**CHAPTER NO- 03**

**Ionic Equilibria**

**3.1 Introduction:**

In the previous chapter, we have studied the principle of chemical equilibrium, now in this chapter, we shall study the principle of ionic equilibrium and the concepts involved in it. The process in which molecules (acids, bases, and salts) when dissolved in water or when melted, dissociates into ions (charged particles) is called ionization.  Another definition of ionic equilibrium is “The equilibrium between ions and unionized molecules in solution is called ionic equilibrium”. Since the ions have positive or negative charges, the aqueous solution of such molecules can conduct electric current, hence such substances are commonly known as electrolytes.  Molecules of substances like

sugar, urea, etc., on dissolution in water or on melting, do not produce ions hence such substances are called non-electrolytes. The conduction of current through electrolytes is due to the movement of ions.

**3.2 Classification of electrolytes:**

The electrolytes are classified into strong electrolytes and weak electrolytes. This classification is based on the ability of ionization in dilute aqueous solution.

**Strong electrolyte:**Those electrolytes which dissociate almost completely into ions in aqueous solutions are known as strong electrolytes.

**Strong electrolytes ionize completely (100%)**

Examples: all salts (except HgCl2, CdBr2), mineral acids like HCl, H2SO4, HNO3, etc.

**Moderate electrolyte**:Those electrolytes which dissociate and form ionic compounds staying in a non-ionic form in the solution. The strong electrolytes can easily dissociate into moderate concentrations while weak electrolytes don't dissociate.

**Moderate electrolytes ionize about 50%**

**Weak Electrolytes:**

Those electrolytes which show poor dissociation into ions in aqueous solutions are called weak electrolytes.

**weak electrolytes ionize only partially (usually on the order of 1–10%).**

Example: All organic acids (except sulphonic acids), and bases like NH3, NH4OH, amines, HCN etc.

**3.2.1 Arrhenius theory of electrolytic dissociation:**

To explain the behavior of electrolytes in solution, Arrhenius postulated the existence of electrically charged particles i.e., ions in the form of theory commonly known as Arrhenius theory of dissociation or ionization.

The main postulates of the theory are given below:

1. In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation to form positive and negative ions.

NaOH → Na + + OH-

KCl → K+ + Cl-

**3.3 Degree of Dissociation or Ionization (α):**

The degree of dissociation of an electrolyte is defined as a fraction of the total number of molecules of the electrolyte that dissociates into its ions when the equilibrium is attained. It is denoted by symbol (α).

Degreeof Dissociation (α) = 

3. At moderate concentrations, there exists an equilibrium between the ions and undissociated molecules, such as

NaOH⇌Na+ + OH-

KCI ⇌ K+ + Cl-

This equilibrium state is called ionic equilibrium.

4. Each ion produced, due to electrolytic dissociation, produces the same effect on osmotic pressure and other colligative properties as an undissociated molecule.

In other words, each ion behaves osmotically as a molecule.

**3.3.1 Factors affecting degree of Ionization:**

**(i) Nature of electrolyte**:

As mentioned earlier, solutions of different electrolytes (strong and week) of same concentration at constant temperature ionize to a different extent. Thus, at normal dilution, value of a is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.

**(ii) Nature of solvent:**

Dielectric constant of a solvent is a measure of its tendency to weaken the forces of attraction between oppositely charged ions of the electrolyte. Higher the dielectric constant of a solvent more is its ionizing power. Water is the most powerful ionizing solvent as its dielectric constant is highest.

* + 1. **Concentration of the Solution:**

Dissociation or Ionization of electrolyte increase with increase in dilution. as the solution is diluted the ions formed moves apart from each other and the attractive as well as repulsive forces between ions becomes negligible and therefore ionization or dissociation increases.

Degree of ionization α

α

**(iv) Temperature:**

Degree of ionization of an electrolyte in solution increases with increase in temperature.

**(v) Presence of common ion:**

The degree of ionization of an electrolyte decreases in the presence of a strong electrolyte having a common ion. For example, ionization of CH3COOH is suppressed in presence of HCI due to common H+ ions.

**3.3.2Ostwald's Dilution Law:**

Since weak electrolytes are not completely dissociated, there exists an equilibrium between the ions and undissociated molecules of the electrolyte. This equilibrium is called ionic equilibrium. Ostwald applied the law of mass action to the ionic equilibrium of weak electrolytes and derived an equation, known as Ostwald's dilution law equation (Ostwald dilution formula).

Let us consider an aqueous solution of the weak electrolyte HA at constant temperature. In aqueous solution, HA remains in equilibrium with its ions.

HA ⇌ H+ + A-

On applying the law of mass action to this equilibrium,

K = [H+] [A-]

[HA]

Where, [H+], [A-] and [HA] are their concentration in mol per lit at equilibrium. K is constant known as ionization or dissociation constant of the electrolyte; its value is constant at constant temperature in a solvent. The value of ‘k’ does not depend on concentration of electrolyte.

Ostwald's Dilution Law is valid only for weak electrolytes in dilute solutions, there for it is also called as dilution law.