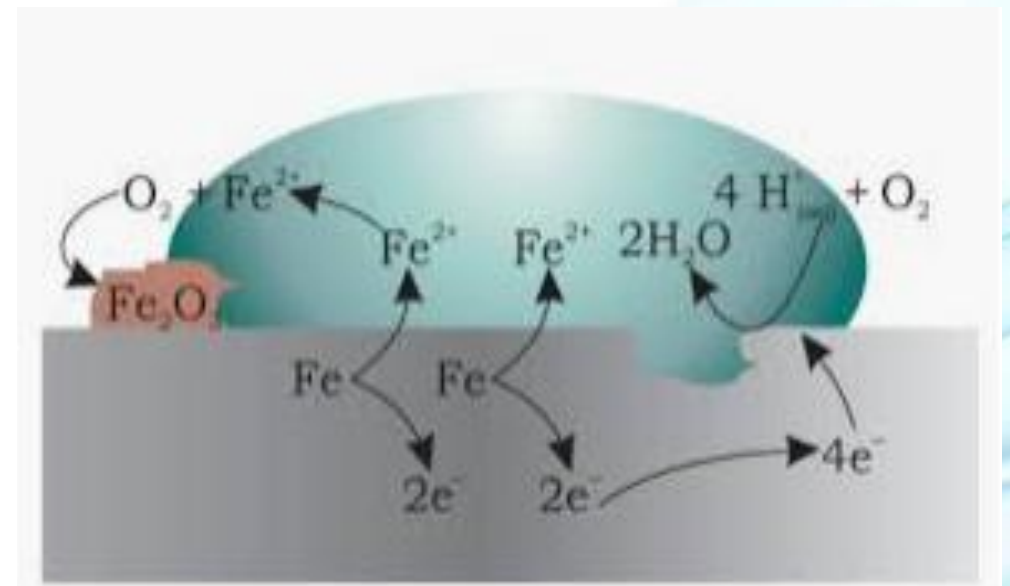
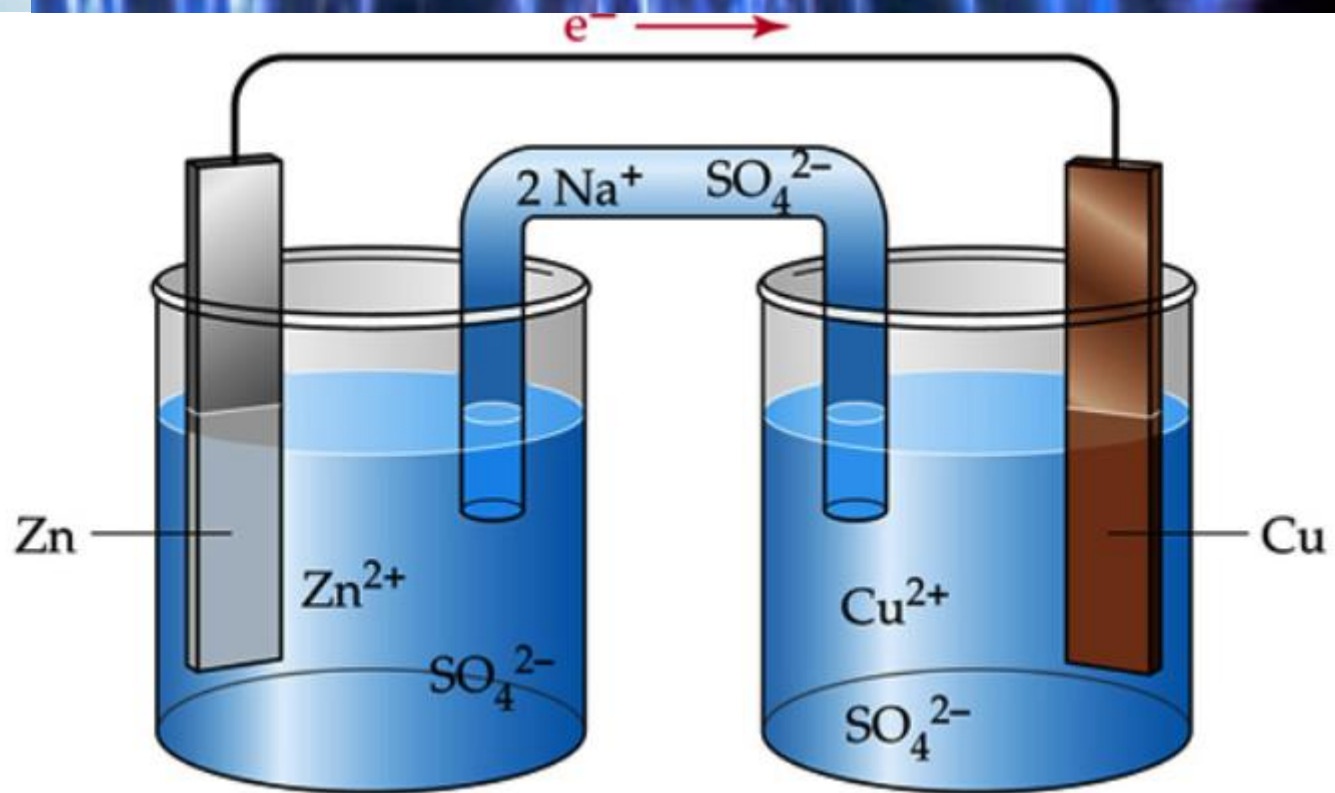


# ELECTROCHEMISTRY

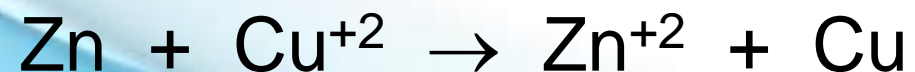
CLASS 12



Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations

## Electrochemical cell/ Galvanic cells/ Voltaic cells

### Example: Daniell Cell



## Electrochemical cell

- ✓ It is a device which **produces electric current** by means of spontaneous redox reaction.
- ✓ It is also called **Galvanic cells or voltaic cells**
- ✓ It consists of two half-cells with an electrode each.
- ✓ **Oxidation** takes place **at anode**
- ✓ ( electrode with negative charge).
- ✓ **Reduction** takes place **at cathode**
- ✓ ( electrode with positive charge).

# Constructuion of electrochemical Cell

- ✓ It consists of **two half-cells**: oxidation & reduction half cell
- ✓ Each half-cell consists of a container of an aqueous solution & an electrode or surface at which the electron transfer takes place.
- ✓ Wire connecting **electrodes**.
- ✓ External circuit carries **electrons**
- ✓ Electrons flow from (anode) oxidized substance to (cathode) reduced substance.
- ✓ **Salt bridge** connects solutions and separates two half-cell reactions .



✓ Half cell reactions:

✓ Anode (Oxidation half reaction)



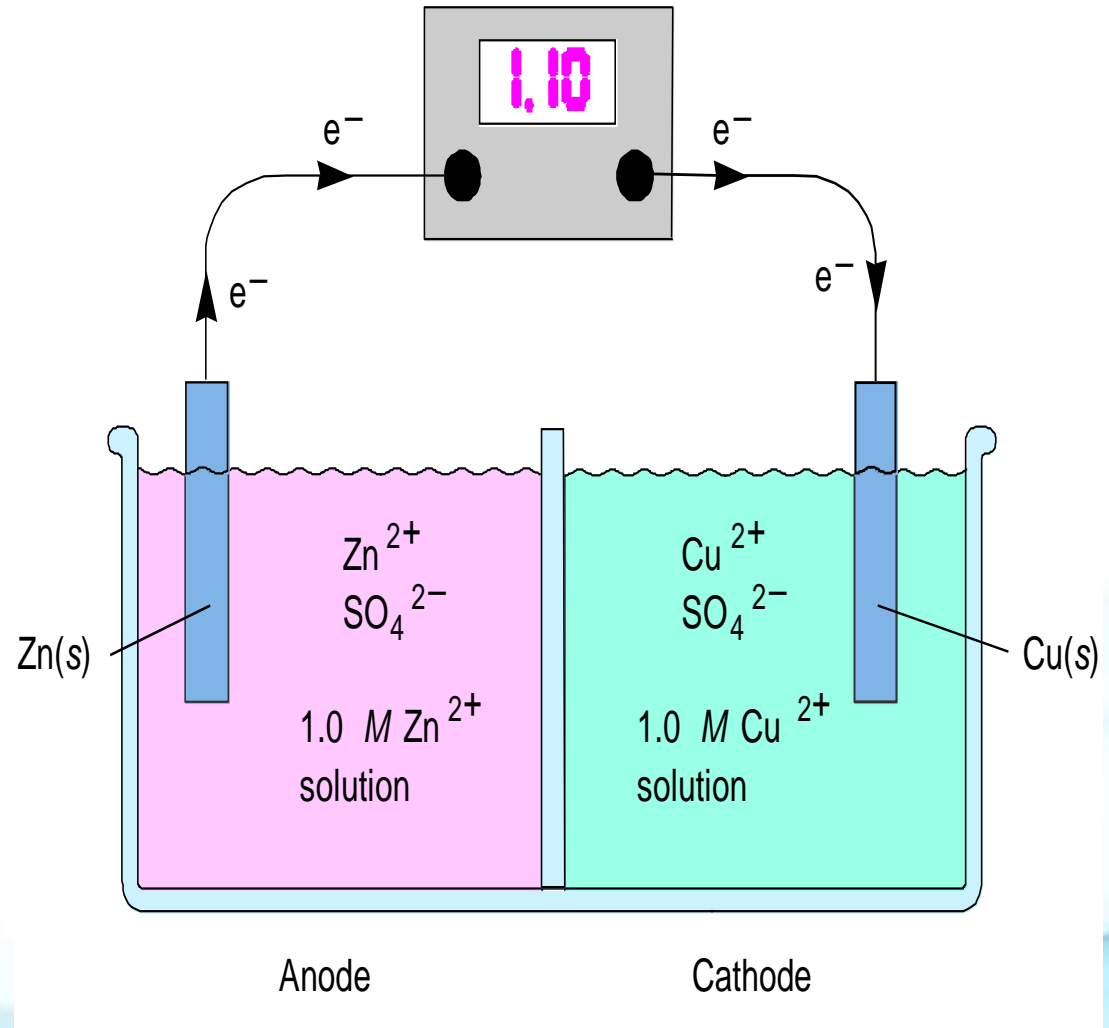
✓ Cathode (Reduction half reaction)

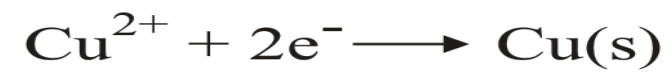
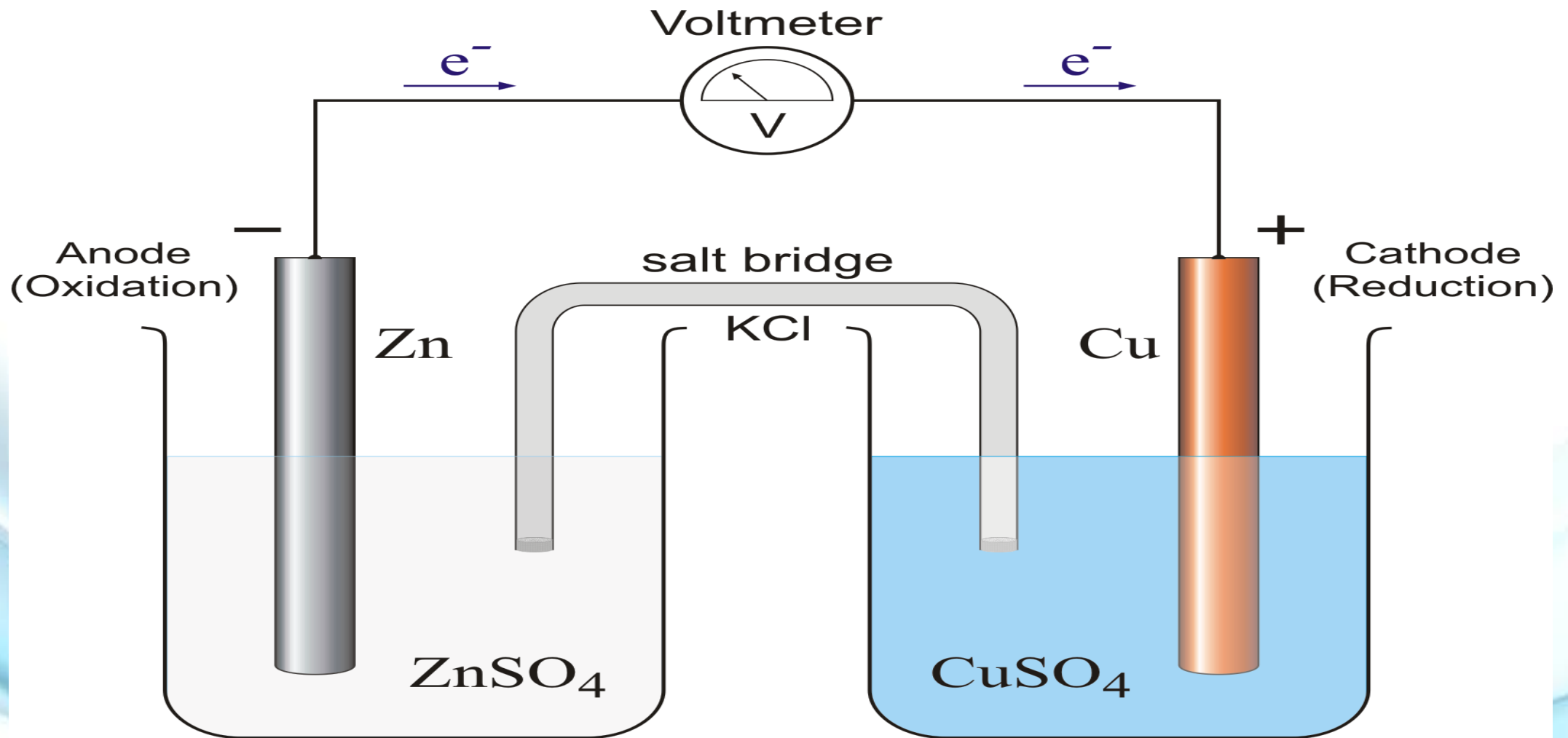


✓ Overall reaction



✓ Half cell is also called **redox couple**.





# REPRESENTATION OF A GALVANIC CELL

## REPRESENTATION OF A DANIELL CELL

Anode

Salt bridge

Cathode



## **(i) Electrode potential**

The electrical potential difference set up between the metal and its solution is known as electrode potential . These are of two types

- Oxidation potential
- Reduction potential

## **(i) Electromotive force(EMF) or cell potential:**

It is the difference between the electrode potential of the two electrodes constituting an electrochemical cell when either no or very little current is drawn from it .

$$E_{\text{cell}} \text{ or EMF} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}}$$

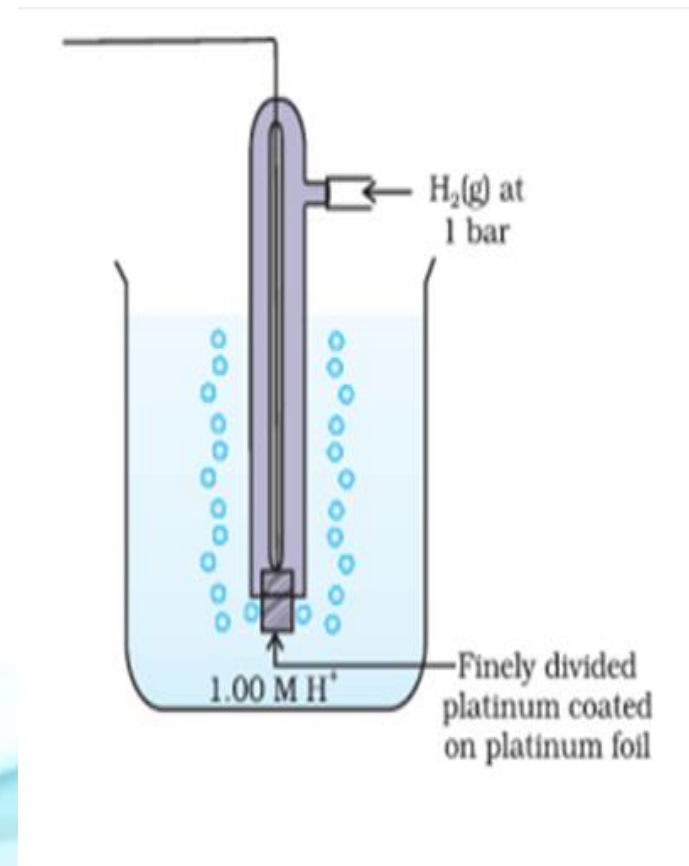
## **(i) Standard electrode potential ( $E^{\circ}$ )**

The electrode potential of an electrode determined relative to the standard hydrogen electrode under the standard conditions is called standard electrode potential. The standard conditions are 1M concentration of ions at 298K and 1atm pressure.



## STANDARD HYDROGEN ELECTRODE (SHE)

- ✓ It is reference electrode consists of a platinum electrode in contact with  $\text{H}_2$  gas (1 atm) and aqueous  $\text{H}^+$  ions (1 M).
- ✓ It is assigned 0.0 V standard electrode potential.
- ✓ It may behave as anodic or cathodic half cell.
- ✓ It is represented as  
$$\text{Pt(s)}|\text{H}_2(\text{g})(1\text{atm})|\text{H}^+(\text{aq})(1\text{ M}).$$
- ✓ When SHE is coupled with an other half cell then cell potential is the value of the electrode potential of half cell.



Q. How will you measure the standard electrode potential of a copper half cell:

To measure the standard electrode potential ( $E^0$ ) of  $\text{Cu}^{2+} / \text{Cu}$  electrode, copper rod is immersed in 1 M solution of  $\text{CuSO}_4$  solution. This half cell is connected to SHE.

The galvanic cell is represented as:



The cell potential is measured using voltmeter. The measured emf of the cell corresponds to the standard electrode potential of the half cell  $\text{Cu}^{2+} / \text{Cu}$ .

Applications of electrochemical series (or) standard electrode potential values:

(i) Calculation of standard EMF of the cell ( $E^0_{\text{cell}}$ ):

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

Q. Calculate the  $E^0$  of the cell whose half cells are given below,

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

(ii) To compare the oxidising and reducing power of various substances:

Substances with higher reduction potentials are stronger oxidising agents and the

Substances with lower reduction potentials are stronger reducing agents.

(iii) Predicting the feasibility of the reaction.

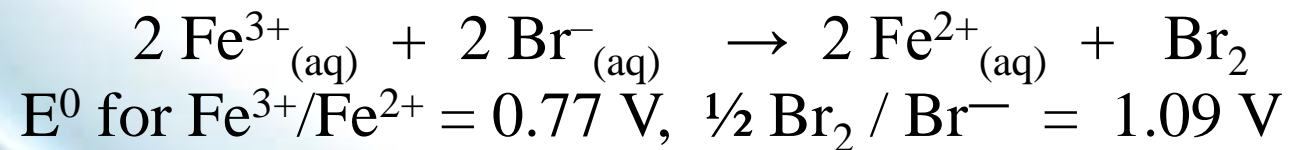
A redox reaction is feasible only when the  $E^0$  value of the reaction is positive.

Otherwise it is not feasible.

Q1. Represent the Galvanic cell using the two half cells  $E^0$  of  $\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}$  and  $E^0$  of  $\text{Sn}^{2+}/\text{Sn} = -0.14 \text{ V}$ .

Determine cell voltage of the cell, write anode and cathode reactions and overall reaction.

Q2. Using the standard electrode potentials given below predict if the following reaction is feasible or not:



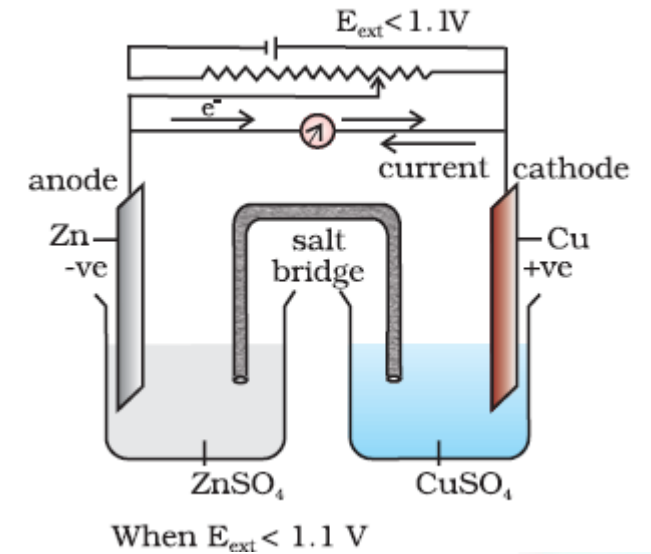
Q3. Using the standard electrode potentials given below predict if the reaction between  $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}^{-}(\text{aq})$  is feasible or not:



Functioning of Daniel cell when external voltage opposing the cell potential is applied.

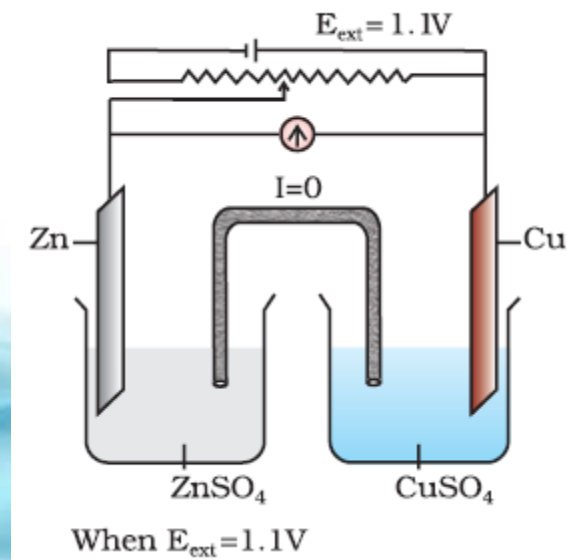
**a) When external voltage is less than 1.1V**

1. Electrons will flow from Zn to Cu rod
2. Current flows from Cu to Zn
3. Zn dissolves at anode and Cu deposits at cathode.



**B) When external voltage = 1.1V**

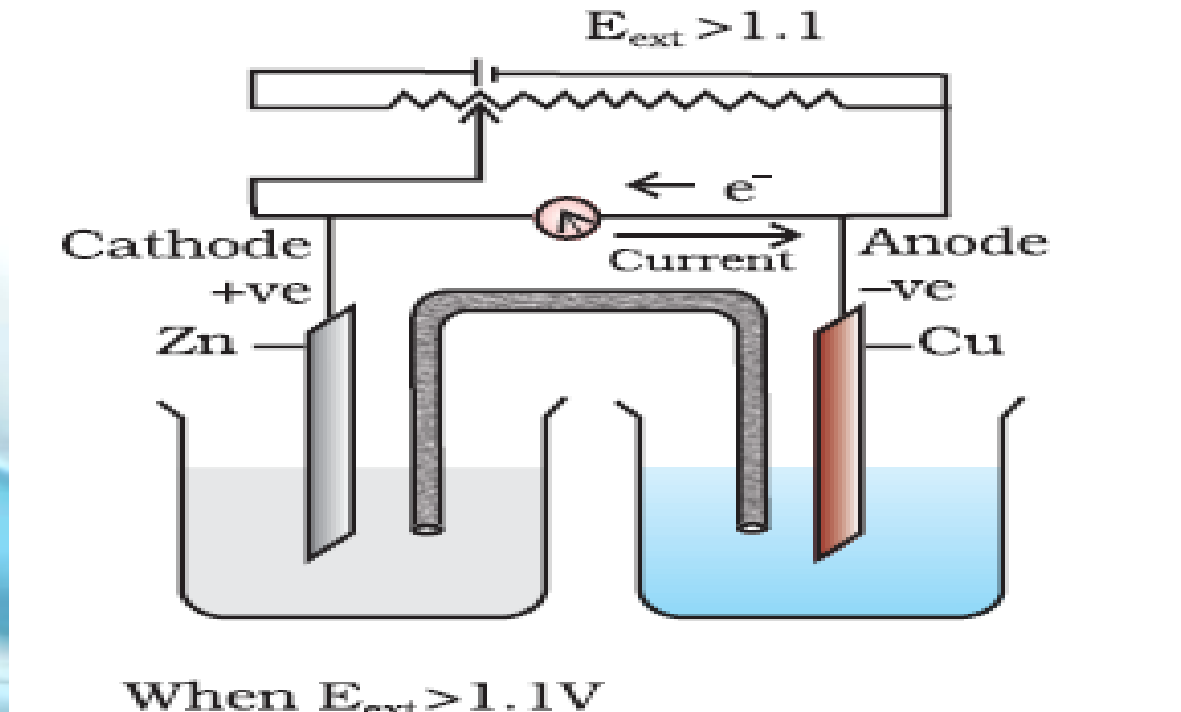
1. There is neither the flow of e-s nor the
2. No chemical change takes place.





**C) When external voltage is more than 1.1V**

1. Electrons will flow from Cu to Zn rod
2. Current flows from Zn to Cu rod
3. Cu dissolves at anode and Zn deposits at cathode



## NERNST EQUATION

The quantitative relationship between the concentration of ions and electrode potential is given by Nernst equation.

### Nernst equation for single electrode

Consider the electrode reaction ,



The Nernst equation is

$$E(\text{Cu}^{2+}/\text{Cu}) = E^{\circ}(\text{Cu}^{2+}/\text{Cu}) - \frac{RT}{nF} \ln \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$E(\text{Cu}^{2+}/\text{Cu})$  = electrode potential

$E^{\circ}(\text{Cu}^{2+}/\text{Cu})$  = standard electrode potential

$[\text{Cu}^{2+}]$  = Molar concentration of ions,  $R = 8.314\text{J/K/mol}$ ,  $n =$  no: of electrons gained ,  $F =$  Faraday's law constant =  $96500\text{ C/mol}$

On substituting the values in Nernst equation at 298K ,

$$E(\text{Cu}^{2+}/\text{Cu}) = E^{\circ}(\text{Cu}^{2+}/\text{Cu}) - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$$E(\text{Cu}^{2+}/\text{Cu}) = E^{\circ}(\text{Cu}^{2+}/\text{Cu}) - \frac{0.059}{n} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

OR

$$E(\text{Cu}^{2+}/\text{Cu}) = E^{\circ}(\text{Cu}^{2+}/\text{Cu}) + \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}]}$$

Q1. Calculate the electrode potential when copper metal is dipped in 4 M solution of  $\text{CuSO}_4$ .

$$E^0 \text{ of } \text{Cu}^{2+} / \text{Cu} = 0.34 \text{ v}$$

Q2. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.



$$E(\text{Cu}^{2+}/\text{Cu}) = E^\circ(\text{Cu}^{2+}/\text{Cu}) + \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}]}$$

$$E(\text{Cu}^{2+}/\text{Cu}) = 0.34 + \frac{0.059}{2} \log 4$$

$$E(\text{Cu}^{2+}/\text{Cu}) = 0.34 + \frac{0.059}{2} \times 0.6021$$

$$E(\text{Cu}^{2+}/\text{Cu}) = 0.3577 \text{ V}$$



$$E_{\text{HE}} = E^0_{\text{SHE}} + \frac{0.059}{n} \log \frac{[\text{H}^+]}{[\text{H}_2]^{1/2}}$$

$$n = 1$$

$$[\text{H}_2]^{1/2} = 1$$

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

$$10 = -\log[\text{H}^+]$$

$$\log[\text{H}^+] = -10$$

$$E^0_{\text{SHE}} = 0$$

$$E_{\text{HE}} = 0 + 0.059 \times -10$$

$$E_{\text{HE}} = -0.59 \text{ V}$$



Nernst equation for Galvanic cell :

Nernst equation for Daniel cell:

Daniel cell is represented as  $\text{Zn} / \text{Zn}^{2+} \parallel \text{Cu}^{2+} / \text{Cu}$

Cell reaction:  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

Nernst Equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}][\text{Cu}]}{[\text{Zn}][\text{Cu}^{2+}]}$$

Since concentration of solids is taken as unity ,  $[\text{Zn}] = [\text{Cu}] = 1$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

OR

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

**Q1. Write Nernst equation and calculate the e.m.f. of the following cell at 298 K.**



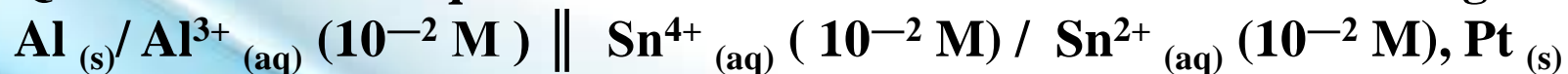
**Given that  $E^0$  of  $\text{Zn}^{2+} / \text{Zn} = -0.76\text{ V}$  and  $E^0$  of  $\text{Cu}^{2+} / \text{Cu} = 0.34\text{ V}$**

**Q2. Write Nernst equation and calculate the e.m.f. of the following cell at 298 K.**



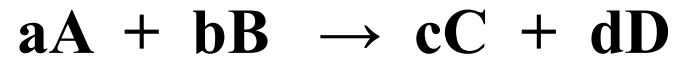
**Given that  $E^0$  of  $\text{Ag}^{+} / \text{Ag} = 0.8\text{ V}$  and  $E^0$  of  $\text{Cu}^{2+} / \text{Cu} = 0.34\text{ V}$**

**Q3. Write Nernst equation and calculate the e.m.f. of the following cell at 298 K.**



**Given that  $E^0$  of  $\text{Al}^{3+} / \text{Al} = -1.66\text{ V}$  and  $E^0$  of  $\text{Sn}^{4+} / \text{Sn}^{2+} = 0.15\text{ V}$**

**For a general redox reaction involving the transfer of n electrons**



**Nernst equation is ;**

$$\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

**On substituting the values at 298K**

$$\mathbf{E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^c}}$$

## Relationship between standard EMF and equilibrium constant

Consider Daniel cell , Zn/Zn<sup>2+</sup> || Cu<sup>2+</sup>/ Cu

The cell reaction is Zn + Cu<sup>2+</sup> → Zn<sup>2+</sup> + Cu

The equilibrium constant for the above reaction is

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Nernst equation for the above reaction is

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

At equilibrium  $E_{cell} = 0$

$$0 = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^{\circ}_{cell} = \frac{RT}{nF} \ln K_c$$

$$E^{\circ}_{cell} = 2.303 \frac{RT}{nF} \log K_c$$

on substituting the value of R, n , and F at 298K,

$$E^{\circ}_{cell} = \frac{0.059}{2} \log K_c$$

Thus for a general reaction at 298K ,

$$E^{\circ}_{cell} = \frac{0.059}{n} \log K_c$$

## Relationship between EMF and Gibbs energy of reaction

Electrical work done in one second is equal to the electrical potential multiplied by total charge passed.

$$W_{\text{Elect}} = \text{electrical charge} \times \text{EMF}$$

If  $n$  moles of electrons are transferred in the cell reaction, then

$$\text{Electrical charge} = nF$$

Since the decrease in Gibbs energy ( $-\Delta G$ ) is a measure of electrical work

$$-\Delta G = nFE_{\text{cell}}$$

$$\Delta G = -nFE_{\text{cell}} \text{ (OR)}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$-\Delta G$  = Maximum work that can be obtained from the cell



# CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

- Resistance (R)
- It is the obstruction to the flow of current. Its unit is ohms.
- R is directly proportional to length and is inversely proportional to area of cross section.
- $R \propto l/A$  ,  $R = \rho l/A$  where  $\rho$  is resistivity
- (b) Resistivity (V) or specific resistance.
- Resistivity is the resistance offered by the conductor of 1m length with area of cross section  $1\text{m}^2$ .
- $\rho = RA / l$
- [c] Conductance [C]
- It is the measure of the ease with which current flows through the conductor. It is the reciprocal of resistance.
- $C = 1/R$  , Its unit is siemens ( $\Omega^{-1}$ )
- (d) Conductivity or specific conductance (K)
- It is defined as the conductance of  $1\text{m}^3$  of a conductor . it is the reciprocal of specific resistance. ( $\rho$ )
- $K = 1/\rho = l/RA$  , unit is  $\text{Sm}^{-1}$  or  $\text{Scm}^{-1}$

**e) Molar conductivity ( $\lambda_m$ )**

It is the conducting power of all the ions produced by dissolving 1gm mole of the electrolyte in solution.

$$\lambda = \frac{1000 \times K}{C} \quad \text{where } C \text{ is the conc: , its unit is } \text{Scm}^2/\text{mol}$$

**f) Cell constant ( $G^*$ )**

It is the ratio of length of the conductor to the area of cross section .

$$G^* = l/A \quad \text{unit is } \text{cm}^{-1} \text{ or } \text{m}^{-1}$$

$$\text{Cell constant } G^* = K/C \text{ or } K \times R$$

## Difference between electronic and electrolytic conduction

Electronic (metallic) conduction	Electrolytic (ionic) conduction
<ul style="list-style-type: none"><li>• Conduction is by the movement of electrons.</li><li>• Conductivity is accompanied by no decomposition</li><li>• Electronic conduction decreases with increase in temp</li><li>• It does not involve any transfer of matter</li></ul>	<ul style="list-style-type: none"><li>• Conduction is by movement of ions.</li><li>• Conductivity is accompanied by decomposition of electrolyte.</li><li>• Electrolytic conduction increases with increase in temp</li><li>• It involves transfer of matter as ions.</li></ul>

## **Factors that affect electronic conductance**

- Nature and structure of the metal
- No: of valence electrons
- Density of metal
- Temperature (as temp increases, conductivity decreases)

## **Factors that affect electrolytic conductance**

- Nature of the electrolyte
- Size of their ions and their solvation
- Nature of the solvent and their viscosity
- Concentration of the electrolyte
- Temperature

## Measurement of conductivity of ionic solutions :

Resistance is measured using Wheatstone bridge. The ionic solution is taken in a conductivity cell which is made of pyrex glass and is fitted with Pt electrodes coated with Pt black. The Pt electrodes have area of cross section equal to  $A \text{ cm}^2$  and are separated by a distance of 1cm

At null point :  $R_1/R_2 = R_3/R_4$

Unknown resistance  $R_2 = R_1 R_4 / R_3$

From the resistance  $R_2$ , conductivity is calculated by ,  $\kappa = G^* / R_2$

Using the  $G^*$  and resistance of the given solution ,we can calculate the conductivity of the given solution i.e;  $\kappa = G^*/R$

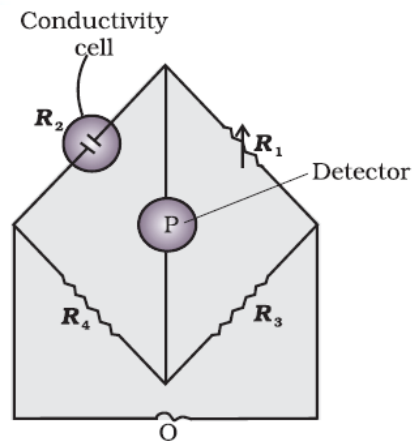
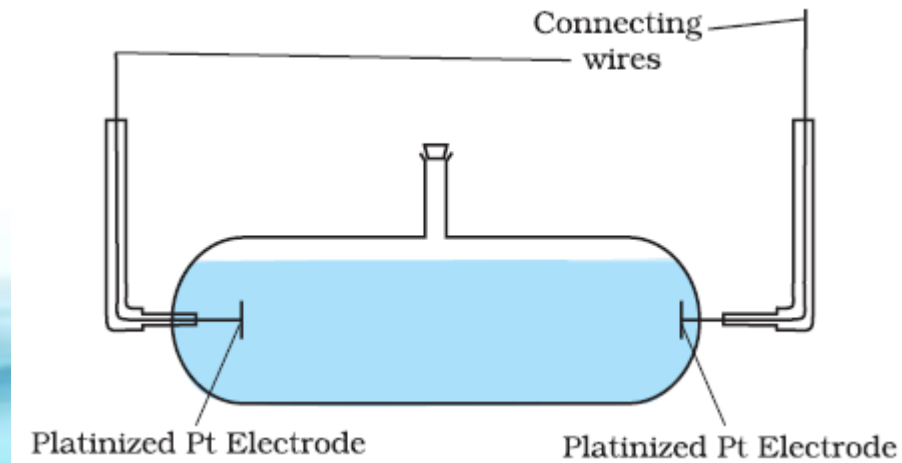


Fig. 3.5: Arrangement for measurement of resistance of a solution of an electrolyte.

$$\text{Unknown resistance } R_2 = \frac{R_1 R_4}{R_3}$$





➤ **Variation of conductivity with dilution**

Conductivity always decreases with dilution for both strong and weak electrolytes because the no: of ions per unit volume that carry current in a solution decreases with increases with dilution.

➤ **Variation of molar conductivity with concentration for strong electrolytes .**

On dilution the no: of ions in the solution donot increase but the inter ionic attractions decreases and mobility of ion increases. Hence molar conductivity ( $\Lambda_m$ ) of strong electrolytes increases slightly on dilution .The variation of molar conductivity with concentration for strong electrolyte is given by

$$\Lambda_m = \Lambda_m^{\circ} - A\sqrt{c}$$

$\Lambda_m^{\circ}$  is molar conductivity at infinite dilution . It can be calculated by extrapolating the graph of  $\Lambda_m$  verses  $\sqrt{c}$ .

The constant A depends on the nature of the solvent , type of solute and temp.

➤ **Variation of molar conductivity with concentration for weak electrolytes.**

On dilution the degree of ionization of weak electrolyte increases and the no: of ions furnished by the electrolyte increases. Hence molar conductivity of weak electrolyte increases largely on dilution.

Molar conductivity at infinite dilution ( $\Lambda_m^0$ ) for weak electrolyte can not be calculated by extrapolating the graph of  $\Lambda_m$  Vs  $\sqrt{c}$ .

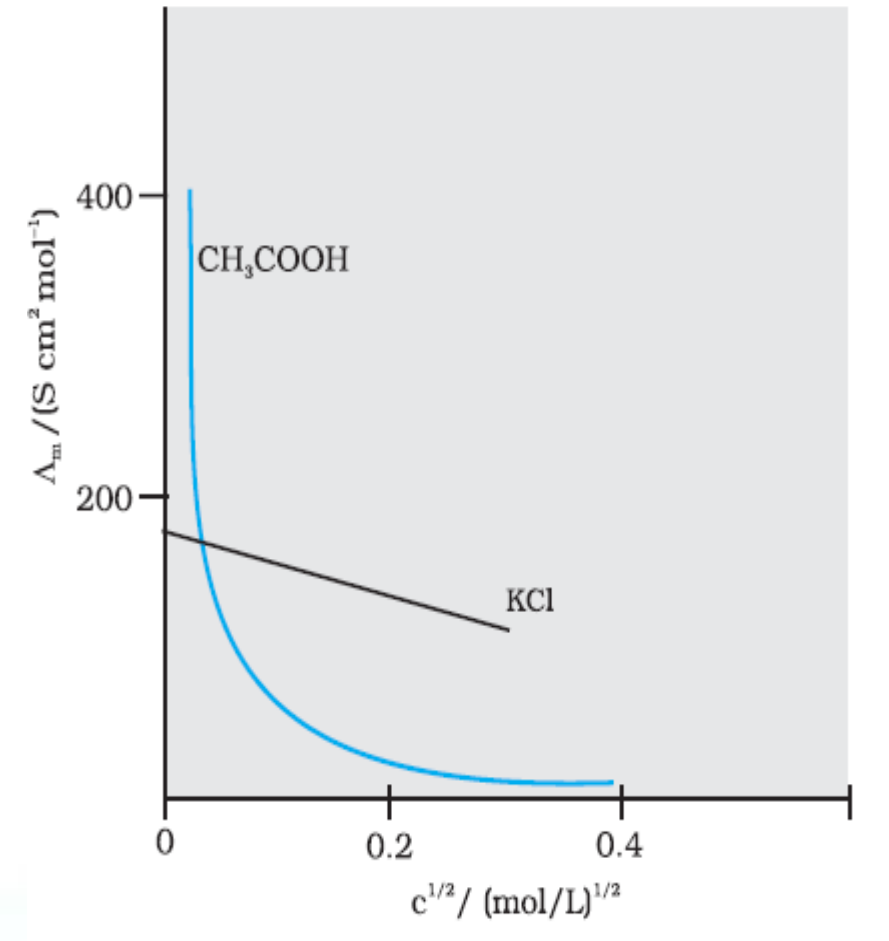
Since ionization of weak electrolyte is complete at infinite dilution, degree of ionization or degree of dissociation ( $\alpha$ ) of weak electrolyte is given as

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

$\Lambda_m^c$  = is molar conductivity at the concentration C mol/L.

Dissociation constant of weak acid ( $K_a$ ) is given as

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$



➤ **Limiting molar conductivity ( $\Lambda^{\circ}_m$ )**

It is the molar conductivity when the concentration approaches zero

➤ **Kohlrausch's law.**

At infinite dilution when the dissociation of the electrolyte is complete, each ion makes a definite contribution towards the molar conductivity of the electrolyte, irrespective of the nature of the other ion with which it is associated.

ie; molar conductivity of an electrolyte at infinite dilution can be expressed as the sum of contribution from individual ions. If  $\lambda^{\circ}_+$  and  $\lambda^{\circ}_-$  represents the molar conductivities of cation and anion at infinite dilution

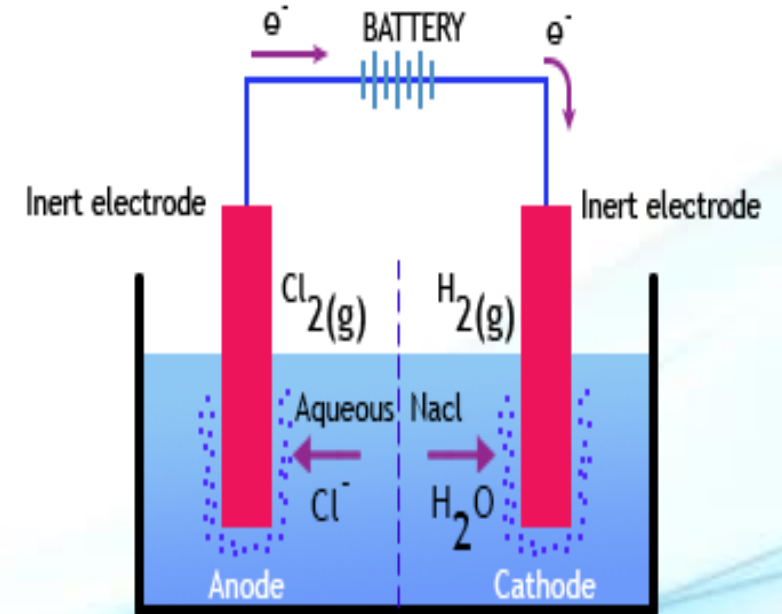
Then for eg:for NaCl the  $\Lambda^{\circ}\text{NaCl} = \lambda^{\circ}\text{Na}^+ + \lambda^{\circ}\text{Cl}^-$

➤ **Applications of Kohlrausch's law.**

- (i) To calculate the molar conductivity of weak electrolyte at infinite dilution
- (ii) To calculate the degree of dissociation of weak electrolytes

## ➤ ELECTROLYTIC CELL

- ✓ This is a device which brings about a chemical change by means of electric current supplied.
- ✓ In this cell two electrodes are dipped in same container.
- ✓ electricity from outside source supplies electrons for the non-spontaneous reaction.
- ✓ Reduction takes place cathode where metal from electrolytic solution gets deposited.
- ✓ oxidation takes place anode from where metal goes into the electrolytic solution.



## Faraday's laws of electrolysis :

### ➤ Faraday's first law

The amount of substance deposited or liberate at an electrode is directly proportional to the quantity of electricity passed through the electrolytic solution.

$$W \propto Q \quad W = ZQ \quad \text{where } Q = It \quad W = Zit$$

Q = quantity of charge in coulombs , I = current in amperes , t = time in seconds

Z = electrochemical equivalent and it is defined as the amount of substance liberated when current of one ampere is passed through the electrolyte for one second.

$$Z = \frac{\text{Atomic mass}}{nF}$$

$$W = \frac{\text{RAM} \times I \times t}{nF}$$



➤ **Faradays second law of electrolysis**

When same quantity of electricity is passed through different electrolytes connected in series then the masses of substances deposited or liberated at the electrodes are proportional to their chemical equivalents.

$$\frac{\text{Mass of X (w}_1\text{)}}{\text{Mass of Y (w}_2\text{)}} = \frac{\text{Equivalent mass of X}}{\text{Equivalent mass of Y}}$$

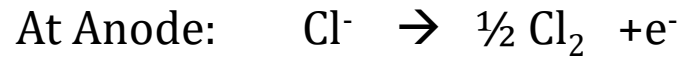
Equivalent mass = atomic mass / valency

## Products of Electrolysis

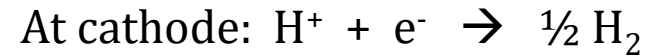
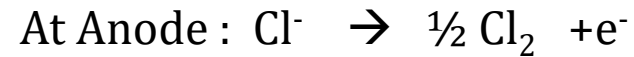
The formation of products during electrolysis depends upon the following factors

- (i) Electrode potential: Cathode reaction will be the one with higher reduction potential values ( $E^{\circ}_{\text{red}}$ ). Anodic reaction will be the one with lower reduction potential values ( $E^{\circ}_{\text{red}}$ ) or higher oxidation potential values ( $E^{\circ}_{\text{ox}}$ ).
- (ii) Concentration of ions
- (iii) Overvoltage
- (iv) Nature of electrodes

### 1. Electrolysis of molten NaCl.



### 2. Electrolysis of aqueous solution of NaCl using Pt electrode



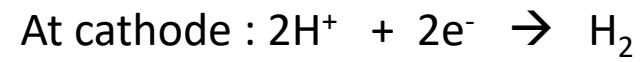
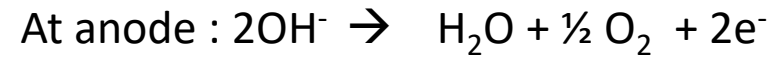
### 3. Electrolysis of aqueous solution of AgNO<sub>3</sub> using Pt electrode



### 4. Electrolysis of aqueous solution of AgNO<sub>3</sub> using Ag electrode



## 5. Electrolysis of dil.H<sub>2</sub>SO<sub>4</sub> solution



## 6. Electrolysis of aqueous solution of AgCl using Ag electrode

