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Ionic Equilibria

IONIC EQUILIBRIA-I

Chemical equilibria involves dissociation of chemical compounds, both solid and gaseous, and the equilibria involving various phase transitions such as solid \rightleftharpoons liquid, liquid \rightleftharpoons vapour, solid \rightleftharpoons vapour and one allotropic form \rightleftharpoons another allotropic form, etc. In this chapter we discuss ionic equilibria involving dissociation of weak acids and weak bases in aqueous medium, dissociation of sparingly soluble salts in aqueous medium, dissociation of water and hydrolytic dissociation of salts etc., in some details.

1.0 STRONG, MODERATE AND WEAK ELECTROLYTES

Electrolytes are classified as strong electrolytes, weak electrolytes and moderate electrolytes.

Strong electrolytes : These are those substances which are almost completely ionized or dissociated into ions in the aqueous solution or in the molten state and hence conduct electricity to a large extent. For example, strong acids (HCl, HNO₃, H₂SO₄ etc.), strong bases (NaOH and KOH etc.) and most of the inorganic salts in fused state, (NaCl, NH₄Cl etc.).

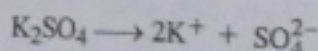
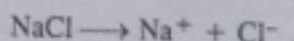
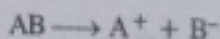
Weak electrolytes : These are those substances which ionize to a small extent into ions in solution phase and hence conduct electricity to a small extent. For example, weak acids such as CH₃COOH, HCN, H₂CO₃ etc. and weak bases such as NH₄OH, Ca(OH)₂ etc.

Moderate Electrolytes : These are those substances which exhibit an intermediate behaviour between strong and weak electrolytes. For example, trichloroacetic acid (Cl₃CHCOOH) etc.

Non-electrolytes : Substances like sugar, urea, alcohol, glycerine etc. which do not conduct electricity (even in solution) are called **non-electrolytes**. These substances do not give ions when dissolved in water or in molten state. Hence, they are unable to conduct electricity.

2.0 DEGREE OF IONIZATION

An electrolyte, when dissolved in water, break up into two charged particles called ions. The positively charged ions are termed cations and negatively charged as anions

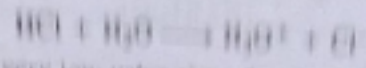


Electrolyte Ions

The process of splitting of the molecules into ions of an electrolyte is called *ionization*. The process may not be completely ionized. The ratio of number of molecules dissociated to the total number of molecules is known as degree of ionization or dissociation. It is denoted by α , i.e.

$$\text{Degree of ionization } (\alpha) = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

In strong electrolytes, it is almost equal to one as they almost completely ionize in aqueous solution. An equation which involves the ionization of strong electrolytes is represented with single headed arrow as follows in the right. For example,



In the weak electrolytes, it has very low value since they ionize to a very small extent. Extent of ionization increases with dilution and becomes maximum at infinite dilution. Complete ionization of the molecule does not occur. The ions formed in solution constantly combine to form neutral molecules and vice versa is a state of dynamic equilibrium between the ions and the unionized molecules i.e.



(By applying the law of mass action to the ionic equilibrium

$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

where K is known as the dissociation or ionization constant.

The electrolytes having high value of K are known as strong electrolytes and those having low value of K as weak electrolytes.

FACTORS CONTROLLING THE DEGREE OF IONIZATION

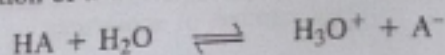
The degree of ionization depends on the following factors :

- (i) **Nature of the electrolyte** : Weak electrolytes such as CH_3COOH , H_2CO_3 , NH_4OH , $\text{Mg}(\text{OH})_2$ etc. can ionize only to a small extent, therefore, their degree of ionization is low. Strong electrolytes such as HCl , NaOH , NaCl which are almost completely ionized have high degree of ionization.
- (ii) **Nature of the solvent** : Every solvent has some definite value of dielectric constant. Generally, solvents with high dielectric constant such as water ($\epsilon = 80$) ionize the electrolytes to greater extent than the solvents with low dielectric constant such as benzene ($\epsilon = 2$). This is due to the fact that solvents having high dielectric constant weakens the forces of attraction between the oppositely charged ions and hence enhance ionization.
- (iii) **Concentration** : Ionization of the electrolyte increases with the increase in dilution and it becomes maximum at infinite dilution i.e. as concentration approaches zero.
- (iv) **Temperature** : The degree of ionization increases with the increase in temperature. This is due to the fact that at higher temperature, molecular speed is increased which overcomes the force of attraction between the ions.
- (v) **Presence of common ions** : The degree of ionization of an electrolyte decreases in the presence of another electrolyte which furnishes, a common ion. For example, ionization of CH_3COOH decreases in the presence of CH_3COONa due to common ion (CH_3COO^-) effect.

2.2 DISSOCIATION OF WEAK ACIDS AND BASES⁷

Dissociation of a Weak Acid

Consider the dissociation of a weak monobasic acid HA in water, represented by the equation



Applying the law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

The square brackets, as usual, represent concentrations in moles per litre of the entities enclosed therein.

Since water is present in large excess in dilute solutions, its concentration may be taken as constant, say, k . Further, since the symbol H_3O^+ simply indicates that hydrogen ion is hydrated, it may be replaced by H^+ , for simplicity. The above equation may then be put as

$$K_c = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}] \times k}$$

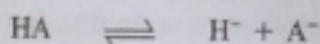
assuming that the activity coefficients of the species involved are equal to unity each.

Since the product of the two constants K_c and k is equal to another constant, say, K_a , Eq. 2 may be written as

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

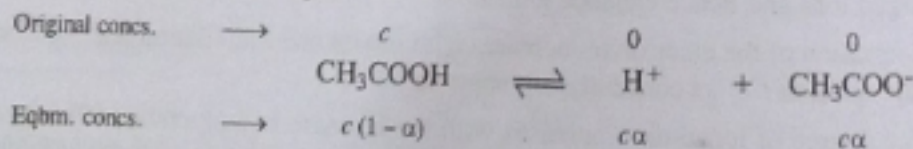
The significance of Eq. 3 is that the product of the concentrations of the hydrogen ion and the anion, irrespective of their source (*i.e.*, whether furnished by the acid itself or by any other substance present in the solution) divided by the concentration of the undissociated acid, is equal to a constant. This constant (K_a) is characteristic of the acid concerned and is known as the **dissociation or ionization constant** of the acid. This varies only with temperature, like other equilibrium constants.

If the dissociation of the acid is represented in accordance with Arrhenius concept*, *i.e.*, as



the same expression as above for the dissociation constant of the acid will be obtained. Therefore, for simplicity, Arrhenius concept may be adopted.

Eq. 3 for the dissociation constant of a weak acid can also be expressed in terms of the degree of dissociation/ionization (α) and the total molar concentration (c) of the acid. Consider, for example, the dissociation of acetic acid, represented below :



$$K = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

* According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in aqueous solution undergo spontaneous dissociation into positive and negative ions and that there is a dynamic equilibrium between ions and the undissociated molecules.

Eq. (4) is the mathematical representation of Ostwald's dilution law. The equilibrium constant K is called the dissociation or ionization constant of the electrolyte. It is constant at a given temperature.

Since for weak acids, α is very small, $1 - \alpha$ in the denominator may be taken as 1. The above expression, therefore, reduces to

$$K = c\alpha^2 \text{ or } \alpha = \sqrt{K/c} \quad \dots(5)$$

Eq. (5) is another form of Ostwald's dilution law which states that

"For a weak binary electrolyte, with a small degree of ionization, the degree of ionization is inversely proportional to the square root of the initial concentration of the electrolyte."

Generally the concentration c is expressed in moles/litre, therefore, the volume (V) of the solution containing 1 mole of electrolyte will be $\frac{1}{c}$ litre.

Putting $\frac{1}{c} = V$ in Eqns. (4) and (5).

$$\text{we get, } K = \frac{\alpha^2}{(1-\alpha)V} \text{ and } \alpha = \sqrt{KV} \quad (\because 1 - \alpha = 1)$$

Thus, Ostwald's dilution law can also be stated as :

"For a weak binary electrolyte with a small degree of ionization, the degree of ionization is directly proportional to the square root of volume in litres containing one mole of electrolyte."

Limitations of Ostwald's Dilution Law

Ostwald's dilution law is obeyed only by weak electrolytes in the dilute solutions and fails completely in case of strong electrolytes such as hydrochloric acid, sodium hydroxide or potassium chloride. The values of K obtained for potassium chloride, for example, varies from 2.350 to 0.015 as the concentration varies from 1.00 M to 0.0001 M. The reason for the failure is that strong electrolytes exist in the form of ions even in the solid state. These electrolytes are completely ionised at all concentrations. There is no equilibrium between the ions and the unionised molecules. Hence, Ostwald's dilution law is not applicable in the case of strong electrolytes.

Relative Strengths of Weak Acids

For two weak acids of dissociation constants K_{a_1} and K_{a_2} , at the same concentration c , it follows from Eq. 5 that

$$\alpha_1/\alpha_2 = \sqrt{K_{a_1}/K_{a_2}} \quad \dots(6)$$

where α_1 and α_2 are the respective degrees of dissociation of the two acids.

But, degree of dissociation of an acid is a measure of its capacity to furnish hydrogen ions and hence a measure of its strength.

$$\frac{\text{Strength of one acid, HA}_1}{\text{Strength of another acid, HA}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} \quad \dots(7)$$

Eq. 5 can also be used for calculating hydrogen ion concentrations of aqueous solutions of acids whose dissociation constants are known. Accordingly,

$$[\text{H}^+] = c\alpha = c\sqrt{K_a/c} = \sqrt{cK_a}$$

Sample Problem 1. The dissociation constants of formic and acetic acids are 1.77×10^{-4} and 1.75×10^{-5} , respectively. Calculate the relative strengths of the two acids.

Solution : According to Eq. 7,

$$\frac{\text{Strength of formic acid}}{\text{Strength of acetic acid}} = \sqrt{\frac{K_a \text{ formic acid}}{K_a \text{ acetic acid}}} = \sqrt{\frac{1.77 \times 10^{-4}}{1.75 \times 10^{-5}}} = 3.18$$

Thus, formic acid is 3.18 times stronger than acetic acid.

Sample Problem 2. A solution of 0.100 M acetic acid is found to be dissociated to the extent of 1.33 per cent at the room temperature. Calculate the dissociation constant of the acid at this temperature.

Solution : Percentage dissociation of acetic acid = 1.33

$$\therefore \text{Degree of dissociation of acetic acid, } \alpha = \frac{1.33}{100} = 0.0133$$

$$\text{Dissociation constant of acetic acid, } K_a = \frac{c\alpha^2}{1-\alpha}$$

$$\text{Since } \alpha \text{ is very small, hence } K_a = c\alpha^2 = 0.1 \times (0.0133)^2 = 1.77 \times 10^{-5}$$

Sample Problem 3. A monobasic acid has a dissociation constant equal to 1.8×10^{-5} at 25°C . Calculate its degree of dissociation at a concentration of 0.20 M at the same temperature. What will be the concentration of hydrogen ions furnished by it?

Solution : Assuming that degree of dissociation is very small,

$$\alpha = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.2}} = 0.009486$$

Thus, degree of dissociation of 0.20 M acid = 0.009486

Further,

$$[\text{H}^+] = \sqrt{cK_a}$$

$$= \sqrt{0.2 \times 1.8 \times 10^{-5}} = 0.001897 \text{ mol dm}^{-3}$$

(Eq. 8)

Practice Problems

- At 25°C , the ionization constant of HCN is 4.9×10^{-10} . Calculate the degree of ionization of HCN, if its concentration are (i) 0.1 M and (ii) 0.01 M. [Ans. 7.0×10^{-5} , 2.21×10^{-4}]
- Acetic acid has a dissociation constant equal to 1.75×10^{-5} at 25°C . What will be the hydrogen ion concentration of a 0.01 M solution of acetic acid. [Ans. 1.32×10^{-4}]

2.3 Dissociation Constants of Polybasic Acids (Di and Triprotic Acids)

Polybasic acids contain two or more hydrogens which can get dissociated. They always dissociate in stages. Consider, for example, the dissociation of carbonic acid in accordance with Arrhenius