5. CHEMICAL EQUILIBRIUM

Synopsis:

- Based on the direction of their occurrence Chemical reactions are two types.
- **Irreversible reactions:** in these reactions reactants are converted into products and products cannot be converted into reactants.
- There are unidirectional as they occur in one direction. i.e. Reactants $\rightarrow$ products.
- These are denoted by single arrow mark.
- These reactions almost go for completion i.e. reactants are almost completely convert into products.
- Precipitation – ionic reactions, explosive reactions, strong acid – strong base neutralisation reactions, combustion- reactions are irreversible.

Eg :1) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$

2) $NH_4NO_{2(s)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

3) $C_2H_5OH_{(l)} \rightarrow 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

4) $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

5) $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

6) $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$

7) $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

Reversible reactions :

- A reaction is said to be reversible, if both the forward and the backward reactions are taking place simultaneously under the given experimental conditions.
- Reactants giving rise to products is known as forward reaction.
- Products giving rise to reactants is known as reverse reaction (or) backward reaction.
- Reversible reactions are represented by writing a pair of half headed – arrows pointing in opposite directions in between the reactants and products.

Reactants $\rightleftharpoons$ products

- A reverse reaction does not go to completion.
- Most of the reversible reactions are carried in the closed vessels.

Eg : 1) $H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)}$

2) $PCl_{5(g)} \Leftrightarrow PCl_{3(g)} + Cl_{2(g)}$

3) $2NO_{2(g)} \Leftrightarrow N_2O_{4(g)}$

4) $N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)}$

5) $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$

6) $CaCO_{3(s)} \Leftrightarrow CaO_{(s)} + CO_{2(g)}$

7) $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \Leftrightarrow CH_3COOC_2H_{5(l)}\ H_2O_{(l)}$

Equilibrium State :

- The stage or state at which the rate of forward reaction is equal to the rate of the reverse reaction in a reversible reaction is known as the equilibrium stage or state.
- The chemical equilibrium is considered as dynamic equilibrium because the forward and the reverse reactions

continue to take place simultaneously at this stage also.

- Equilibrium is established in

  i) a reversible reaction ii) in a closed vessel
- In the beginning in a reversible reaction the rate of forward reaction is more since the concentration of reactants is more.
- As time proceeds the rate of forward reaction decreases as the concentrations of reactants decreases.
- In the beginning in a reversible reaction the rate of backward reaction is absolutely zero because the concentration of products is zero.
- AS time proceeds the rate of backward reaction increases since the concentrations of products also increases.
- At one stage the rate of forward reaction becomes equal to rate of backward reaction and no further change occurs in the concentration of reactions or products.
- At equilibrium, the concentration of reactants and products may not be equal but they remain constant.

Characteristics of chemical equilibrium :

- The rate of the forward reaction is equal to the rate of the reverse reaction.
- The concentrations of the reactants and the products remain unchanged with time.
- The observable properties such as pressure, concentration, density, colour also remain unchanged with time.
- The attainment of chemical equilibrium can be recognised by the constancy in some macroscopic potteries like pressure, concentration, density, color etc.
- The equilibrium is dynamic in nature. Both the forward reaction and the reverse reaction continue to take place simultaneously with equal rates.
- A catalyst does not alter the state of equilibrium or the composition of the chemical substances of the reaction at the equilibrium. It only speeds up the attainment of the equilibrium.
- Chemical equilibrium can be established from either side of the reversible reaction.
- Chemical equilibrium can be homogeneous or heterogeneous and also ionic or molecular.
- The factors such as pressure, concentration temperature presence of inert gas influence the position of the equilibrium.
- At equilibrium, the value of Gibbs free energy change (ΔG) is zero ($\Delta G = 0$).
- At equilibrium, ΔS is maximum.
- The equilibrium does not tell us how long it takes for a reaction to attain equilibrium.
- Once equilibrium is reached, it continues forever until the conditions like pressure, temperature, concentration etc, are altered.
- At equilibrium the concentration of reactants may be equal or less or more than the concentration of products.

Law of mass action :

- This laws stated by C.M. Guldberg and P. Wage in 1863.
- This law gives the relation between the rate of a reaction and the concentration of the reactants.
- The rate of a chemical reaction at a temperature at any instant is proportional to the product of the active masses of the reactants.
- This law is applicable to all reactions i.e. reversible and irreversible occurring in the gas phase or in the liquid phase.

- $aA + bB \Leftrightarrow cC + dD$, the equilibrium constant.

$$k_c = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_f = forward reaction rate constant.

K_b = backward reaction rate constant.

- The equilibrium constant

$$k_c = \frac{\text{product of the concentration of products}}{\text{product of the concentration of reactants}}$$

- Partial pressure of the gas = mole fraction of gas $\times$ total pressure.

$$K_p = \frac{k_f}{k_b} = \frac{p_C^c . p_D^d}{p_A^a . p_B^b}$$

- $$K_p = \frac{\text{prodct of patial pressures of products}}{\text{product of partial pressures of reactants}}$$

k_c= equilibrium constant in terms of molar concentration.

k_p=equilibrium constant in terms of partial pressure.

$$\text{Active mass} = \frac{\text{no.of moles}}{\text{volume in litres}}$$

Active mass is considered for gas or liquid.

- The active mass of a solid is unity whatever may be its mass.

Types of chemical equilibrium:

- Based on the physical states of substances equilibrium is of two types.

1) Homogeneous equilibrium : All the reactants and products are present in same physical state. i.e same phase.

Eg :1) $2SO_{2(g)} + O_2 \rightleftharpoons 2SO_{3(g)}$

2) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

3) $CH_3COOC_2H_{5(l)} + H_2O_{(l)} \; CH_3COOH_{(l)} + C_2H_5OH_{(l)}$

4) $CH_3COOH_{(l)} \rightleftharpoons CH_3COO^-_{(l)} + H^+_{(l)}$

2) Heterogeneous equilibrium : Reactants and products are in different physical states or different phase.

Eg : 1) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

2) $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

3) $Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

- Relationship between k_p and k_c:

$k_p = k_c (RT)^{\Delta n}$

R = gas constant, T = absolute temperature

Δn = change in number of moles

$= n_P - n_R$ (no.of moles of gaseous products – no.of moles of gaseous reactants)

case (i) if $n_P = n_R$, $\Delta n = 0$, $k_p = k_c$

Eg. $H_2 + I_2 \Leftrightarrow 2HI$

(ii) if $n_P > n_R$, Δn = +ve, $k_p > k_c$

$PCl_5 \Leftrightarrow PCl_3 + Cl_2$

iii) If $n_P < n_R$, Δn = -ve, $k_p < k_c$

$N_2 + 3H_2 \Leftrightarrow 2NH_3$

- **Units of equilibrium constant :**

  Unit of $k_c = (\text{mol. lit}^{-1})^{\Delta n}$

  Unit of $k_p = (\text{atmosphere})^{\Delta n}$

- Writing k_c and k_p expressions and expressing their units

  I) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

  $$k_c = \frac{[HI]^2}{[H_2][I_2]}$$

  No unit for K_c

  $$k_p = \frac{P_{HI}^2}{p_{H_2} \times p_{I_2}}$$

  No unit for K_p

  ii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

  $$k_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}; \; k_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 \times P_{O_2}}$$

  $k_c = \text{lit . mol}^{-1}$; $k_p = \text{atm}^{-1}$

  iii) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

  $k_c = [CO_2]$; $k_c = \text{mol. lit}^{-1}$

  $k_p = P_{CO_2}$; $k_p = \text{atm}$

Characteristics of equilibrium constant : (k_p or k_c)

- The value of k depends on the nature of the reaction.
- The value of k will be a constant for a given reaction at a given temperature.
- The value of k depends on temperature of reaction.
- The value of k is independent of concentration and pressure.
- The value of k is independent of presence of catalyst and presence of inert gas.
- The value of k depends on stoichiometry of the equation.
- The value of k depends on mode of writing the equilibrium reaction.

Lechattelier's principle and its application to industrial processes ;

- The effect of change of pressure, concentration and temperature on equilibrium was studied by Henry Lewis Lechatterlier in 1885 and F. Brawn. So this is called Lechattelier- Brawn Principle or simply Lechattelier's principle.
- If a system at equilibrium is subjected to a stress, the system shifts the equilibrium in such a way to reduce or nullify the stress.
- Effect of concentration : Increase in concentration of reactants or decrease in concentration of products favours the shift of equilibrium towards products side and rate of forward reaction is increased.

  Increase in the concentration of the products or decrease in the concentration of reactants favours the shift of

equilibrium towards the reactant side and rate of backward reaction is increased.

Effect of pressure :

- Pressure has no effect on equilibrium if Δv or $\Delta n=0$, ($n_p= n_r$).

  Eg : $H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)}$

- Pressure has effect on equilibrium if $\Delta v \neq 0$ or $\Delta n \neq 0$, ($n_p \neq n_r$). When pressure increases, equilibrium shifts in a direction of decrease of volume or towards less mole number and vice vessa.

  Eg: $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

  When pressure increases, equilibrium shifts towards right and forward reaction rate increases.

- Pressure does not show any marked effect on equilibrium reactions taking place in the solution phase or in the solid phase.

- **Effect of temperature** : increase of temperature of the equilibrium system favours endothermic reactions, and decrease of temperature of the equilibrium system favours exothermic reactions.

- **Effect of Catalyst** : Catalyst has no net effect on equilibrium. It helps the system to attain equilibrium at a faster rate by increasing the rate of forward as well as backward reaction to the same extent.

  Eg:**(1)** Synthesis of ammonia by Haber's process:

  $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$ + heat $\Delta H = -92.0$ K.J

  Favourable conditions for high yield of NH_3:

  High pressure:200atm, Catalyst : Fe as catalyst

  Low temperature : 773 K, Promoter: small amount of molybdenum or Al_2O_3 and K_2O.

  (2) Manufacture of H_2SO_4 by the contact process.

  $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$ + Heat; $\Delta H = -189$ K.j

- Favourable conditions for higher yield of SO_3.

  I) High pressure : 1.5 – 1.7 atm.

  ii) Low temperature : 673 k

  iii) Catalyst : V_2O_5 or platinised asbestos

  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ – heat

  i) High temperature ii) No effect of pressure

  Melting of ice :

  $H_2O_{(s)}$+ heat $\rightleftharpoons H_2O$

  I) high temperature ii) high pressure