Chapter-5 Electrochemistry

⇒ **Introduction:**

The branch of Chemistry which deals with the study of relationship between electrical energy and chemical energy and interconversion of one form into another is called Electrochemistry.

Depending upon electrical conductivity, substances can be classified into the following types:

- **Substances**
  - Conductors
    - Metallic Conductors
    - Electrolytes
      - Strong Electrolytes
      - Weak electrolytes
  - Non-conductors
    - Insulators
    - Non-Electrolyte

* **Electrolytes:** The chemical substances which allows electricity to pass through its aqueous solution or in the fused state are called electrolytes.

Ex:- All acids, alkalies and salts.

Characteristics:-

(i) They conduct electricity in their aqueous solutions.

(ii) They are chemically decomposed.

(iii) They form ionic solutions (cations and anions) when dissolved in water.

* **Non-electrolytes:**

The chemical substances which donot allow electricity to pass through their aqueous solution or in the fused state are called Non-electrolytes.

Ex: Urea, Sugar, glucose, fructose, maltose, lactose etc.

⇒ **Types of electrolytes:-**

Depending upon the strength, electrolytes may be classified into following types:

i. Strong electrolytes

ii. Weak electrolytes.

i. **Strong electrolytes:**

Substances which get completely ionised in solution or which have high degree of ionisation are strong electrolytes.

Example: ⓐ acids like HCl, HNO_3, H_2SO_4 etc.

ⓑ alkalies like $NaOH$, KOH, $Ca(OH)_2$, $Mg(OH)_2$ etc.

ⓒ Salts like $NaCl$, KCl, $CaCl_2$, $MgCl_2$ etc.

$$HCl \rightleftharpoons H^+ + Cl^-$$ (Almost fully ionised)

$$KOH \rightleftharpoons K^+ + OH^-$$ (Almost fully ionised)

$$NaCl \rightleftharpoons Na^+ + Cl^-$$ (Almost fully ionised)

ii. **Weak electrolytes :**

Substances which get ionised only slightly or which have low degree of ionisation are weak electrolytes.

A large fraction of such substances exist as undissociated molecules in solution and a very small fraction of it ionises in solution.

Example :- (a) Organic acids like CH_3COOH, $HCOOH$, $(COOH)_2$ etc.

(b) Inorganic acids like H_2CO_3, HCN etc.

(c) Bases like NH_4OH

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$ (Very slight dissociation)

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$ (Very slight dissociation)

Note :- **Degree of dissociation** :- The fraction of the total substance which exists as ions in solution is called its degree of dissociation.

$$\therefore \text{Degree of dissociation} = \frac{\text{No. of molecules split into ions}}{\text{Total no. of molecules dissolved}}$$

⇒ **Electrolysis :-**

The process of chemical decomposition of an electrolyte in solution or in the fused state by the passage of electric current is known as electrolysis.

* **Process of Electrolysis :-**

The process of electrolysis is carried out in a vessel known as electrolytic tank. It is made up of some insulating material such as glass, stone etc. Fused electrolyte or an aqueous solution of the electrolyte is taken in the electrolytic tank and two metallic plates are dipped in the electrolyte. These plates known as

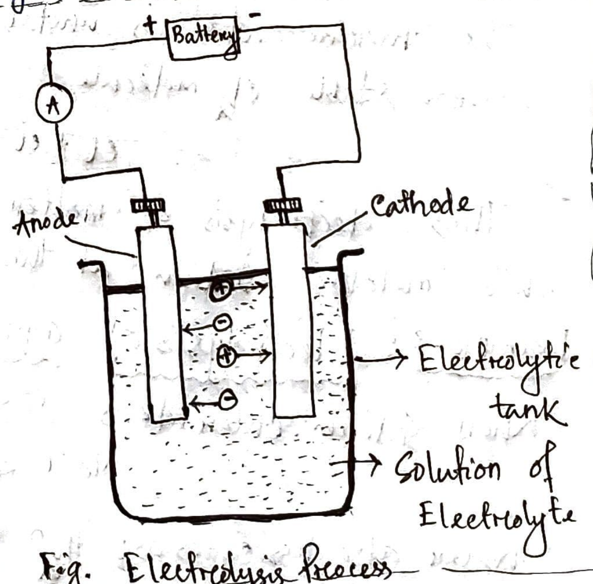


Fig. Electrolysis Process

electrodes are then connected with the poles of a battery. The electrode which is connected with the positive pole of the battery is called anode and the other, connected with the negative pole of the battery is called Cathode. Current enters the electrolyte through the anode and leaves through the cathode.

* **Working Process :**

When an electrolyte is dissolved in water it breaks up into cations and anions. When an electric current is passed through the solution, cations (+ve ions) move towards the cathode (negative electrode), whereas anions (-ve ions) move towards anode (+ve electrode) as shown in figure. This movement of ions towards oppositively charged electrodes is called electrolytic conduction. While reaching at the electrodes, the ions get discharged at their respective electrodes to give neutral species (primary change). The neutral species may further undergo secondary change to give stable substances.

* **Example-1 : Electrolysis of fused sodium chloride (or molten NaCl) :**

When NaCl (solid) is heated to high temperature, it melts and ionises as

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

When electric current is passed through this molten NaCl using Platinum electrodes :

ⓐ Na^+ ions move towards cathode, lose their charge by gain of electrons and changed into neutral atoms.

At Cathode; $Na^+ + e^- \longrightarrow Na$ (metal) {Primary change)

ⓑ Cl^- ions move towards anode, lose their charge by loss of electrons and change into neutral atoms.

At anode; $Cl^- - e^- \longrightarrow Cl$ (atom) { Primary change }

The chlorine atom is unstable and combines with another atom of Cl to form stable Cl_2 molecule :

$$Cl + Cl \longrightarrow Cl_2 \quad \text{(Secondary change)}$$

Thus, electrolysis of molten NaCl liberates Cl_2 gas at the anode while metallic sodium at the cathode.

Example-2 : Electrolysis of aqueous NaCl :-

When sodium chloride is dissolved in water, it ionises as :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Water also dissociates as: $H_2O \rightleftharpoons H^+ + OH^-$ (Slight ionisation)

When electric current is passed through aqueous NaCl solution using Platinum electrodes :

ⓐ Out of Na^+ and H^+ ions, only H^+-ions are discharged more readily than Na^+-ions because of their low discharge potential and

Preefarably gets discharged at the cathode.

At Cathode ; $H^+ + e^- \longrightarrow H$ (unstable atom) (Preimary change)

$H + H \longrightarrow H_2$ (stable) (Secondary change)

(b) Out of $Cl^\ominus$ and $OH^\ominus$ ions, only $Cl^\ominus$ ions are discharged more readily than OH^- ions because of theire low discharege potential and preefarably gets discharged at the anode.

At anode ; $Cl^\ominus - e^\ominus \longrightarrow Cl$ (atom, unstable) (Preimary change)

$Cl + Cl \longrightarrow Cl_2$ (stable) (Secondarey change)

Hence in the electreolysis of aqueous solution of sodium chloreide, hydreogen is libereated at cathode while chloreine is libereated at ~~cathode~~ anode.

⇒ Fareaday's Laws of Electreolysis :-

* 1. Fareaday's 1st Law of Electreolysis :

Statement: The mass of the substance libereated (W) or deposited at the electreode as a reesult of electreolyses is direectly preoporetional to the quantity of electreicity passed (Q) through the electrolyte.

Mathematically, $W \propto Q$

But, $Q = I \times t \Rightarrow W \propto I \times t$

$$\Rightarrow \boxed{W = Z \times I \times t}$$

Where,
- W = Amount of substance libereated in gm
- Q = Quantity of electreicity ore Charge in Coulomb
- I = Curerent in ampere.
- t = time of flow of curerent in seconds.
- Z = Constant Called Electreochemical Equivalent (ECE)

When, I = 1 ampere and t = 1 second

then $\boxed{W = Z}$

Thus Electreochemical Equivalent of a substance is defined as the mass of substance libereated when one ampere of curerent is passed through the electreolyte fore one second.

(ore) It is the mass of the substance libereated by the passage of one coulomb of electreicity.

A Faraday is a bigger unit of electricity.

1 Faraday = 96500 Coulombs.

Experimentally, it is observed that when 1 faraday (96500c) of electricity is passed through an electrolyte, then 1 gm equivalent of the substance is deposited at the electrode.

∴ 96500 Coulombs of charge deposits 1 gm equivalent

⇒ 1 coulomb of charge deposits = $\frac{1 \text{ gm equivalent}}{96500\ c}$

Hence, Electrochemical Equivalent (Z) = $\frac{1 \text{ gm equivalent}}{96500c} = \frac{\text{Atomic mass/valency}}{96500}$

Unit of 'Z' is gm equivalent / Coulomb.

Note: 1 mole of electrons carry 1 Faraday or 96500 Coulombs of charge.

Question-1: How many grams of silver will be deposited at the Cathode by the presence of 10 ampere of current through an aqueous solution of $AgNO_3$ for 1 hour?

Solution: Given data,

$I = 10$ ampere

$t = 1$ hour $= 3600$ sec

$Z = \frac{1 \text{ gm equivalent}}{96500\ c} = \frac{108/1}{96500} = \frac{108}{96500} = 0.0011$

Since $W = ZIt = 0.0011 \times 10 \times 3600 = 39.6$ gram.

Question-2: How many coulombs are required for the following changes?

i. One mole Ca^{2+} into Ca.

ii. Two moles of Al^{3+} into Al.

Solution: i. $Ca^{2+} + 2e \longrightarrow Ca$

1 mole of electrons carries 96500 Coulombs

⇒ 2 moles of electrons carry (2×96500) coulomb = 193000 Coulombs.

ii. $2Al^{3+} + 6e \longrightarrow 2Al$

1 mole of electrons carries 96500 coulombs

⇒ 6 moles of electrons carry (6×96500) coulombs = 579000 Coulombs.

Question-3: How many coulombs of charge are required to get 10 gms of Ca from molten $CaCl_2$?

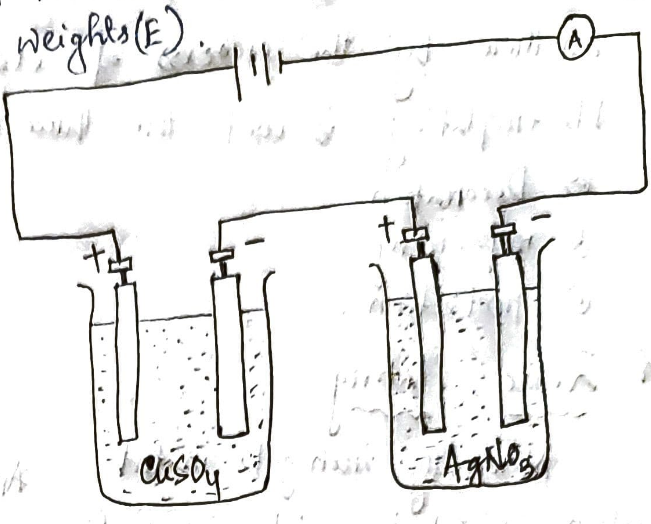
Solution: Given data, W = 10 gm, Q = ?

Since $W = ZQ = \frac{\text{Eq. mass/valency}}{96500} \times Q \Rightarrow Q = \frac{10 \times 96500 \times 2}{40}$ (cancelled to 48250)

∴ **Q = 48250 coulombs**

* 2. Faraday's 2nd law of Electrolysis :-

It states that when the same quantity of electricity is passed through different electrolyte solutions connected in series, the amount (W) of different substance produced at various electrodes are directly proportional to their equivalent weights (E).



Let us consider two electrolytic solutions $AgNO_3$ and $CuSO_4$ taken in two different electrolytic cells. Both the cells are connected in series and the same quantity of electricity is passed through the electrolytes.

According to Faraday's 2nd law,

$$W_{Ag} \propto E_{Ag} \quad \text{---} \; (1)$$

$$W_{Cu} \propto E_{Cu} \quad \text{---} \; (2)$$

from equation (1) and (2) we, have

$$\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} \Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}/96500}{E_{Cu}/96500} = \frac{Z_{Ag}}{Z_{Cu}}$$

$$\therefore \boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}} \quad \text{or} \quad \boxed{W \propto E \propto Z}$$

Question-1 : The same quantity of electricity is passed simultaneously through acidulated water and $CuSO_4$ solution. Weights of hydrogen and copper are 0.0132 and 0.4164 gram respectively. Find out the equivalent weight of copper.

Solution :- Wt. of hydrogen, W_{H_2} = 0.0132 gm

Wt. of copper, W_{Cu} = 0.4164 gm

Eq. wt. of hydrogen, E_{H_2} = 1.008

Eq. wt. of copper, E_{Cu} = ?

Applying Faraday's 2nd law of electrolysis,

$$\frac{W_{H_2}}{W_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \Rightarrow E_{Cu} = E_{H_2} \times \frac{W_{Cu}}{W_{H_2}} = 1.008 \times \frac{0.4164}{0.0132} = 31.79 \text{ Ans}$$

⇒ Industreial Application of Electreolysis :

1. Electreoplating :

The process of applying a coating of one metal overe another by the process of electrolysis is called electreoplating. Electreoplating is used fore three main purposes:

ⓐ Decoreation
ⓑ reepairing
ⓒ Preotection.

★ Zinc Plating

Noremally ireon gets reusted when exposed to moist aire. Rusting of ireon can be preevented by applying a coating of Zn ore Cr overe it. The process of applying a coating of Zn overe ireon with a view to preotect it from reusting is called Galvanization.

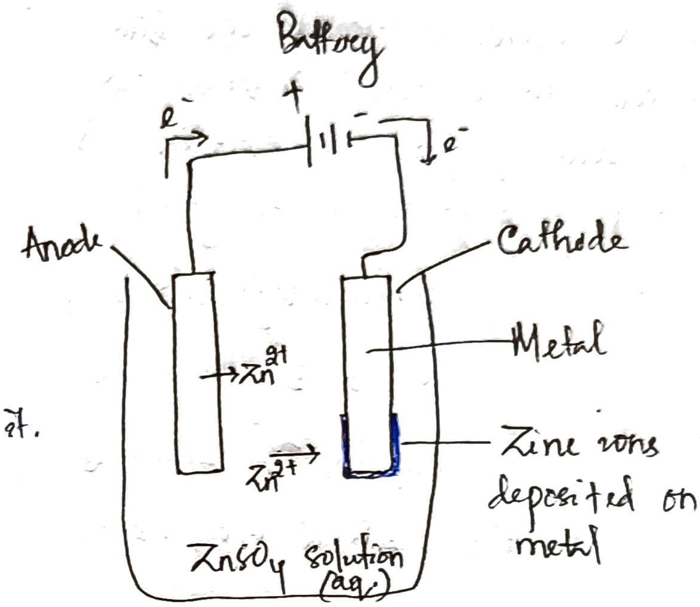


Fig:- Zinc plating

During the process of galvanisation, Zinc plate is used as anode and ireon areticle is used as cathode. Both the electreodes are connected to the teremenals of a batterey. The electreodes aree dipped in an aqueous solution of Zinc sulphate. When electreicity is passed, the anode, i.e., Zn plate dissolves in its aqueous salt solution to liberate Zn ion (Zn^{2+}), which get discharged and deposited overe the cathode. In this way a coating of Zn is applied overe the surface of the ireon areticle.