Chapter 10 : ELECTROCHEMISTRY

The branch of physical chemistry which study about the relation between electricity and chemical process involved is called electrochemistry.

Electrolytes:

Electrolytes are the aqueous solution of chemical substance like acid, base and salt which conduct electricity in aqueous medium.

For examples:- Aqueous solution of H_2SO_4, NaOH, NaCl, etc.

Electrolytes are ionized into charge particles (ie. Cation and anion) when electricity is passed through them.

$$NaOH \xrightarrow{water} Na^+ + OH^-$$

Depending upon the strength of electrolytes, they can be classified into two types.

1. Strong electrolytes
2. Weak electrolytes

Strong electrolytes:-

The electrolytes which are completely ionized in aqueous medium are called strong electrolytes. It can conduct electricity easily.

Examples- Solution of H_2SO_4, HNO_3, HCl, NaOH, NaCl,etc.

Weak electrolytes:-

The electrolytes which are partially ionized in aqueous medium are called weak electrolytes. It conducts electricity partially.

Examples- Solution of CH_3COOH, NH_4OH, H_2CO_3, etc.

Non – Electrolytes :

Non – electrolytes are the aqueous solution of chemical substance which do not conduct electricity in aqueous medium.

Examples – Solution of glucose, sugar, urea etc.

Electrolysis :

The process of chemical decomposition of an electrolytes in solution by using electric current is called electrolysis.

This process is carried out in a vessel called electrolytic cell or voltameter. The two metallic rods are connected to two terminals of battery in electrolytic solution with the help of electric wire. These metallic rods are called electrodes. The electrode connected to positive terminal of battery is called anode and the electrode connected to negative terminal of battery is called cathode. In cathode reduction takes place whereas in anode oxidation takes place.

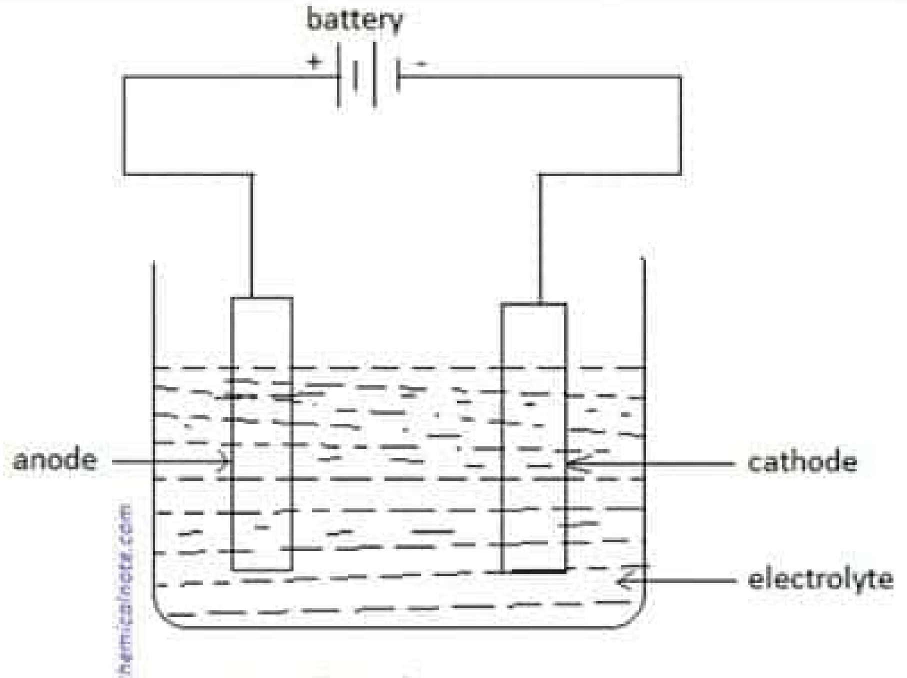

Fig. Electrolysis

If the electrolyte is NaCl solution, then,

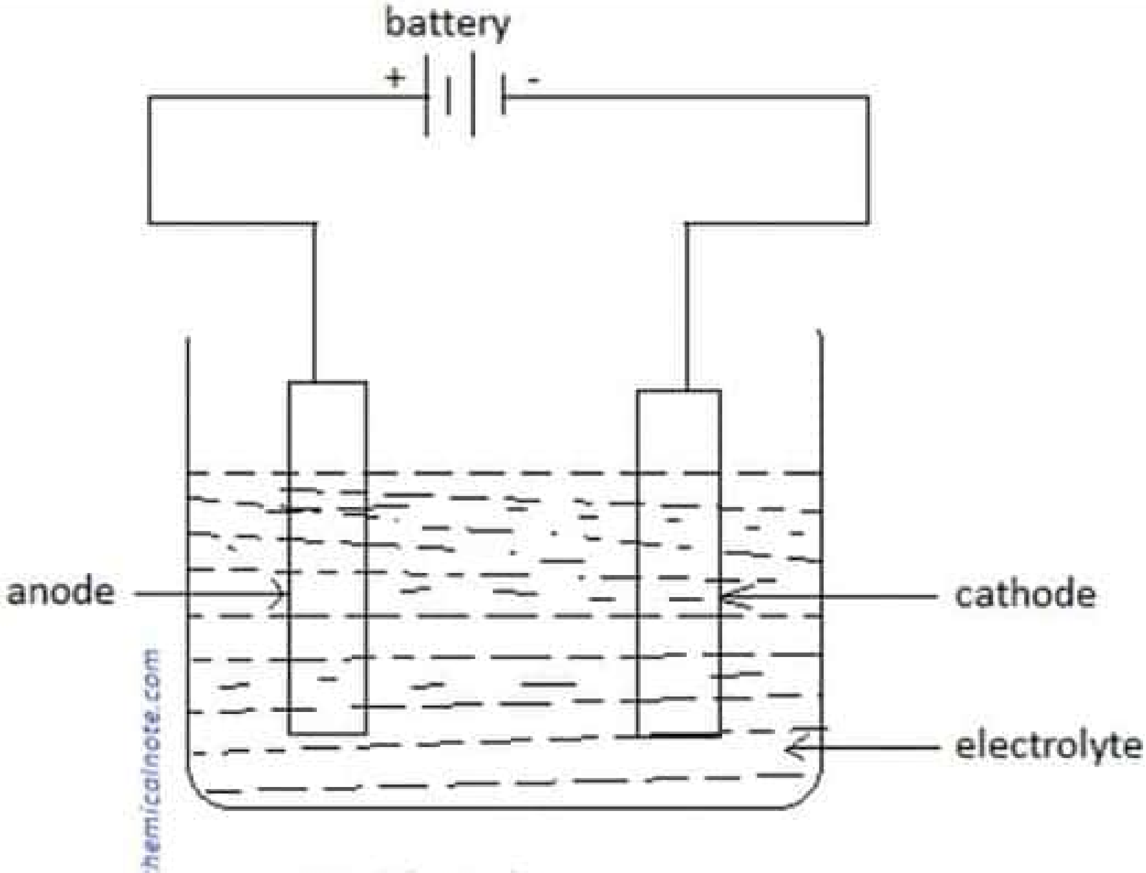

Fig. Electrolysis

If the electrolyte is NaCl solution, then,

At cathode : Reduction

$$Na^{+} + e^{-} \longrightarrow Na$$

At anode : Oxidation

$$Cl^{-} - e^{-} \longrightarrow Cl$$

Faraday's first laws of electrolysis :

This law state that, "The mass of the substance deposited at the electrode during electrolysis is directly proportional to the quantity of electricity passed through the solution."

Mathematically, $w \propto Q$

But, we know, $Q=It$, then,

$w \propto It$

Or, $w= ZIt$

Where, w = mass(weight) of the substance deposited at the electrode in gram.

Q = quantity of electricity passed through the solution in coulomb.

I= current in ampere

t= time in second

Z= constant known as electrochemical equivalent (ECE).

If I = 1 ampere and t = 1 sec then,

If I = 1 ampere and t = 1 sec then,

[w = Z]

Hence, electrochemical equivalent is the mass of the substance deposited at the electrode by passing 1 Ampere current for 1 second.

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{ Note : Z = E/F also. Where F

i.e. Z= E/96500

1 Faraday's charge : Charge of

We know, charge of an electron

1 mole of electron = 6.023x1023

Therefore, charge of 1 mole ele

= 9.6488x104 = 96488  = 96500 c

i.e. 1 faraday's charge = 96500
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Faraday's Second laws of electrolysis :

This law states that " the mass(weight) of different substances deposited or liberated at electrode by the same amount of electricity is directly proportional to the equivalent weight of substances".

Mathematically, W α E

Or, W = K E

Or, W/E = K

Therefore, Weight of substance (W) / Eq. wt. of substance (E) = Constant (K)

For example, when the same current is passed through the solution of H_2SO_4, $CuSO_4$ and $AgNO_3$ for the same period of time as shown in figure, then,

Wt. of the H_2 liberated/ Equivalent weight of H_2 = Constant(K) – – – -(i)

Wt. of the Cu deposited / Equivalent weight of Cu = Constant(K) – – – (ii)

Wt. of the Ag deposited / Equivalent weight of Ag = Constant(K) – – – -(iii)

On combining (i), (ii) and (iii),

$$\frac{\text{Wt. of the } H_2 \text{ liberated}}{\text{Equivalent weight of } H_2} = \frac{\text{Wt. of the Cu deposited}}{\text{Equivalent weight of Cu}} = \frac{\text{Wt. of the Ag deposited}}{\text{Equivalent weight of Ag}}$$

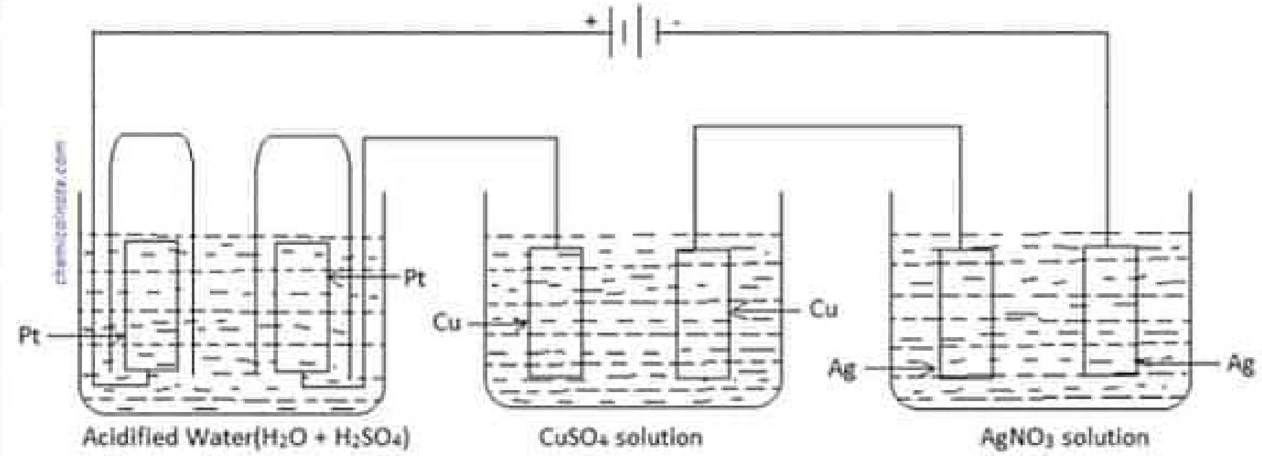

Fig. Illustrating Faraday's second law of electrolysis.

It is found that when 1.008 gram of H_2 is evolved from acidified water, then the masses of copper and silver deposited are 31.75 gram and 108 gram respectively, which are the equivalent weight of copper and silver respectively. Hence, this verifies Faraday's second law of electrolysis.

Applications of Electrolysis :

1. Electrolysis can be used to extract the pure metals in electroplating, electro refining, etc.
2. It can be used to manufacture oxygen and hydrogen gas from water.

Postulates of Arrhenius theory of ionization :

The main postulates of Arrhenius theory of ionization are given below.

- When an electrolyte is dissolved in water or any polar solvent, it's molecules are dissociated into charged particles called ions. The process of breaking down of molecules into ions is called ionization.
- Positively charged ions are called cations and negatively charged ions are called anion.
- Number of cations and anions in the solutions is always equal. So, the solution becomes electrically neutral.

$$AB \longrightarrow A^+ + B^-$$

- Ions have tendency to reunite to form unionized molecules too. So an equilibrium exists between the ions and unionized molecules.

$$AB \rightleftharpoons A^+ + B^-$$

- The degree of ionization vary with concentration . Lower the concentration of dissolved substance, greater is the degree of ionization.

$$\text{Degree of ionization} = \frac{[A^+]\,[B^-]}{[AB]}$$

Thus complete ionization(dissociation) may be expected to take place only in infinitely dilute solutions.

- The properties of an electrolyte in solution are the properties of it's ions.

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pH : pH may be defined as negative logarithm of hydrogen ion concentration.

i.e. pH = -log $[H^+]$

Auto – ionization of water/ Relation between pH and pOH :

Water is a weak electrolyte which ionizes weakly as,

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying law of mass action,

$$\text{Degree of ionization (k)} = \frac{[H^+][OH^-]}{[H_2O]}$$

Or, $k[H_2O] = [H^+]\,[OH^-]$

Or, $k_w = [H^+]\,[OH^-]$

Where K_w is a constant called ionic product of water and is defined as the product of molar concentration of H^+ and OH^- ions at temperature of 25^0C. it's value at 25^0C is found to be 1×10^{-14}

Therefore, $[H^+]\,[OH^-] = 1\times10^{-14}$

Taking −log on both sides,

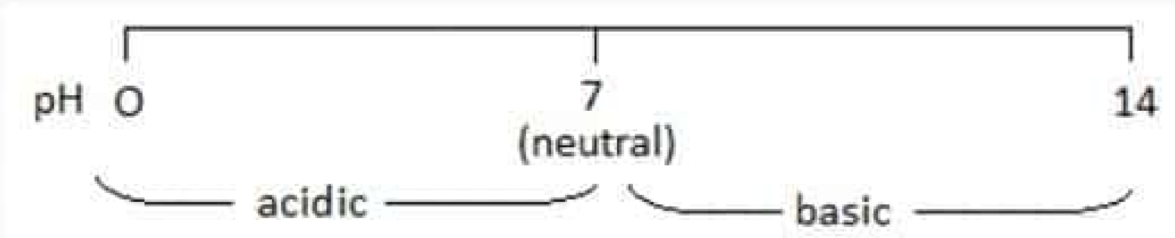
$$-\log [\,H^+\,] - \log [\,OH^-\,] = -\log [\,1\times10^{-14}\,]$$

$$p^H + p^{OH} = 14 \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;(\,i\,)$$

This equation (i) is the relation between p^H and p^{OH}.

p^H Scale :

The scale or the instrument which is used to measure the p^H of the solution is called p^H scale.



If a solution have:

$p^H = 7$ (Then solution is neutral.)

$p^H < 7$ (Then solution is acidic.)

$p^H > 7$ (Then solution is alkaline.)

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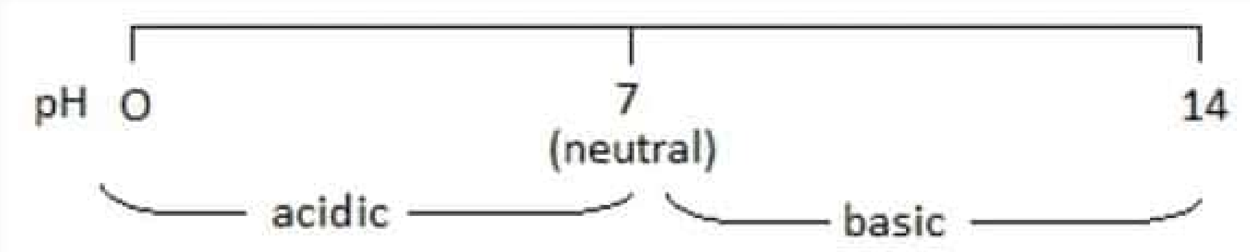

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Importance of p^H

1. p^H plays important role in the digestion of food and other biochemical activities. Examples : p^H of gastric juice is 1 – 2 which help in digestion of food.
2. Enzymes function effectively at certain p^H. Example : Trypsin acts best in alkaline p^H.
3. p^H of blood is maintained at the p^H of 7.35 – 7.42 which is due to the buffer action of bicarbonate and carbonic acid system.

Buffer solution :

The solution which can resist the p^H of the solution when small amount of acid or base is mixed in it is called buffer solution.

OR, The solution of equimolar mixture of a weak acid and its salt with strong base or weak base and its salt with strong acid is called buffer solution.

There are two types of buffer solution.

- **Acidic Buffer :** It is the solution of equimolar mixture of a weak acid and its salt with strong base. Eg. Equimolar mixture of CH_3COOH and CH_3COONa . The pH value of acidic buffer is less than 7.

- **Basic(alkaline) Buffer:** It is the solution of equimolar mixture of a weak base and its salt with strong acid. Eg. Equimolar mixture of NH_4OH and NH_4Cl. The pH value of acidic buffer is more than 7.

Applications of buffer solution:

1. Buffer action maintains the p^H of blood at about 7.35 – 7.42. If p^H is slightly changed then it may cause death.
2. It is used in many industrial processes like electroplating, manufacture of dyes, food, etc.
3. It is used in analytical chemistry.
4. It is used in bacteriological research.

Common – ion effect :

When a strong electrolyte having a ion common to weak electrolyte is mixed, then the ionization of weak electrolyte is totally suppressed. This effect of ion is called common ion effect.

$$\underset{\text{(weak electrolvte)}}{CH_3COONa} \rightleftharpoons Na^+ + CH_3COO^-$$

$$\underset{\text{(strong electrolyte)}}{NaCl} \longrightarrow \underset{\text{(common ion)}}{Na^+} + Cl^-$$

This effect is used in soap industries to make the precipitate of soap from soap solution.

Numerical solved problems :

- **Find the p^H of 0.1 Molar (M) of HCl.**

<u>Solution</u>:-

$HCl \rightarrow H^+ + Cl^-$

0.1M 0.1M 0.1M

We know that,

$p^H = -\log [H^+]$

$= -\log [0.1] = 1$ ans.

- **Calculate the p^H of 0.5 M solution of sulphuric acid.**

Solution:-

$H_2SO_4 \rightarrow 2H^+ + SO_4^{--}$

0.5M 2×0.5M 0.5M

We know,

$p^H = -\log [H^+] = -\log [2\times0.5] = 0$ ans.

- **Calculate the pH of solution containing $[OH^-]$ ions concentration of 10^{-6} mol L^{-1}**

Solution:

Given, $[OH^-] = 10^{-6}$ mol L^{-1}

pH = ?

we know $pOH = -\log[OH^-]$

$= -\log 10^{-6} = 6$

Now , pH + pOH = 14

Therefre, pH = 14 – pOH = 14 – 6 = 8 ans.

- **A current of 2.5 Ampere is passed through a solution of $ZnSO_4$ for 30 minutes and deposits 1.52 gram at cathode. Calculate the equivalent weight of zinc.**

Solution:-

Given, Current (I) = 2.5 A

Time (t) = 30 minutes = 30×60 sec = 1800 seconds

Weight of zinc deposited(w) = 1.52 gram

Equivalent weight of Zinc (E) = ?

We know from first law of electrolysis,

$w = ZIt$

$w = E/96500 \times It$

$1.52 = E/96500 \times 2.5 \times 1800$

$E = 32.59$

Thus, equivalent weight of zinc is 32.59.

- **0.383 gram of divalent metal was deposited by passing 2 Ampere of current for 50 minutes. Calculate the atomic weight of metal.**

Solution:-

Given,

Weight of metal (w) = 0.383 gram

Current (I) = 2 A

Time (t) = 50 minutes = 50×60 sec = 3000 second

Valency of metal (V) = 2

Atomic weight of Metal (At. Wt.) = ?

We know,

m = Zit

m = E/96500 x It

0.383 = E/96500 x 2 x 3000

E = 6.15

Atomic weight of Metal (At. Wt.) = ?

We know,

$m = Zit$

$m = E/96500 \times It$

$0.383 = E/96500 \times 2 \times 3000$

$E = 6.15$

Again,

Equivalent weight (E) = Atomic weight/Valency

$6.15 = At.\ Wt./2$

$At.Wt. = 12.30$

Therefore, atomic weight of zinc is 12.30 gram.

- **How many coulombs of electricity is required to discharge 0.1 M of sodium.**

Solution:-

We know,

1 mole of Na discharge 1 Faraday's coulombs charge.

i.e. 1 mole of Na discharges 96500 coulombs.

0.1 M of Na discharge 96500 x 0.1 Coulombs.

= 9650 coulombs

Therefore, 9650 coulombs of electricity is required to discharge 0.1 M of sodium.