Unit

7 Equilibrium

- **Equilibrium** is the state of process, in which the concentration of reactants and products becomes constant until the conditions of temperature and pressure are changed. At equilibrium state both the forward and backward reactions move with equal speed.

PHYSICAL EQUILIBRIUM

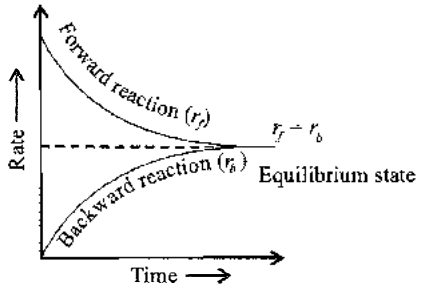
- It is the process which involves physical changes only, like equilibrium between different states of substances at a particular temperature.
  - Solid $\rightleftharpoons$ liquid : ice $\rightleftharpoons$ water at 0°C
    rate of melting = rate of freezing
  - Liquid $\rightleftharpoons$ gas (vapour) : water $\rightleftharpoons$ water at 100°C (vapours)
    rate of evaporation = rate of condensation
  - Solid $\rightleftharpoons$ gas (vapour) : CO_2 (solid) $\rightleftharpoons$ CO_2 (vapours)
    rate of sublimation = rate of condensation
  - Solid $\rightleftharpoons$ saturated solution of solid in liquid
    rate of dissolution = rate of precipitation
  - Gas $\rightleftharpoons$ saturated solution of gas in liquid
    always exothermic and spontaneous
- **Freezing point / melting point :** The temperature at which the solid-liquid equilibrium is reached for a pure substance under one atmospheric pressure is called normal melting point or normal freezing point of the substance.
- **Boiling point :** The temperature at which liquid-gas equilibrium is attained for a pure substance under normal atmospheric pressure (1 atm) is called normal boiling point of the substance.

CHEMICAL EQUILIBRIUM

- If the process involves only chemical change, the equilibrium is called chemical equilibrium.
- **Reversible reaction :** A reaction in which the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. These reactions if carried out in a closed vessel do not go to completion.
  e.g., $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- **Irreversible reaction :** These are the reactions in which products do not react back to give the reactants, *i.e.*, reaction can not be retraced at any point.
  e.g., $AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$
  $SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$
- **State of equilibrium :** Chemical equilibrium is that state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.

Characteristics of chemical equilibrium

- Equilibrium state is attained only when reaction is carried out in a closed vessel.
- At equilibrium, concentration of all reactants and products becomes constant.
- Equilibrium is dynamic in nature *i.e.*, reaction seems to be static but actually takes place in both the directions with same speed.
- Chemical equilibrium can be attained from either direction *i.e.*, from the side of reactants or products.
- At the stage of equilibrium free energy change is zero *i.e.*, $\Delta G = 0$.



Variation of reaction rates of forward and backward reaction with time.

- **Law of chemical equilibrium**
  For a given reversible reaction,
  $aA + bB \rightleftharpoons cC + dD$
  Rate of forward reaction (R_f) $\propto [A]^a [B]^b$ (law of mass action)
  $= k_f [A]^a [B]^b$
  Rate of backward reaction (R_b) $\propto [C]^c [D]^d = k_b [C]^c [D]^d$
  At equilibrium, $R_f = R_b$; $k_f [A]^a [B]^b = k_b [C]^c [D]^d$

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

$$\frac{k_f}{k_b} = K_c = \text{equilibrium constant}$$

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