

- **Strong Electrolytes.** Those substances which are almost completely ionized or dissociates into ions in the aqueous solution or in molten state and hence conduct electricity to a large extent. For example HCl, HNO<sub>3</sub>, NaOH, NaCl etc.
- **Weak Electrolyte.** Those substances ionizes to a small extent into ions in the solution phase and hence conduct electricity to a small extent. For example CH<sub>3</sub>COOH, HCN, NH<sub>4</sub>OH etc.
- **Moderate Electrolytes.** Those substance which exhibit an intermediate behaviour between strong and weak electrolytes. For example, Cl<sub>3</sub>CHCOOH etc.
- **Degree of ionization ( $\alpha$ ).**

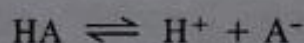
$$\text{Degree of ionization } \alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

**Factors affecting degree of ionization.**

- Nature of Electrolyte.** Strong electrolytes such as HCl, NaOH, NaCl which are almost completely ionized have high degree of ionization.
  - Nature of Solvent.** Solvents with high dielectric constant ionize the electrolytes to greater extent than solvents with low dielectric constant.
  - Concentration.** Ionization of electrolyte increases with the increase in dilution.
  - Temperature.** The degree of ionization increases with increase in temperature.
  - Presence of Common Ions.** The degree of ionization of an electrolyte decreases in the presence of another electrolyte which furnishes a common ion.
- **Dissociation of a Weak Acid.** For a weak acid, HA, the dissociation equilibrium is represented by the equation



or simply as



The equilibrium constant of this reaction, which is also called **dissociation/ionization constant of the acid**, is given by

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

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

which is mathematical representation of Ostwald's dilution law.

For a weak electrolyte degree of ionization  $\alpha$  is very small, therefore

$$K_a = c\alpha^2 \text{ or } \alpha = \sqrt{K_a / c}$$

which another form of Ostwald's dilution law which states that "For a weak binary electrolyte, with a small degree of dissociation, the degree of dissociation is inversely proportional to the square root of the initial concentration of the electrolyte."

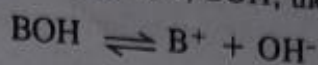
The H<sup>+</sup> ion concentration of the acid would be given by

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

where  $c$  is the molar concentration of the acid.

- **Dissociation Constants of Polybasic acid.** Polybasic acids contain two or more hydrogens which can get dissociated. For example  $\text{H}_2\text{CO}_3$ ,  $\text{H}_3\text{PO}_4$  etc. They always dissociate in stages. The successive dissociation constant is always found to be smaller than first dissociation constant.

- **Dissociation Constant of a Base.** For a weak base, BOH, the dissociation equilibrium is represented as



and the ionization or dissociation constant of the base is given by

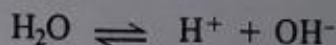
$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]}$$

The  $\text{OH}^-$  ion concentration of the base would be given by

$$[\text{OH}^-] = \sqrt{cK_b}$$

where  $c$  is the molar concentration of the base.

**Ionic Product of Water.** Water, being a weak electrolyte, dissociates to a very small extent into  $\text{H}^+$  and  $\text{OH}^-$  ions, as represented by the equation :



The dissociation constant  $K$  of this reaction is given by

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{[\text{H}^+][\text{OH}^-]}{k}$$

since  $[\text{H}_2\text{O}]$  is taken as constant.

$$\therefore K \times k = K_w = [\text{H}^+][\text{OH}^-]$$

$K_w$  is called the dissociation constant or **ionic product of water**. Numerically,

$$K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ\text{C}$$

**The pH Scale.** The concentration of  $\text{H}^+$  ions in a solution is most conveniently represented with the help of a quantity called  $p\text{H}$ . The  $p\text{H}$  of a solution is given by

$$p\text{H} = -\log [\text{H}^+]$$

The  $p\text{H}$  of a solution in which  $[\text{H}^+]$  is  $1 \text{ mol dm}^{-3}$  (as in  $1 \text{ M HCl}$  solution) is zero and the  $p\text{H}$  of a solution in which  $[\text{H}^+] = 10^{-14} \text{ mol dm}^{-3}$  (as in  $1 \text{ M NaOH}$  solution), is 14. Thus, the scale of  $p\text{H}$  is 0 to 14.

Other logarithmic expressions are :

$$p\text{OH} = -\log [\text{OH}^-]$$

$$pK_w = -\log K_w$$

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

$$p\text{H} + p\text{OH} = 14 \text{ at } 25^\circ\text{C}$$

- **Common Ion Effect :** The suppression of the dissociation of a weak acid or a weak base on the addition of its own ions is called common ion effect. For example, the addition of sodium acetate to a solution of acetic acid suppresses the dissociation of acetic acid which is already very small.



- **Hydrolysis of Salts.** Certain salts when dissolved in water, give acidic or alkaline solutions. This phenomenon, which can be considered as reverse of neutralisation, is known as **hydrolysis**. It is due to the interaction of anions and cations of the salt with  $H^+$  and  $OH^-$  ions furnished by water.

Salts of strong acids and strong bases do not undergo hydrolysis.

Salts of strong acids and weak bases give acidic solution on hydrolysis.

Salts of strong bases and weak acids give alkaline solution on hydrolysis.

Salts of weak acids and weak bases undergo hydrolysis to give practically neutral (or very very weak acidic or alkaline) solutions.

Some useful information in respect of various categories of salts is given below :

1. **Salts of Weak Acids and Strong Bases.** Salts of this category undergo hydrolysis to give alkaline solution. The hydrolytic reaction in the case of  $CH_3COONa$ , for example, is written as



feebly dissociated

**Hydrolysis Constant,  $K_h$**  is given by

$$(i) \quad K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$$

The following relation holds good between  $K_h$ ,  $K_a$  and  $K_w$  :

$$(ii) \quad K_h = K_w/K_a$$

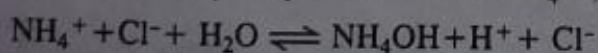
**Degree of hydrolysis,  $h$ ,** is given by

$$(iii) \quad h = \sqrt{\frac{K_w}{K_a \times c}}$$

**The pH of the hydrolysed solution** is given by

$$(iv) \quad pH = 14 - \frac{1}{2} pK_w + \frac{1}{2} \log c + \frac{1}{2} pK_a \quad \text{where } c \text{ is the molar concentration of the salt.}$$

2. **Salts of Weak Bases and Strong Acids.** The salts of this category undergo hydrolysis to give acidic solution. The hydrolytic reaction of  $NH_4Cl$ , for instance, would be written as



Feebly dissociated

**Hydrolysis Constant,  $K_h$ ,** is given by

$$(i) \quad K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$$

$K_h$ ,  $K_w$  and  $K_b$  are related as

$$(ii) \quad K_h = K_w/K_b$$

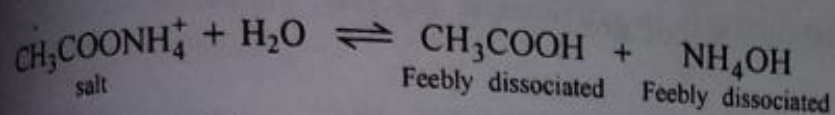
**Degree of hydrolysis,  $h$ ,** is given by

$$(iii) \quad h = \sqrt{\frac{K_w}{K_b \times c}}$$

The pH of the hydrolysed solution is given by

$$(iv) \text{pH} = \frac{1}{2} \text{p}K_w - \frac{1}{2} \log c - \frac{1}{2} \text{p}K_b$$

For the Hydrolysis of Salts of Weak Acids and Weak Bases, as for example, the hydrolysis of ammonium acetate,



the following relations hold good :

$$(i) K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$$

$$(ii) K_h = \frac{K_w}{K_a \times K_b}$$

$$(iii) h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$(iv) \text{pH} = \frac{1}{2} \text{p}K_w + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b$$

• **Buffer Solutions.** There are solutions whose pH does not change much even on the addition of appreciable amounts of strong acids and bases. Such solutions are called **buffer solutions**. Thus, a buffer solution is one which can resist change in pH on the addition of small amounts of an acid or a base.

Some of the best known buffers are :

1. A mixture of a weak acid and its salt with a strong base, *e.g.*, a mixture of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ . The pH of such a buffer is given by the **Henderson-Hasselbalch** equation, *viz.*,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

2. A mixture of a weak base and its salt with a strong acid, *e.g.*, a mixture of  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ . The pOH of such a buffer is given by

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Knowing that  $\text{pH} + \text{pOH} = 14$  at  $25^\circ\text{C}$ , the pH of the above buffer can be easily determined.

A solution of  $\text{CH}_3\text{COONH}_4$  alone also acts as a buffer.

**Buffer Capacity.** The capacity of a solution to resist alteration in its pH, is known as its buffer capacity.

**Buffer Range.** It is the pH range where a buffer effectively neutralizes acids and bases, while maintaining a relatively constant pH. For example  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer has pH range is 3.7 - 5.6.



### Applications of Buffers.

#### In Analytical Chemistry

$\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  buffer is used in removal of phosphate ion during the qualitative analysis.  $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$  buffer is used for the precipitation of hydroxides of third group in qualitative analysis.

For precipitation of lead chromate quantitatively in gravimetric analysis, the buffer  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$  is used.

**In Biochemical Processes :** A buffer of carbonic acid ( $\text{H}_2\text{CO}_3$ ) and bicarbonate ( $\text{HCO}_3^-$ ) is present in blood plasma to maintain a  $\text{pH}$  between 7.35 and 7.45.

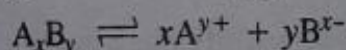
**In Industries :** In industries, buffer solutions are used in alcoholic fermentation, tanning of leather, electroplating, manufacture of sugar, paper etc.

- **Solubility Product.** For the saturated solution of a sparingly soluble salt (such as  $\text{AgCl}$ ) in water, we can write the solubility equilibrium as



and the solubility product,  $K_{sp}$ , is given by  $K_{sp} = s^2$  where  $s$  is the molar solubility of the salt. From a knowledge of  $K_{sp}$ ,  $s$  can be determined :  $s = \sqrt{K_{sp}}$ .

In a general case, in which a sparingly soluble salt  $\text{A}_x\text{B}_y$  dissociates as



the solubility product of the salt is given by

$$K_{sp} = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

Thus, the **solubility product** of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte.

The principle of solubility product is used in

1. Determining solubilities of sparingly soluble salts,
2. Predicting precipitation reactions,
3. Precipitation of soluble salts,
4. Inorganic qualitative analysis,
5. Dissolution of precipitates of carbonates, phosphates, sulphides, etc. in acidic solutions.

- **Hydrogen Ion Indicators or Acid-Base Indicators**

A hydrogen ion (or acid-base) indicator is a substance which changes its colour within limits with variation in  $\text{pH}$  of the solution to which it is added. This gives an easy method of determining  $\text{pH}$  of a solution by simply adding a *suitable* indicator and noting the colour. The  $\text{pH}$  range, over which the colour change occurs, varies considerably from one indicator to another. For example, methyl orange gives full acid colour (red) when added to a solution the  $\text{pH}$  of which is 3 or below and full basic colour (yellow) in a solution whose  $\text{pH}$  is 4.4 or above. In solutions having  $\text{pH}$  between 3 and 4.4, methyl orange gives a colour intermediate between red and yellow. Thus, the  $\text{pH}$  range over which methyl orange can be used as an indicator lies between 3 and 4.4.