

ELECTROCHEMISTRY

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- *Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions*

Electrochemistry is the area of chemistry concerned with the interconversion of chemical and electrical. A battery is an electrochemical cell, a device for interconverting chemical and electrical energy. A battery takes the energy released by a spontaneous chemical reaction and uses it to produce electricity.

Electrochemical cell

Electrochemical cell are of two types



Galvanic cells or Voltaic cell

- A spontaneous chemical reaction generates an electric current.

Electrolytic cell.

- An electric current drives a nonspontaneous reaction.

Electrolysis-

- *The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**.*
- Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerine, alcohol etc., are examples of **non-electrolytes**

Continue..

- Voltmeter convert ***electrical energy into chemical energy***.
- **Electrolytic cell or Voltmeter** : The device in which the process of electrolysis or electrolytic decomposition is carried out is known as ***electrolytic cell*** or ***voltmeter***.

Continue..

- **Electrode-**
- The electrode on which oxidation takes place is called ***anode*** (or +ve pole) and the electrode on which reduction takes place is called ***cathode*** (or –ve pole).
- During electrolysis in voltameter ***cations are discharged on cathode and anions on anode.***
- In voltameter, outside the ***electrolyte*** electrons flow from ***anode to cathode*** and ***current*** flow from ***cathode to anode.***

Anode and Cathode

- The anions on reaching the anode give up their electrons and converted into the neutral atoms.
- **At anode** : $A^{-} \longrightarrow A + e$ (Oxidation)
- (vi) On the other hand cations on reaching the cathode take up electrons supplied by battery and converted to the neutral atoms.
- **At cathode** : $B^{+} + e^{-} \longrightarrow B$ (Reduction)
- This overall change is known as **primary change** and products formed is known as **primary products**.

Points about anode and cathode

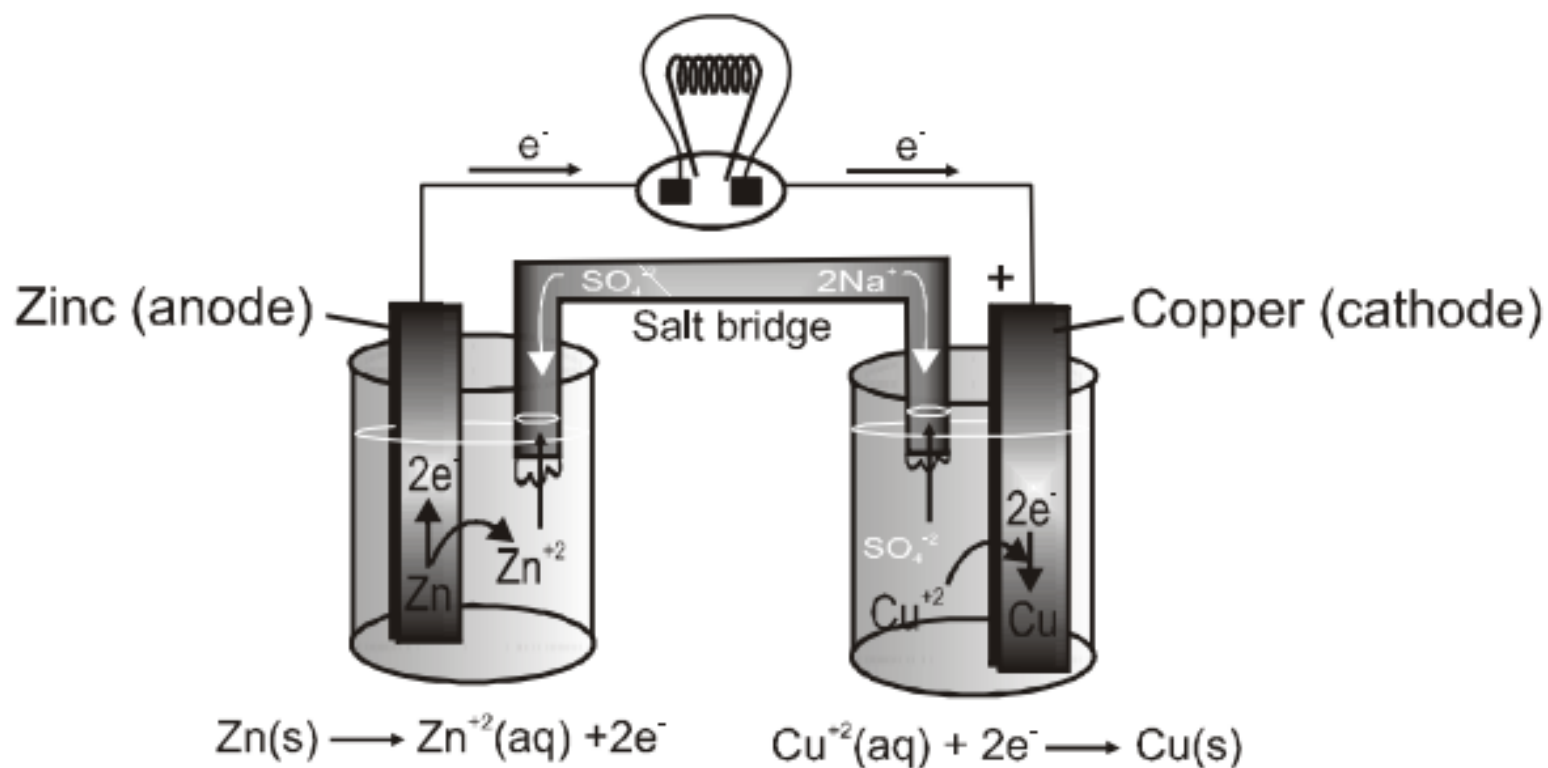
This particular electrode is known as anode :

- On anode oxidation will take place. (release of electron).
- To act as source of electrons.
- It is of negative polarity.

This will be known as cathode.

- At cathode reduction will take place.(gain of e^- will take place)
- To act as sink of electron.
- Positive polarity will be developed.

Construction of cell



Continue..

- It has two **half-cells**, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called **electrodes** and are connected by an conducting wire.
- Two solutions are connected by a **salt bridge**.
- The oxidation and reduction half reactions occur at a separate electrodes and electric current flows through the wire.

Selection of salt bridge

The electrolyte in salt bridge should be such that speed of its cation equals speed of its anion in electrical field.

For that charge and sign of the ions should be almost equal.

Transport number of cation = Transport number of anion

or

Mobility of cation = Mobility of anion

KCl is generally preferred but KNO_3 or NH_4NO_3 can also be used.

Function of salt bridge

A **salt bridge** is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte. It connects the solution of two half cell to complete the circuit.

It minimise the liquid junction potential. The potential difference between the junction of two liquids.

It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.

" The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.

If the salt bridge is removed then voltage drops to zero.

The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.

Generally tube is filled with a paste of agar-agar powder with a neutral electrolyte/generally not common to anodic/cathodic compartment with porous plugs at each mouth of tube.

It prevents mechanical mixing of two electrolytic solution.

Electrode potential

The potential difference developed between metal electrode and its ions in solution is known as electrode potential.

Electrode potential depends upon :

- Concentration of the solution.
- Nature of the metal.
- Nature of the electrolyte.
- Pressure temperature conditions.

The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as standard electrode potential.

Continue..

Shorthand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by following few rules;
 - The anode half-cell is always written on the left followed on the right by cathode half cell.
 - The separation of two phases (state of matter) is shown by a vertical line.
 - The various materials present in the same phase are shown together using commas.
 - The salt bridge is represented by a double slash (||).
 - The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
 - For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e $\text{Pt H}_2 / \text{H}^+$ or $\text{H}^+ / \text{H}_2 \text{ Pt}$)

Standard electrode potential

• Standard Electrode Potential



Oxidation Potential (O.P.) :

- The electrode potential for oxidation half reaction
- Tendency to get oxidised.
- **Greater the O.P. than greater will be tendency to get oxidised.**

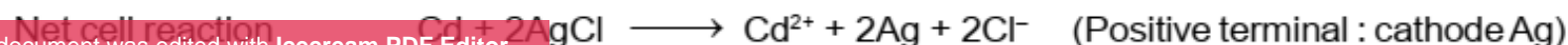
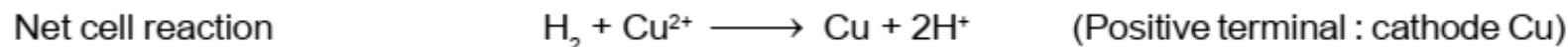
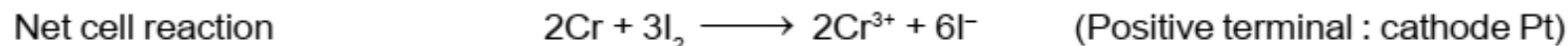
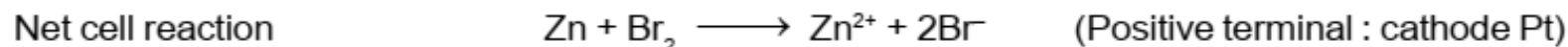
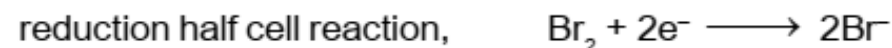
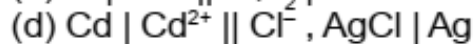
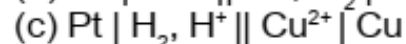
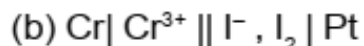
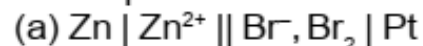
Reduction Potential (R.P.)

- The electrode potential for reduction half reaction
- Tendency to get reduced.
- **Greater the R.P. greater will be tendency to get reduced.**

Question

Write short hand notation for the following reaction, $\text{Sn}^{2+}(\text{aq}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\text{Ag}(\text{s})$.
The cell consists of a platinum wire anode dipping into an Sn^{2+} solution and a silver cathode dipping into an Ag^+ solution therefore $\text{Pt}(\text{s}) | \text{Sn}^{2+}(\text{aq}), \text{Sn}^{4+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}(\text{s})$.

Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?



Cell potential

The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.

The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half cell constituting the cell. The following three methods are in use :

- › When oxidation potential of anode and reduction potential of cathode are taken into account :

$$E^{\circ}_{\text{cell}} = \text{oxidation potential of anode} + \text{reduction potential of cathode}$$
$$E^{\circ}_{\text{ox}}(\text{anode}) + E^{\circ}_{\text{red}}(\text{cathode})$$

- › When reduction potential of both electrodes are taken into account :

$$E^{\circ}_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$
$$= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \quad \text{C both are reduction potential.}$$

- › When oxidation potential of both electrodes are taken into account :

$$E^{\circ}_{\text{cell}} = \text{oxidation potential of anode} - \text{Oxidation potential of cathode}$$
$$= E^{\circ}_{\text{ox}}(\text{anode}) - E^{\circ}_{\text{ox}}(\text{cathode})$$

The standard cell potential E° is the cell potential when both reactants and products are in their standard states – solutes at 1 M concentration, gases at a partial pressure of 1 atm, solids and liquids in pure form, with all at a specified temperature, usually 25° C.

E°_{cell} is intensive property so on multiplying/Dividing cell reaction reaction by any number, the E°_{cell} value would not change.

Question

Calculate E^0_{cell} of (at 298 K),



given that $E^0_{\text{Zn/Zn}^{2+}(\text{aq})} = 0.76 \text{ V}$

$$E^0_{\text{Cu(s)} / \text{Cu}^{2+}(\text{aq})} = -0.34 \text{ V}$$

$$\begin{aligned} E^0_{\text{cell}} &= (\text{S.R.P})_{\text{cathode}} - (\text{S.R.P})_{\text{anode}} \\ &= 0.34 - (-0.76) = 1.1 \text{ V} \end{aligned}$$

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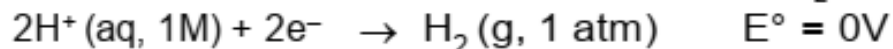
In the galvanic cell $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$, the electrons flow from Cu-electrode to Ag-electrode. Answer the following questions regarding this cell :

- (a) Which is the anode ?
- (b) Which is the cathode ?
- (c) What happens at anode-reduction or oxidation ?
- (d) What happens at cathode-oxidation or reduction ?
- (e) Which electrode loses mass ?
- (f) Which electrode gains mass ?
- (g) Write the electrode reactions.
- (h) Write the cell reaction
- (i) Which metal has greater tendency to loss electron-Cu or Ag ?
- (j) Which is the more reactive metal-Cu or Ag ?
- (k) What is the function of salt bridge represented by the symbol \parallel ?

Standard Hydrogen Electrode (SHE)

Standard Hydrogen Electrode (**SHE**) is taken as standard reference electrode. Its electrode potential is arbitrarily assumed to be 0.00 volt.

Standard Hydrogen Electrode (**SHE**) consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard state conditions (1 atm H_2 gas, 1 M H^+ (aq), 25°C).



Continue..

- For SHE reference potential is taken to be zero at all temperature.
SOP = – SRP = 0 for SHE.
- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and it's potential is measured that gives the value of electrode potential of that electrode.

Anode : Zinc electrode

Cathode : SHE

Cell : Zinc electrode || SHE

Cell potential :

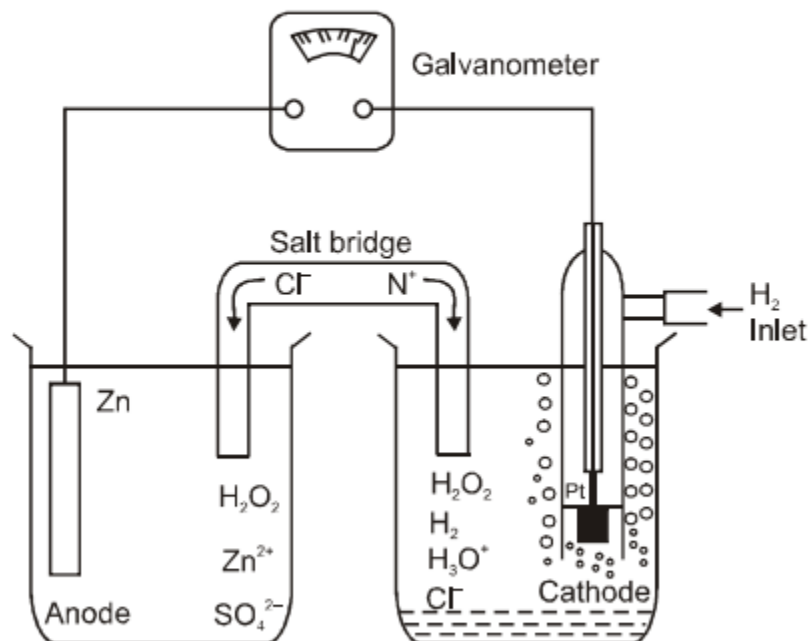
$$E_{\text{cell}} = E_{\text{H}^+/\text{H}_2(\text{g})} - E_{\text{Zn}^{2+}/\text{Zn}}$$

$$= 0.76 \text{ V (at 298 K experimentally)}$$

$$\text{So, } E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V (SRP)}$$

$$E_{\text{Zn}/\text{Zn}^{2+}(\text{aq})}^0 = 0.76 \text{ V (SOP)}$$

- So, w.r.t. H_2 , Zn has greater tendency to get oxidised.
In similar manner reduction potentials (SRP) at 298 K for many other electrodes are calculated and are arranged in a series increasing order known as electro chemical series.



A galvanic cell measuring the Zn^{2+}/Zn half-cell potential

Calculation of ΔG^0

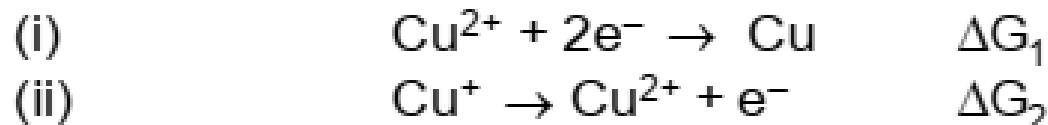
Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.

- Obtain the reaction of the 3rd electrode with the help of some algebraic operations on reactions of the given electrodes.
- Then calculate ΔG of the 3rd reaction with the help of some algebraic operations of ΔG^0 of 1st and 2nd reactions.
- Use $\Delta G^0 = -nF E_{\text{elec}}^0$ to calculate unknown E.P.
- E_{cell}^0 is intensive property so if we multiply/Divide electrode reaction by any number the E_{cell}^0 value would not be changed

Question

Given that $E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.337 \text{ V}$ and $E^0_{\text{Cu}^+/\text{Cu}^{2+}} = -0.153 \text{ V}$. Then calculate $E^0_{\text{Cu}^+/\text{Cu}}$

Solution



after adding



$$\Delta G_1 + \Delta G_2 = \Delta G_3$$

$$-2F E_1^0 - F E_2^0 = -F E_3^0$$

$$E_3 = 2E_1^0 + E_2^0$$

$$= 2 \times 0.337 - 0.153$$

$$= 0.674 - 0.153 = 0.521 \text{ V}$$

Electrochemical Series :

Increasing strength of reducing agent	Electrode	Reaction	SRP (at 298 K)	Increasing strength of oxidising agent
	* Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li(s)}$	- 3.05 V	
	K	$\text{K}^+ + \text{e}^- \rightarrow \text{K (s)}$	- 2.93 V	
	Ba			
	Ca	$\text{Ca}^{+2} + 2\text{e}^- \rightarrow \text{Ca(s)}$	- 2.87 V	
	Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na(s)}$	- 2.71 V	
	Mg	$\text{Mg}^{+2} + 2\text{e}^- \rightarrow \text{Mg(s)}$	- 2.37 V	
	Al			
	Electrolytes (H ₂ O)	$\text{H}_2\text{O(l)} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^-$	- 0.828 V	
	* Zn	$\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn(s)}$	- 0.76 V	
	Cr	$\text{Cr}^{+3} + 3\text{e}^- \rightarrow \text{Cr(s)}$	- 0.74 V	
	* Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	- 0.44 V	
	Cd	$\text{Cd}^{+2} + 2\text{e}^- \rightarrow \text{Cd(s)}$	- 0.40 V	
	Co			
	Ni	$\text{Ni}^{+2} + 2\text{e}^- \rightarrow \text{Ni(s)}$	- 0.24 V	
	Sn	$\text{Sn}^{+2} + 2\text{e}^- \rightarrow \text{Sn(s)}$	- 0.14 V	
	Pb	$\text{Pb}^{+2} + 2\text{e}^- \rightarrow \text{Pb(s)}$	- 0.13 V	
	* H ₂	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{(g)}$	0.00 V	
	Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$	0.34 V	
	I ₂			
	Fe	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77 V	
	Hg	$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg(l)}$	0.79 V	
	Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80 V	
	Hg	$\text{Hg}^{2+} \rightarrow \text{Hg(l)}$	0.85 V	
	Br ₂	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.06 V	

Question

1. The reduction potential values are given below
 $\text{Al}^{3+}/\text{Al} = -1.67$ volt, $\text{Mg}^{2+}/\text{Mg} = -2.34$ volt, $\text{Cu}^{2+}/\text{Cu} = +0.34$ volt
 $\text{I}_2 / \text{I}^- = +0.53$ volt. Which one is the best reducing agent ?
2. The standard reduction potential value of the three metallic cations X, Y and Z are 0.52, -3.03 and -1.18 V respectively. Write the decreasing order of reducing power of the corresponding metals :

Nernst Equation

- Cell potentials depend on temperature and on the composition of the reaction mixtures.
- It depends upon the concentration of the solute and the partial pressure of the gas, if any.
- The dependence upon the concentration can be derived from thermodynamics.

From thermodynamics

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + 2.303 R T \log Q$$

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

Take $T = 298 \text{ K}$, $R = 8.314 \text{ J/mol K}$, $F = 96500 \text{ C}$

$$\text{Now we get, } E = E^\circ - \frac{0.059}{n} \log Q$$

Where n = number of transferred electron, Q = reaction quotient

- Nernst equation can be used to calculate cell potentials for non standard conditions also.
- Nernst equations can be applied to half cell reactions also.

Application of Nernst equation

- Nernst Equation for Electrode Potential**



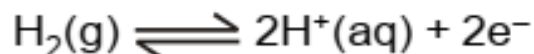
$$E_{Red^n} = E_{red}^0 - \frac{RT}{nF} \ln \left[\frac{M(s)}{M^{n+}} \right]$$

$$E_{Red^n} = E_{red}^0 - \frac{2.303RT}{nF} \log \left[\frac{M(s)}{M^{n+}} \right]$$

at 298K ,

$$E_{Red^n} = E_{Red^n}^0 - \frac{0.059}{n} \log \left[\frac{1}{M^{n+}} \right]$$

- Hydrogen Electrode**



$$E = E^0 - \frac{0.059}{2} \log \left[\frac{(H^{+})^2}{P_{H_2}} \right]$$

Concentration of cell

- A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.
- The two solutions are separated by a salt bridge.

e.g. $\text{Ag(s)} \mid \text{Ag}^+ (a_1) \parallel \text{Ag}^+ (a_2) \mid \text{Ag(s)}$ ($a_1 < a_2$) a_1, a_2 are concentrations of each half cell

At LHS electrode Anode : $\text{Ag (s)} \longrightarrow \text{Ag}^+(a_1) + e^-$

At RHS electrode Cathode : $\text{Ag}^+(a_2) + e^- \longrightarrow \text{Ag(s)}$

The net cell reaction is : $\text{Ag}^+ (a_2) \longrightarrow \text{Ag}^+ (a_1)$

The nernst eq. is

$$E_{\text{cell}} = - \frac{0.059}{n} \log \frac{a_1}{a_2} \quad (\text{Here } n = 1, \text{ Temp, } 298 \text{ K})$$

- Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and P_2 ($P_1 > P_2$) and dipping into a solution HCl is :

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{P_1}{P_2} \quad (\text{at } 298 \text{ K})$$

Useful work of cell

Work done by a cell :

- (i) Let 'n' faraday charge be taken out of a cell of EMF 'E'; then work done by the cell will be calculated as : $\text{work} = \text{Charge} \times \text{Potential} = nFE$
- (ii) Work done by cell = Decrease in free energy
so $-\Delta G = nFE$
or $W_{\text{max}} = + nFE^{\circ}$ where E° is standard EMF of the cell

Thermodynamics of cell Potential

We know that :

$$\Delta G^0 = -nF E_{\text{cell}}^0$$

$$\Delta G = -nF E_{\text{cell}}$$

$$G = H - TS$$

From thermodynamics $H = E + PV$ enthalpy function.

Substituting $G = E + PV - TS$

By partial differentiation

$$\partial G = \partial E + P \partial V + V \partial P - T \partial S - S \partial T \quad \text{..... (i)}$$

according to **1st law** of thermodynamics

$$E = q + W \quad dW = -PdV$$

$$\partial E = \partial q - PdV$$

$$\partial q = \partial E + P \partial V \quad \text{..... (ii)}$$

according to **2nd law**

$$ds = \frac{dq}{T} = dq = Tds \quad \text{..... (iii)}$$

$$S = \frac{-\partial G}{\partial T}$$

$$\Delta S = -\frac{\partial(\Delta G)}{\partial T}$$

Electrolytic cell and Electrolysis

Electrolysis :

- Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- This is possible due to the movement of ions from which it is made of and electrolyte.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and reduction due to current in the electrolyte.
- The product obtained during electrolysis depends on following factors.
 - The nature of the electrolyte
 - The concentration of electrolyte
 - The charge density flowing during electrolysis.
 - The nature of the electrode

Active and Inactive electrode

- The metal electrodes in the cell that are active because the metals themselves are components of the half reactions.
- As the cell operates, the mass of the zinc electrode gradually decreases, and the $[\text{Zn}^{2+}]$ in the anode half – cell increases. At the same time, the mass of the copper electrode increases and the $[\text{Cu}^{2+}]$ in the cathode half – cell decreases; we say that the Cu^{2+} „plates out" on the electrode.
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half -reactions.

Faraday's Law of Electrolysis-

- **1st Law** : The mass deposited/released/produced of any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$$W \propto Q$$

$$W = ZQ$$

Z – electrochemical equivalent of the substance.

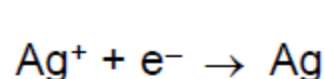
$$\text{Unit of } Z = \frac{\text{mass}}{\text{coulomb}} = \text{Kg/C or g/C}$$

Z = Mass deposited when 1 C of charge is passed into the solution.

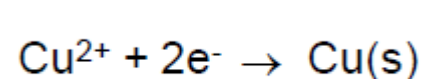
Equivalent mass (E) : mass of any substance produced when 1 mole of e^- are passed through the solution during electrolysis.

$$E = \frac{\text{Molar mass}}{\text{no. of } e^- \text{ involved in oxidation / reduction}}$$

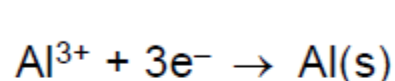
Example



$$E = \frac{M}{1}$$



$$E = \frac{M}{2}$$



$$E = \frac{M}{3}$$

1 mole of e^- = 1 Faraday of charge.

\therefore 96500 C – Charge deposit E gram metal charge

$$\therefore 1\text{C} \rightarrow \left(\frac{E}{96500} \right) \text{g} \quad Z = \frac{E}{96500}$$

$$\int dQ = i \int dt \quad Q = it$$

$$W = \frac{i \times t}{96500} \times \frac{\text{Molar mass}}{(\text{no. of } \text{e}^- \text{ involved})}$$

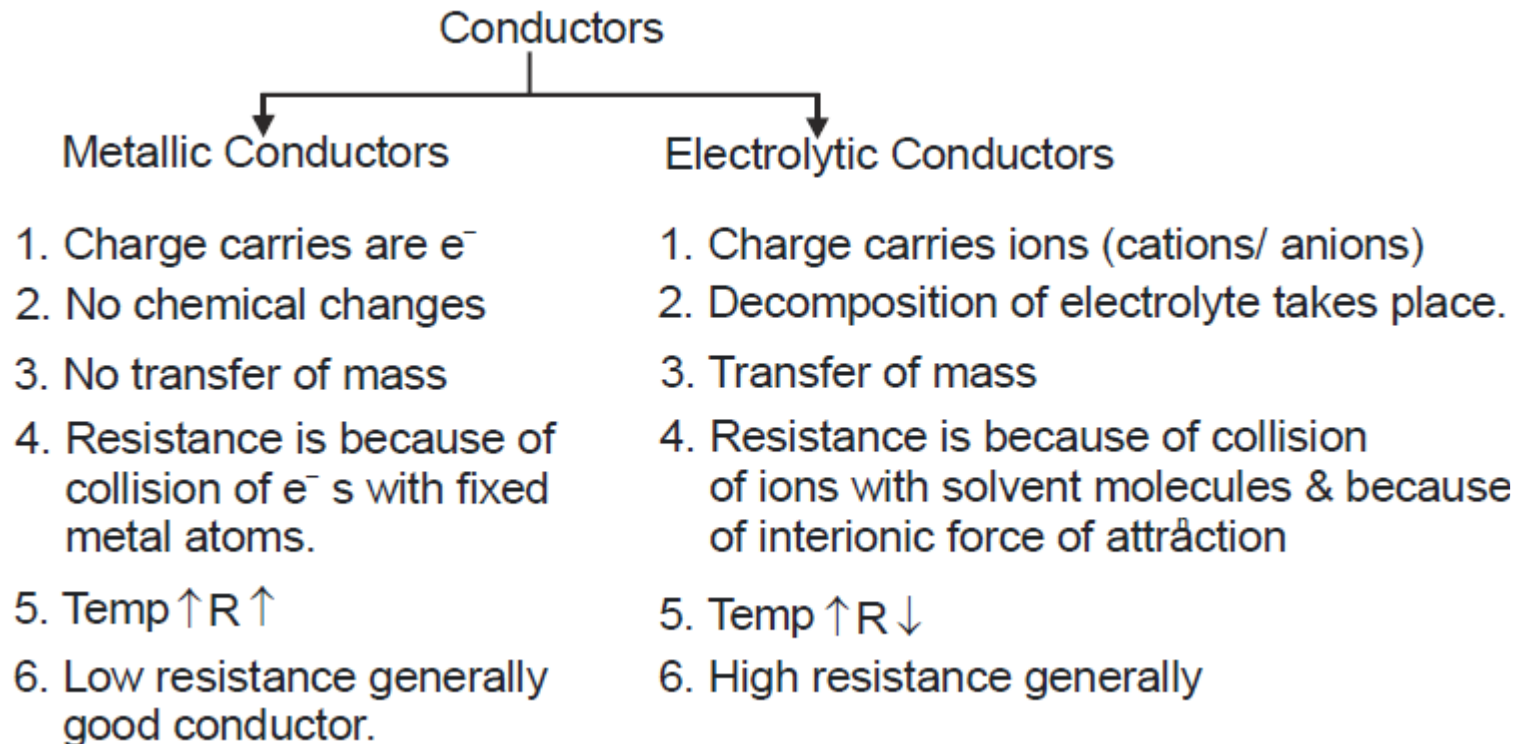
2nd law of Electrolysis

- **2nd Law :** When equal charge is passed through 2 electrolytic cells and this cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$$W = ZQ = \frac{EQ}{96500}$$

$$\frac{W_1}{W_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2} \text{ (} Q = \text{ same)}$$

Difference of Metallic and Electrolytic conductance



Factor affecting the Electrolytic Conductance

1. Solute – Solute interactions (Inter – Ionic force of attraction) Greater the force of attraction, greater will be the resistance.
Force \propto Charge
2. Solute – Solvent Interaction (Hydration/Solvation of Ions)
Greater the solvation
Solvation \propto Charge $\propto \frac{1}{\text{size}}$ greater will be resistance
Li⁺ (Hydrated largest) Cs⁺ (Hydrated smallest)
resistance of LiCl > resistance of CsCl
3. Solvent solvent interaction (Viscosity) : greater the viscosity greater will be resistance
4. Temperature
T \uparrow R \downarrow
5. Nature of electrolyte
Weak electrolyte – high resistance strong electrolyte – Low resistance