By- SHAILENDRA SHUKLA SIR

Ionic Equilibrium

Electrolytes

The substances which pass electricity through them, either in their aqueous solutions or in their molten form are called electrolytes.

When electrolytes are dissolved in water or melted they get splitted into ions. This phenomenon is called ionization or dissociation. For example,

$$NaCl\ (s) \xrightleftharpoons{\text{Water}} \underbrace{Na^+\ (aq) + Cl^-\ (aq)}_{\text{Ions}}$$

$$NaCl\ (s) \xrightleftharpoons{\text{Melt}} \underbrace{Na^+ + Cl^-}_{\text{Ions}}$$

The conduction of electricity through aqueous solutions or molten form of electrolytes is due to flow of ions.

All acids (e.g. HCl, H_2SO_4, HNO_3, CH_3COOH etc.), bases (e.g. NaOH, KOH, NH_4OH, $Ba(OH)_2$ etc.) and salts (e.g. NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are electrolytes.

Types of Electrolytes

Depending upon the degree of dissociation or ionization, the electrolytes may be of following two types-

(1) Strong electrolytes- Such electrolytes which dissociate almost completely in their aqueous solutions are called strong electrolytes. For example,

(i) All strong acids- e.g. HCl, H_2SO_4, HNO_3, $HClO_4$ etc.

(ii) All strong bases- e.g. NaOH, KOH, $Ba(OH)_2$ etc.

(iii) Salts of strong acids and strong bases- e.g. NaCl, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3 etc.

(iv) Salts of strong acids and weak bases- e.g. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3 etc.

(v) Salts of weak acids and strong bases- e.g. CH_3COONa, CH_3COOK, Na_2CO_3, K_2CO_3, NaCN, KCN etc.

(2) Weak electrolytes- Such electrolytes which dissociate very feebly or partially in their aqueous solutions are called weak electrolytes. For example,

(i) All weak acids- e.g. CH_3COOH, H_2CO_3, HCN etc.

(ii) All weak bases- e.g. NH_4OH, $Mg(OH)_2$, $Ca(OH)_2$ etc.

CHEMISTRYFORCOMPETITION.COM

(iii) Salts of weak acids and weak bases- e.g. CH_3COONH_4, $HCOONH_4$, $(NH_4)_2CO_3$, NH_4CN etc.

Degree of dissociation or Degree of ionization (α)

"The fraction of total number of molecules which remains dissociated at equilibrium is called degree of dissociation or degree of ionization of the electrolyte."

Mathematically,

Degree of dissociation, $\alpha = \frac{The\ number\ of\ molecules\ dissociated\ at\ equilibrium}{Total\ number\ of\ molecules}$

Strong electrolytes (e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, $Ba(OH)_2$, NaCl, KCl, NH_4Cl, K_2SO_4, CH_3COONa etc.) are electrolytes are almost completely dissociated in their aqueous solutions. Hence, for these electrolytes, the number of molecules which remain dissociated at equilibrium is almost equal to the total number of molecules. Thus, the degree of dissociation of these electrolytes is almost equal to 1. Thus, for strong electrolytes,

$$\alpha \approx 1$$

On the other hand, weak electrolytes (e.g. CH_3COOH, H_2CO_3, HCN, NH_4OH, CH_3COONH_4, $(NH_4)_2CO_3$, NH_4CN etc.) are very feebly dissociated in their aqueous solutions at equilibrium. Hence, for these electrolytes, the number of molecules which remain dissociated at equilibrium is much lesser than the total number of molecules. Hence, for these electrolytes, the degree of dissociation is very very less than 1. Thus, for weak electrolytes,

$$\alpha << 1$$

Ostwald's dilution law

This law is in fact, the law of mass action applicable for weak electrolytes. Let, a sparingly soluble binary salt AB dissociates in its aqueous solution and establishes following equilibrium-

$$AB\ (aq) \rightleftharpoons A^+\ (aq) + B^-\ (aq)$$

Let, 1 mole of AB is dissolved in V litre of its aqueous solution and its degree of dissociation is α, then,

$AB\ (aq)$	$\rightleftharpoons$	$A^+\ (aq)$	+	$B^-\ (aq)$	
1		0		0	(Initial no. of moles)
$(1-\alpha)$		α		α	(No. of moles at equilibrium)
$\frac{(1-\alpha)}{V}$		$\frac{\alpha}{V}$		$\frac{\alpha}{V}$	(Molar Conc. at equilibrium)

CHEMISTRYFORCOMPETITION.COM

Applying law of mass action, dissociation constant,

$$K = \frac{[A^+(aq)]\,[B^-(aq)]}{[AB\,(aq)]}$$

or $$K = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\frac{(1-\alpha)}{V}}$$

or $$K = \frac{\alpha^2}{V^2} \times \frac{V}{(1-\alpha)}$$

or $$K = \frac{\alpha^2}{V\,(1-\alpha)} \quad \text{---------- (1)}$$

For weak electrolytes,

$$\alpha << 1$$

$$\therefore \quad (1-\alpha) \approx 1$$

$$\therefore \quad K = \frac{\alpha^2}{V}$$

or $$\alpha = \sqrt{KV} \quad \text{---------- (2)}$$

Thus, "At constant temperature the degree of dissociation of a weak electrolyte is directly proportional to the square root of the dilution of the solution."

This law is called the Ostwald's dilution law.

$$\because \quad C = \frac{1}{V}$$

$$\therefore \quad \alpha = \sqrt{\frac{K}{C}}$$

Thus, "At constant temperature the degree of dissociation of a weak electrolyte is inversely proportional to the square root of the molar concentration of the solution."

This is another form of the Oswald's dilution law.

Ionic Product of water (K_w)

Water is a very weak electrolyte and undergoes autoionization (self-ionisation) to establish following equilibrium-

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

Applying law of mass action, dissociation constant,

$$K = \frac{[H_3O^+(aq)]\,[OH^-(aq)]}{[H_2O\,(l)]^2}$$

or $$K \times [H_2O(l)]^2 = [H_3O^+][OH^-]$$

Being very weak electrolyte, the degree of dissociation of water is very small. Hence, the molar concentration of undissociated water can be taken to be almost constant. Hence,

CHEMISTRYFORCOMPETITION.COM

$$K \times (\text{Constant})^2 = [H_3O^+][OH^-]$$

or $$[H_3O^+]\,[OH^-] = K_w$$

Where, K_W is a new constant called ionic product of water.

Thus, "At constant temperature, in pure water the product of the molar concentration of H_3O^+ and OH^- ions is constant, which is called ionic product of water."

At 298 K temperature, the value of K_W is found to be 1.0×10^{-14} gram-ion^2/litre^2. Thus, at 298 K temperature,

$$[H_3O^+][OH^-] = 1.0\times10^{-14} \text{ gram-ion}^2/\text{litre}^2$$

This value of K_W depends only upon temperature and remains constant as long as temperature is constant, but it gets changed with change of temperature.

For pure water (neutral solution),

$$[H_3O^+] = [OH^-]$$

$$\therefore \quad [H_3O^+][H_3O^+] = 1.0\times10^{-14} \text{ gram-ion}^2/\text{litre}^2$$

or $$[H_3O^+] = \sqrt{1.0 \times 10^{-14} \text{ gram} - \text{ion}^2/\text{litre}^2}$$

$$= 1.0\times10^{-7} \text{ gram-ion/litre}$$

Thus, in pure water (neutral solution), H_3O^+ and OH^- ion concentrations are same and at 298K temperature its value is 10^{-7} gram-ion/litre.

For acidic solutions-

$$[H_3O^+] > [OH^-]$$

$$> 1.0\times10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$

For basic solutions -

$$[H_3O^+] < [OH^-]$$

$$< 1.0\times10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$

Effect of temperature on K_W- Auto ionization of water is an endothermic process.

$$2H_2O\,(l) + \text{Heat} \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

Hence, on increasing temperature, following Le-chatelier's principle, this equilibrium will shift in forward direction i.e. there will occur more dissociation of water producing more concentration of H_3O^+ and OH^- ions. Thus, the ionic product of water will increase with increase of temperature. For example, at 363 K temperature, the value of K_w is found to be 10^{-12} gram-ion^2/litre^2. This value of K_w remains constant as long as the temperature is constant, but it gets changed with change of temperature.

CHEMISTRYFORCOMPETITION.COM

pH value or pH Scale

In order to express acidic, basic or neutral nature of the aqueous solutions, Sorenson has introduced a scale called pH scale. On this scale, the molar concentration of H_3O^+ ions of the solution is expressed as the negative power of the base 10, where the numerical value of the negative power of the base 10 corresponds to the pH value of the solution. Thus,

If in a solution,

$$[H_3O^+] = 10^{-x} \text{ gram-ion/litre}$$

Then, pH of the solution = x

Thus, $[H_3O^+] = 10^{-pH}$ ---------- (1)

"The numerical value of the negative power raised to the base 10 to express the molar concentration of H_3O^+ ions of the solution is called the p^H value of the solution."

Taking algorithm of eq. (1),

$$\log [H_3O^+] = - pH \ (\log 10)$$

$\because$ $\log 10 = 1$

$\therefore$ $\log [H_3O^+] = - pH$

or $pH = - \log [H_3O^+]$ ---------- (2)

Thus, "The negative logarithm of the molar concentration of H_3O^+ ions of a solution is called pH value of the solution."

From eq. (2)-

$$pH = \log \frac{1}{[H_3O^+]} \quad \text{---------- (3)}$$

Thus, "The logarithm of the reciprocal of the molar concentration of H_3O^+ ions of a solution is called pH value of the solution."

At 298 K temperature, in pure water (neutral solution),

$$[H_3O^+] = 10^{-7} \text{ gram-ion/litre}$$

$\therefore$ $pH = - \log (10^{-7})$

$= 7$

Thus, at 298K temperature, the pH value of pure water (neutral solution) is 7.

For acidic solutions-

$[H_3O^+] > 10^{-7}$ gram-ion/litre (at 298K temperature)

$\therefore$ $pH < 7$

For basic solutions -

$[H_3O^+] < 10^{-7}$ gram-ion/litre (at 298K temperature)

$\therefore$ $pH > 7$

CHEMISTRYFORCOMPETITION.COM

In fact, at 298K temperature, the pH value of the aqueous solutions ranges from 0 to 14. Here, if the pH value of the solution is from 0 – 2, it is highly acidic. If it is 2 – 5, then the solution is moderately acidic and if it is from 5 – 7, then the solution is weakly acidic in nature. At pH 7, the solution is completely neutral. On the other hand, if the pH value of the solution is from 7 – 9, it is weakly basic. If it is 9 – 12, then the solution is moderately basic and if it is from 12 – 14, then the solution is highly basic in nature.

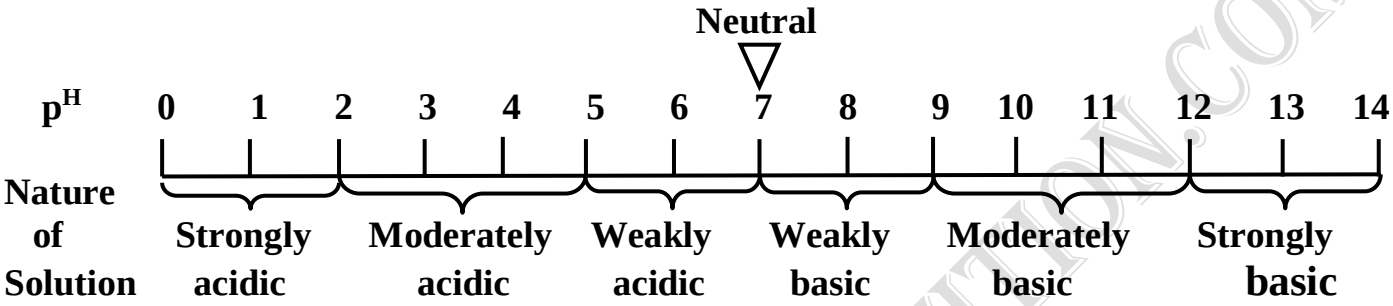


Fig. - pH Scale

pOH value or pOH Scale

If in a solution,

$[OH^-] = 10^{-x}$ gram-ion/litre

Then, pOH of the solution = x

Thus, $[OH^-] = 10^{-pOH}$ ---------- (1)

"The numerical value of the negative power raised to the base 10 to express the molar concentration of OH^- ions of the solution is called the pOH value of the solution."

Taking algorithm of eq. (1),

$\log [OH^-] = -pOH \ (\log 10)$

$\because \log 10 = 1$

$\therefore \log [OH^-] = -pOH$

or $pOH = -\log [OH^-]$ ---------- (2)

Thus, "The negative logarithm of the molar concentration of OH^- ions of a solution is called pOH value of the solution."

From eq. (2)-

$$pOH = \log \frac{1}{[OH]^-} \text{ ---------- (3)}$$

Thus, "The logarithm of the reciprocal of the molar concentration of OH^- ions of a solution is called pOH value of the solution."

At 298 K temperature, in pure water (neutral solution),

CHEMISTRYFORCOMPETITION.COM

$$[OH^-] = 10^{-7} \text{ gram-ion/litre}$$
$$\therefore \quad pOH = -\log(10^{-7})$$
$$= 7$$

Thus, at 298K temperature, the pOH value of pure water (neutral solution) is 7.

For acidic solutions-

$$[OH^-] < 10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$
$$\therefore \quad pOH > 7$$

For basic solutions -

$$[OH^-] > 10^{-7} \text{ gram-ion/litre (at 298K temperature)}$$
$$\therefore \quad pOH < 7$$

Numericals Based on pH-

Q.1.-Find the pH value of an aqueous solution containing H_3O^+ ion concentration 0.001 mol L^{-1}.

Soln.- Given that,

$$[H_3O^+] = 0.001 \text{ mol } L^{-1}$$
$$= 10^{-3} \text{ mol } L^{-1}$$
$$pH = ?$$
$$\because \quad pH = -\log [H_3O^+]$$
$$= -\log 10^{-3}$$
$$= -\{-3 \log 10\}$$
$$= -\{-3\} \qquad (\because \log 10 = 1)$$
$$= 3$$

Q.2.-Find the pH value of an aqueous solution containing H_3O^+ ion concentration 0.02 mol L^{-1}.

Soln.- Given that,

$$[H_3O^+] = 0.02 \text{ mol } L^{-1}$$
$$= 2 \times 10^{-2} \text{ mol } L^{-1}$$
$$pH = ?$$
$$\because \quad pH = -\log [H_3O^+]$$
$$= -\log (2 \times 10^{-2})$$
$$= -\{(\log 2) + (-2 \log 10)\}$$
$$= -\{0.3010 - 2\} \qquad (\because \log 10 = 1)$$
$$= 1.6990$$

CHEMISTRYFORCOMPETITION.COM

Q.3.-Find the pH value of an aqueous solution at 298 K temperature, if it contains OH^- ion concentration 0.001 mol L^{-1}.

Soln.- Given that,

$[OH^-] = 0.001 \text{ mol } L^{-1}$

$= 10^{-3} \text{ mol } L^{-1}$

pH = ?

I[st] Method-

Here, $pOH = - \log [OH^-]$

$= - \log 10^{-3}$

$= -\{-3 \log 10\}$

$= -\{-3\}$ ($\because \log 10 = 1$)

$= 3$

Now since,

$pH + pOH = 14$ (at 298K)

$\therefore pH = 14 - pOH$

$= 14 - 3$

$= 11$

II[nd] Method-

At 298K temperature,

$[H_3O^+] [OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 L^{-2}$

$\therefore [H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$

$= \frac{1.0 \times 10^{-14}}{[10^{-3}]}$

$= 10^{-11} \text{ mol } L^{-1}$

Now $\because pH = - \log [H_3O^+]$

$= - \log (10^{-11})$

$= - (- 11 \log 10)$

$= - (-11)$ ($\because \log 10 = 1$)

$= 11$

Q.4.-Find the pH value of 0.002 M aqueous solution of HCl.

Soln.- Given that,

$[HCl] = 0.002 \text{ M}$

$= 2 \times 10^{-3} \text{ mol } L^{-1}$

pH = ?

HCl is a strong electrolyte and ionises almost completely in its aqueous solution as under-

$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

CHEMISTRY FOR COMPETITION.COM

Here, $[H_3O^+] \approx [HCl]$

$= 2 \times 10^{-3}$ mol L^{-1}

Now $\because$ pH $= - \log [H_3O^+]$

$= - \log (2 \times 10^{-3})$

$= -\{(\log 2) + (- 3 \log 10)\}$

$= -\{0.3010 - 3\}$ $(\because \log 10 = 1)$

$= 2.6990$

Q.5.-Find the pH value of 0.01 M aqueous solution of H_2SO_4.

Soln.- Given that,

$[H_2SO_4] = 0.01$ M

$= 10^{-2}$ mol L^{-1}

pH = ?

H_2SO_4 is a strong electrolyte and ionises almost completely in its aqueous solution as under-

$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{2-}$$

Here, $[H_3O^+] \approx 2 \times [H_2SO_4]$

$= 2 \times 10^{-2}$ mol L^{-1}

Now $\because$ pH $= - \log [H_3O^+]$

$= - \log (2 \times 10^{-2})$

$= -\{(\log 2) + (- 2 \log 10)\}$

$= -\{0.3010 - 2\}$ $(\because \log 10 = 1)$

$= 1.6990$

Q.6.-The pH value of an aqueous solution is 5.6. Find $[H_3O^+]$ ion concentration in the solution.

Soln.- Given that,

pH = 5.6

$[H_3O^+]$ = ?

$\because$ pH $= - \log [H_3O^+]$

$\therefore$ $[H_3O^+]$ = Antilog (-pH)

= Antilog (-5.6)

= Antilog ($\bar{6}$.4)

$= 2.512 \times 10^{-6}$ mol L^{-1}

CHEMISTRYFORCOMPETITION.COM