Equilibrium

1. **Equilibrium in Physical and Chemical Processes**
2. **Law of Chemical Equilibrium and Equilibrium Constant**
3. **Factors Affecting Equilibria**
4. **Ionization of Acids and Bases**
5. **Buffer Solutions and Solubility Equilibria**

- When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal.

- **Equilibrium involving physical processes:** When equilibrium is attained for physical process, it is characterised by constant value of one of its parameters at a given temperature.

  Equilibrium involving chemical processes: In chemical equilibrium, when the rates of forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant.

- Equilibrium constant, Kc is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient.
  For Reaction $\mathrm{a\,A} + \mathrm{b\,B} \rightleftharpoons \mathrm{c\,C} + \mathrm{d\,D}$
  $\mathrm{K}_c = [\mathrm{C}]^c[\mathrm{D}]^d/[\mathrm{A}]^a[\mathrm{B}]^b$
- Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant.
- For a gaseous reaction equilibrium constant is expressed as Kp and is written by replacing concentration terms by partial pressures in Kc expression. The direction of reaction can be predicted by reaction quotient Qc which is equal to Kc at equilibrium.
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Homogeneous equilibrium reaction -when all reactants and products are in same phase it is called homogeneous equilibrium reaction.

- Heterogeneous equilibrium reaction – when all reactants and products are in different phases it is called heterogeneous equilibrium reaction.
- Law of mass action states: Rate of a chemical reaction is directly proportional to the product of molar concentration of the reactants at a constant temperature at any given time.

Characteristic features of equilibrium constant

- Equilibrium constant is applicable only when the concentration of reactants and products have attained their equilibrium state.
- Equilibrium constant has a definite value for every reaction at a particular temperature.
- Equilibrium constant is independent of presence of catalyst.
- The value of equilibrium constant is independent of initial concentrations of the reactants and products.

Applications of equilibrium constant

1) Helps in predicting the extent of a reaction

- If Kc > 103 , products predominate over reactants, the reaction proceeds nearly to completion
- If Kc < 10-3 , reactants predominate over products, the reaction proceeds rarely to completion
- If Kc is in the range of 10-3 to 103 , considerable concentrations of both reactants and products are present, similar to equilibrium mixture.

2) Predicting the direction of the reaction

- Reaction quotient (Q) is the ratio of product of concentration (or partial pressure) of products to that of reactants at any stage of the reaction
- If Qc >Kc , the reaction will proceed in the direction of reactants (reverse reaction).
- If Qc < Kc , the reaction will proceed in the direction of the products (forward reaction)
- If Qc = Kc , the reaction mixture is already at equilibrium.

Le Chatelier's principle

- Le Chatelier's principle states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors.
- Catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa.
- All substances that conduct electricity in aqueous solutions are called electrolytes. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution.
- Substances which ionize almost completely into aqueous solutions are called strong electrolytes
- Ionic Equilibrium: Equilibrium established between unionized molecules and anions in solution of weak electrolytes.
- The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions.

  Limitation of Arrhenius concept: The concept is applicable only to aqueous solutions and it does not account for the basicity of substances like ammonia which does not have hydroxyl group.
- Brönsted-Lowry on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a conjugate pair of acid-base differs only by one proton. Lewis further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition.

- The degree of ionization and its dependence on concentration and common ion are discussed.
- Common ion Effect: The shift in equilibrium position caused by the addition or presence of an ion involved in the equilibrium reaction is known as common ion effect
- Strength of acid or base is determined with the help of extent of ionization in aqueous solution.
- The pH scale ($pH = -\log[H^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ($pOH = -\log[OH^-]$) ; $pKa = -\log[Ka]$;$pKb = -\log[Kb]$; and $pKw = -\log[Kw]$ etc.).
- The ionization of water has been considered and we note that the equation: $pH + pOH = pKw$ is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution.
- Buffer solutions: are the solutions which resist change in pH on dilution or addition of small amount of acid or alkali.
- Acidic buffers contain equimolar quantities of a weak acid and one of its salt with a strong base.
- Basic buffers contain equimolar quantities of a weak base and one of its salt with a strong acid.
- The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as solubility product constant (Ksp). Its relationship with solubility of the salt is established. Under equilibrium conditions, $Ksp = Qsp$ The solubility of salts of weak acids, like phospates, increases with decrease in pH. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out.