B. Sc. Hons Part I

Paper : Physical Chemistry (IA)
Topic : Chemical Equilibrium

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CHEMICAL EQUILIBRIUM

Concept of Equilibrium :—

Equilibrium is a state of a system in which there are no observable changes as time goes by. One of the key factors which dictates the position of equilibrium in any physical and chemical process is the tendency for materials to exist in the most stable thermodynamic state under given set of conditions. In equilibrium state, all the variables (viz. P, T, conc. etc.) associated with system attain a definite, constant-value, which do not change with time. The state of equilibrium may be classified into different types as given below:

A. Mechanical Equilibrium : The equilibrium in which position (or speed) ystem do not change with time is known as mechanical equilibrium. It may be of two types:

(i) Static mechanical equilibrium, e.g. a ladder placed with wall.
(ii) Dyanic mechanical equilibrium, e.g., train moving with a constant-speed.

B. Thermal Equilibrium : In thermal equilibrium, heat-content (or say temperature) of a system becomes constant- and the heat-taken or given

by the system are equal

C. Thermodynamic Equilibrium : In this state of equilibrium, the system loses its tendency for a change and all the thermodynamic properties associated with system become constant and do not change without external stimulation. It may be of two types :
(i) Physical Equilibrium
(ii) Chemical Equilibrium

D. Stable Equilibrium : In this equilibrium state, when the equilibrium of the system is slightly disturbed by an external stimulus and if this disturbance is removed then the system regains initial state of equilibrium.

E. Unstable Equilibrium : In this type of equilibrium, system can not regain the initial state of equilibrium, if it is disturbed slightly.

F. Neutral Equilibrium : An equilibrium which remains unaffected by slight disturbance is called neutral equilibrium.

G. Static Equilibrium : — In this equilibrium state the factor responsible for establishment of equilibrium does not change with time. In this equilibrium, there is no change in position.

H. Dynamic Equilibrium : In dynamic equilibrium changes occur but in opposite directions and at constant rate.

I. Pseudo Equilibrium : Sometimes a process occurs at so slow rate that it appears to be in a state of equilibrium. It is called state of pseudo equilibrium.

J. Metastable Equilibrium : If a system in equilibrium attains a new equilibrium when it is disturbed by changing reaction conditions, then it is called metastable equilibrium.

Reversible and Irreversible Reactions :→

Consider a process in which substance A is to be converted into B.

$$A \longrightarrow B$$

This change may occur in two ways :

(a) A gets converted into B, but B is not converted back into A. Such a change is known as irreversible process.

(b) A gets converted into B and simultaneously B is also converted back into A. Such changes are known as reversible processes.

Irreversible Reactions :—

In these reactions, reactants are converted into products, but products are not converted back into reactants simultaneously.

In irreversible reactions reactant/s and product/s are separated by arrow (⟶), e.g.

$A \longrightarrow B$.

Irreversible reactions always go for completion and reactants are completely converted into products. Such reactions never attain equilibrium.

Those reactions in which one or more products get separated from reaction mixture either in the form of gas or in the form of precipitate, are always irreversible.

Some irreversible reactions are given below :

(i) Thermal Decomposition : A thermal decomposition reaction having at least one gaseous product, will be irreversible, if it is carried out in open vessel; where gas/es escapes out from reaction mixture, e.g.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2(\uparrow)$$

$$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2(\uparrow)$$

(ii) Neutralisation reactions: Neutralisation reactions of strong acids and strong bases are irreversible.

e.g. $HCl + NaOH \longrightarrow NaCl + H_2O$

(iii) Precipitation reactions: These are irreversible reactions because in them products get separated as precipitates. e.g.

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl\,(\downarrow)$$

(iv) Redox reactions: eg.,

$$X + O_2 \longrightarrow XO_2\,(\uparrow) \quad (X = C \text{ or } S)$$

Reversible Reactions :—

In these reactions, reactants are converted into products and simultaneously the products are converted back into reactants. In other words, a reaction which can go in the forward and backward direction simultaneously is called a reversible reaction.

In reversible reactions, reactants and products are separated by a pair of arrows ($\rightleftharpoons$)

Reactant $\underset{\text{Backward Reaction}}{\overset{\text{Forward Reaction}}{\rightleftharpoons}}$ Product

Reversible reactions never go for completion, i.e. as soon as the reactants react to give the products and if the products are not allowed to escape, then these products react to reform the reactants. Here comes an stage where the rate of forward reaction becomes equal to the rate of backward reaction, and a reaction never goes to completion. When a reaction reaches this stage, it is said to be in a stage of chemical equilibrium, a state at which the compositions of reactants and products get fixed.

Some examples of reversible reactions are given below:

(i) Thermal Dissociation : Thermal dissociation reaction taking place in closed vessel are reversible. e.g.;

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

(ii) Neutralisation reactions : Neutralisation reactions of weak acid, weak base or both are reversible. e.g.

$$CH_2COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$HCN + NH_4OH \rightleftharpoons NH_4CN + H_2O$$

(iii) Hydrolysis : Hydrolysis of esters, inorganic salts (except those of strong acid and strong base) is also reversible. e.g.

$$RCOOR' + H_2O \overset{H^+}{\rightleftharpoons} RCOOH + R'OH$$

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$$

(iv) Esterification : e.g.

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

Physical Equilibrium

The equilibrium attained between different physical forms of a chemical entity is referred as physical equilibrium. In this state, the concentrations of different forms of substance become constant. Such equilibrium is attained in physical processes, such as fusion, freezing, evaporation etc. e.g.

$$Ice \rightleftharpoons Water$$

$$H_2O(l) \rightleftharpoons H_2O(V)$$

$$C\ (graphite) \rightleftharpoons C\ (diamond)$$

General characteristics of Physical Equilibrium :-

1. Equilibrium can be attained in closed systems

only, i.e. a system which can not exchange the mass with its surroundings. It can not be attained in open systems. e.g. It can be attained if a liquid is being evaporated in closed vessel but not in open vessel.

2. At equilibrium, all the measurable properties of system become constant and rates of two opposing processes become equal. e.g.,

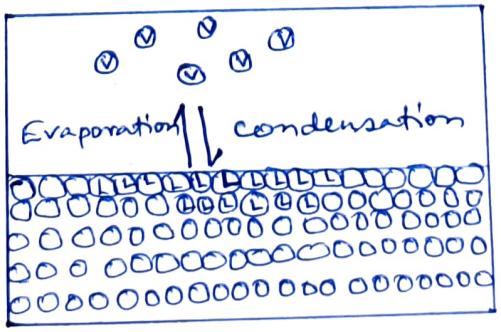
$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapour}$$

At equilibrium, rate of evaporation is equal to the rate of condensation, and vapour pressure of system becomes constant.

3. The ratio of concentrations of products and reactants becomes constant (Equilibrium constant) and value of equilibrium constant indicates the extent to which reaction has proceeded. Higher is the value of equilibrium constant, higher is the concentration of product in equilibrium mixture.

Some Important Physical Equilibria :-

(a) Liquid - vapour Equilibrium in Evaporation Process :- Let a liquid is being evaporated in a closed container. Initially only liquid molecules



are present but after sometime, the vapours above the liquid surface achieve an equilibrium with liquid. e.g.; $\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapour}$

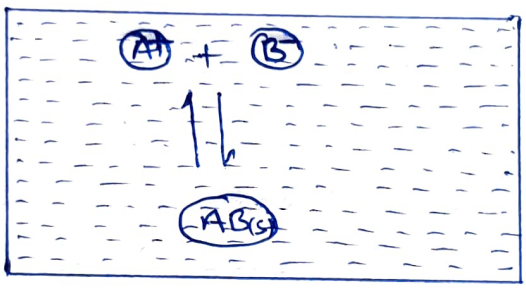
At equilibrium,

Rate of evaporation = Rate of condensation

Thus at equilibrium, the two opposing processes occur simultaneously at equal rates and so it is a dynamic equilibria.

(b) Solute + Solvent – Saturated Solution Equilibria in Dissolution Process :— A saturated solution is also an example of physical equilibria where solute (solid) is in equilibrium with the ions dispersed in solvent (liquid). In saturated solution undissolved solute is in equilibrium with dissolved solute. Additional solute will not dissolve if added to a saturated solution. e.g. Saturated solution of AB :

$$AB + H_2O \underset{\text{Crystallisation}}{\overset{\text{Dissolution}}{\rightleftharpoons}} AB_{(\text{saturated solution})}$$



As a solid solute starts to dissolve in a solvent, the concentration of solute particles in solution increases, so the chances of their collisions with the surface of the solid increases. Such collisions may result in the solute particles to become a part of the solid (Crystallization).

At equilibrium the rate at which ions leave the solid surface (dissolution) is equal to the rate at which ions are removed from the solution to become part of solid (crystallization), and then no further net increase in the amount of solute in solution occurs.

The solubility of a solid in a liquid depends upon temperature, nature of solute, nature of solvent etc. It is also a dynamic equilibrium.

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