operatorname{PCL}_{3}(g) + \operatorname{CL}_{2}(g) \text{ temperature pressure} \\ t = 0 & a & 0 & 0 & T_{1} & P_{1} \\ t_{eq} & a - a\alpha & a\alpha & a\alpha & T_{2} & P_{2} \\ \Rightarrow & \alpha = \frac{T_{1} P_{2} - T_{2} P_{1}}{T_{2} P_{1}} \end{array}$$

5.9 LE CHATELIER'S PRINCIPLE AND ITS APPLICATION

Le Chatelier's Principle: According to this principle, if an equilibrium is subjected to a stress, the equilibrium adjusts in such a manner that the effect of the disturbance is minimized.

(i) **Effect of change of pressure:** By increasing the pressure, equilibrium shifts in the direction in which there is decrease in volume or less number of molecules and vice versa.

E.g., (i) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; By increasing the pressure, more NH_3 will be formed. (ii) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

By increasing the pressure less PCl₅ will be dissociated.

(ii) Effect of change of temperature: By increasing the temperature the equilibrium shifts in the direction in which heat is absorbed, i.e., in which direction reaction is endothermic. E.g., (i) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92.38 \text{ kJ}$

By increasing the temperature, formation of NH₃ decreases.

Effect of adding inert gases:

- (i) If P is a constant and Δn , = 0, K_p is unaffected by the addition of the inert gas.
- (ii) If P is constant and $\Delta n_g \neq 0$, and if we add an inert gas, equilibrium will shift in the direction where Δn_g is positive.
- (iii) If V is a constant and an inert gas is added, no change in equilibrium takes place.
- (iii) **Effect of change of concentration:** In a chemical equilibrium increasing the concentration of the reactants results in shifting the equilibrium in favour of the products while increasing the concentration of the products results in shifting equilibrium in favour of the reactants.

Le Chatelier's principle in case of physical equilibrium:

(i) Effect of pressure on boiling point:

Water = Vapour

An increase in pressure will favour backward reaction, i.e., the reaction in which volume decreases ($V_{vapour} > V_{water}$). Thus, more water will exist at equilibrium, i.e., boiling point of water (solvent) increases with increase in pressure.

- (ii) Effect of pressure on the freezing point of a liquid (or melting point of a solid)
 - (a) For ice → water equilibrium: An increase in pressure will favour forward reaction because V_{ice} is greater than V_{water}. Thus, more and more ice will melt or the melting point of ice is lowered with increase in pressure.
 - (b) For a solid \rightleftharpoons liquid equilibrium: An increase in pressure will favour backward reaction because $V_{Liquid} > V_{solid}$ and thus more solid will exist at equilibrium, i.e., melting point of solid increases with increase in pressure.

(iii) Effect of pressure on solubility of gases:

 $Gas + Solvent \Longrightarrow Solution$

 (V_{F}) (V_{b})

Since $V_F > V_b$, an increase in pressure will favour forward reaction and thus solubility of gas increases with increase in pressure.

Henry's law: It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

W(g) μ P(g) or W(g) = KP(g); where W(g) is amount of gas dissolved in solution and P(g) is the partial pressure of the gas over the solution and K is Henry's constant which is different for each gas.

(iv) Effect of temperature on solubility of solids:

(a) Solute + Solvent \implies Solution; $\Delta H = +ve$

An increase in temperature always favours endothermic process and thus solutes having endothermic dissolution (e.g., urea, glucose) show an increase in their solubility with increase in temperature.

(b) Solute + Solvent \implies Solution; $\Delta H = -ve$

Solutes having exothermic dissolution (e.g., lime, NaOH, acids, etc.) show a decrease in their solubility with increase in temperature. Le Chatelier principle is not valid for solid-solid heterogeneous equilibrium.