EQUILIBRIUM

EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

✤ CHEMICAL EQUILIBRIUM

The state of the reversible chemical reaction at which rate of forward reaction becomes equal to rate of backward reaction.

$$\begin{array}{c} R_{f} \\ A + B \\ \hline \\ R_{b} \\ R_{f} = \text{forward rate of reaction} \\ R_{b} = \text{backward rate of reaction} \\ R_{f} = R_{b} \end{array}$$

i.e.

or the state of the reversible chemical reaction at which the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time at the given set of conditions is said to be chemical equilibrium conditions. Rate of forward reaction decreases as the concentration of products increases; rate of backward reaction also starts increasing.



At a certain stage, rate of forward reaction becomes equal to rate of backward reaction called equilibrium state.

AT EQUILIBRIUM STATE

Rate of forward reaction = Rate of backward reaction

- At this state of equilibrium forward and backward reactions proceeds with same speed.
- > The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.
- > The equilibrium state is dynamic in nature.
- The reaction does not stop, but both the opposing reactions are going on continuously with same speeds.

CHARACTERISTICS OF EQUILIBRIUM

- (a) Chemical equilibrium is dynamic in nature means the reaction, although appears to be stopped, but actually takes place in both the directions with the same speed.
- (b) To obtain equilibrium, if anyone of the reactant or product is in gaseous state then the reaction should be carried out in closed vessel.
- **(c)** At a given temperature and pressure of equilibrium the properties like concentration, colour, density remains constant.
- (d) In a reversible chemical reaction, the equilibrium state can be attained in lesser time by the use of positive catalyst.

A catalyst doesn't change the equilibrium state because it increases the rate of both forward and backward reaction simultaneously by changing the path of reaction and it helps in attaining equilibrium rapidly.

- (e) In order to prevent escape of products, equilibrium is reached in only in closed vessels in reversible reactions.
- (f) Homogeneous equilibrium is the equilibrium in which the reactants and products are in the same phase.
- (g) Heterogeneous equilibrium is the equilibrium in which the reactants and products are in two or more phases.

 $Zn(s) + CO_2(g) \longrightarrow ZnO(s) + CO(g)$

TYPES OF EQUILIBRIA

There is two types of equilibria:

1. Physical Equilibria

If in a system only physical state (phase) is changed and then equilibrium is established, (i.e. there is no chemical change) the equilibrium is called physical equilibrium.

Ex. Fusion of ice, evaporation of water, dissolution of salts and absorption of gases in liquid etc.

Following are the types of common physical equilibria: -

(i) Liquid-Vapour Equilibria : In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.

Ex.
$$H_20(\ell) \longrightarrow H_20(g)$$

(ii) Solid-Liquid Equilibria: This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.

Ex. $H_20(s) \longrightarrow H_20(\ell)$ at melting point

- (iii) (Solute-Solvent), Saturated Solution Equilibria : If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.
- **Ex.** NaI (s) \longrightarrow Na⁺ (aq.) + I⁻ (aq.)
- **Note:** Above example is of solubility of sparingly soluble salt, which only depends on temperature.
- (iv) (Gas + Solvent), Saturated Solution Equilibria: In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature.
- **Ex.** Dissolved CO_2 in cold drinks. Dissolved O_2 in water etc.

Note

(i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

Henry's Law can be applied on such system, that states, the mass of gas (ii) dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

 $C_g \propto P_g$ or $C_g = k P_g$

where

k = Henry's constant

 C_g = Solubility of gas in the solution (mol L⁻¹)

 $P_g = Pressure of the gas$

One should not compare it with liquid vapour equilibria. (iii)

2. Chemical Equilibria

When chemical change occur in a reversible reaction i.e. reactants convert into products and products also convert into reactants under similar conditions of pressure and temperature, the reaction is said to be in chemical equilibria.

(i)
$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$
 (formation of HI)

(ii)
$$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(g)$$
 (formation of SO_2Cl_2)

 $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$ (formation of PCl_5) (iii)

 $2NH_3$ (g) \longrightarrow N₂ (g) + $3H_2$ (g) (Decomposition of NH₃) (iv)

Ex. Chemical equilibrium is a condition:

(A) where all species have same concentration

(B) where all species have constant concentration with respect to time.

(C) where all species have concentration = 1

(D) all of above

Sol. (B)

Chemical equilibrium defined as when all species have constant concentration with respect to time.

Example of physical equilibria, is: Ex.

(A) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$ (B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

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(C)
$$H_2O(s) \longrightarrow H_2O(\ell)$$
 (D) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

Sol. (C)

Physical equilibria does not include any chemical change.

Ex. At equilibrium:

(A) the energy of system is minimum (B) the entropy of system is maximum

(C) the energy of system is maximum (D) the entropy of system is minimum

Sol. (A,B)

It is the compromising stage of minimum energy and maximum entropy.