

PHYSICAL CHEMISTRY

CHAPTER NUMBER: 03

CHAPTER NAME: ELECTROCHEMISTRY

CLASS-XII

CHANGING YOUR TOMORROW

Lecture – 01:

Electrochemical cell, Electrode potential, Standard Electrode potential

Introduction

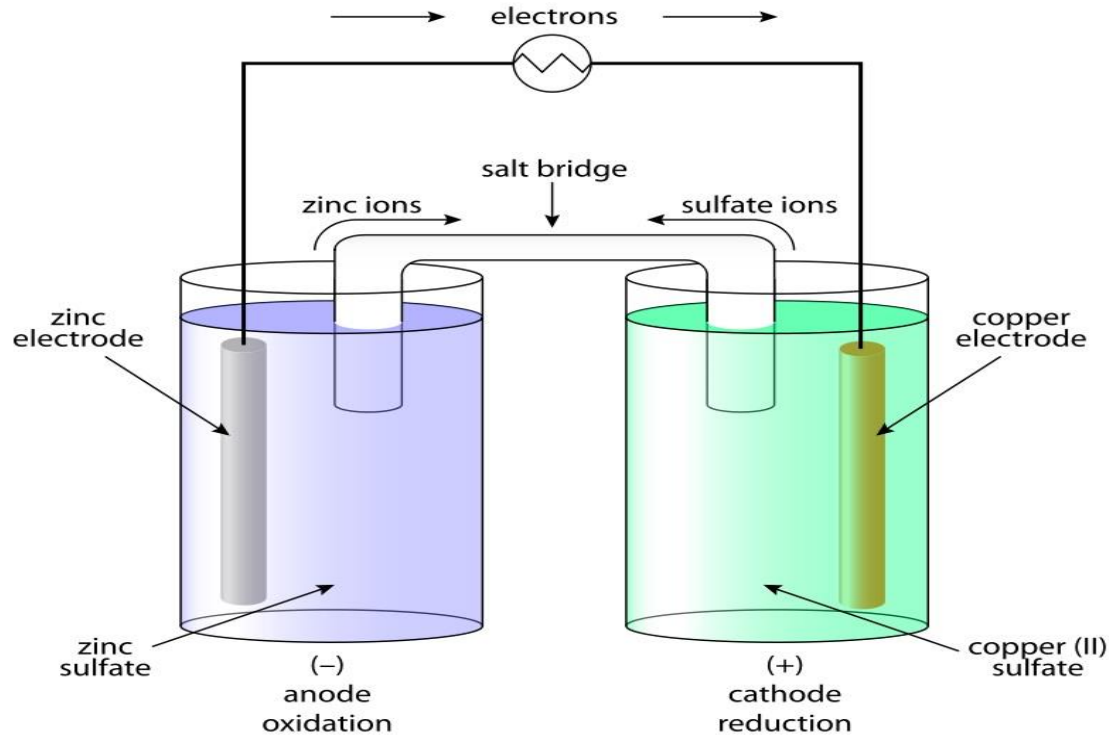
- English chemist John Daniell and physicist Michael Faraday both credited as founder of electrochemistry
- Electrochemistry is the study of chemical reaction which take place at the interface of an electrode usually solid metal, semiconductor and an ionic conductor, the electrolyte.
- It deals with the interaction between electrical energy and chemical change.
- Study of electrochemistry is important for creating new technologies that are eco-friendly. The transmission of sensory signals through cells to brain and vice versa is also of electrochemical origin.

ELECTROCHEMICAL CELL

- A device which is used to convert chemical energy produced in a spontaneous redox reaction into electrical energy is called electrochemical cell or Galvanic Cell.
- Galvanic cell consists of two half cells and the reaction occurring in half cells are called half cell reactions. Each half cell consists of metallic electrode dipped in an electrolyte.
- The half cell in which oxidation occurs is called oxidation half cell and the reaction taking place is called oxidation half cell reaction. The half cell in which reduction occurs is called reduction half cell and the reaction taking place is called reduction half cell reaction .
- The electrode where oxidation occurs is called anode and the electrode where reduction occurs is called cathode.

- Since at anode electrons are released, this electrode is rich in electrons and hence assigned negative charge and at cathode, electrons are gained and it is deficient of electrons and acts as positively charged electrode.
- The electrodes of the two half cells are connected by a metallic wire through a voltmeter externally.
- Electrons flow from anode to cathode in the external circuit and conventionally current flow in opposite direction i.e. from cathode to anode.
- The two half cells are joined by a salt bridge internally that maintains electrical neutrality of the two half cells and complete the electrical circuit by allowing the ions to flow.
- The salt bridge containing inert electrolytes like KCl , KNO_3 , K_2SO_4 etc or solidified solution of such an electrolyte in gelatin or agar-agar. The ions of inert electrolytes don't take part in redox reaction.

ELECTROCHEMICAL CELL: SCHEMATIC REPRESENTATION

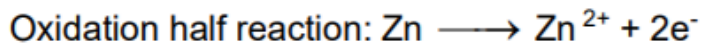
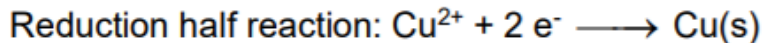


DANIELL CELL

- The Electrochemical cell which converts the chemical energy liberated in the redox reaction between zinc and cupric ions to produce electrical energy is called Daniell cell.

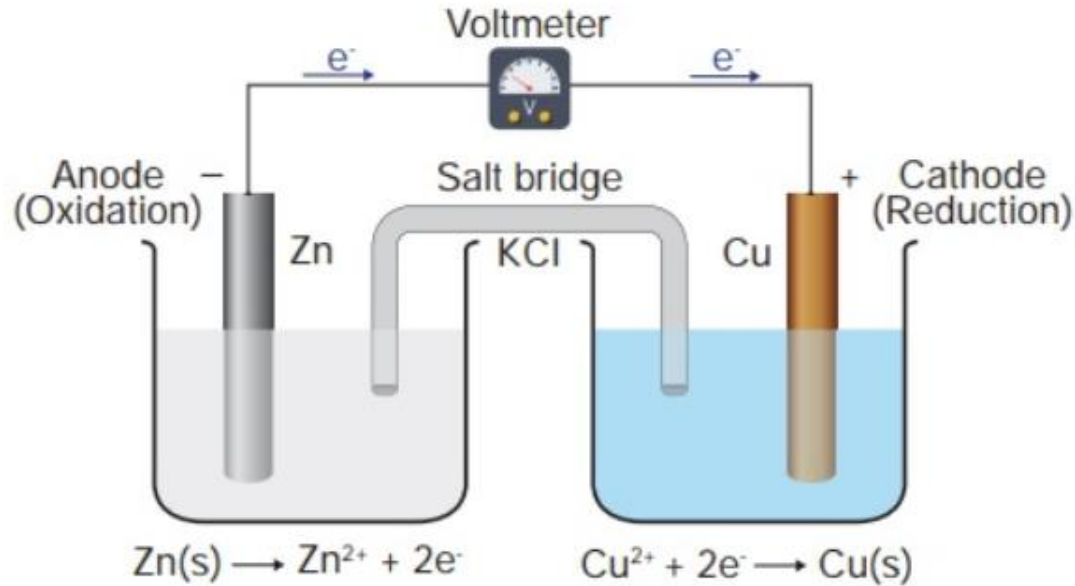


- The reaction is a combination of two half cell reactions:



- Daniell cell has an electrode potential of 1.1 V when concentration of ions are unity.
- When an external opposite potential is applied in Daniell cell then reaction continues till the opposite voltage reaches the value 1.1 V.
- When the opposite potential is 1.1 V then reaction stops. When opposite potential is greater than 1.1 V then the reaction starts in opposite direction and it function as electrolytic cell, which is defined as the cell in which non-spontaneous reaction occurs using electric current.

DANIELL CELL:



Zn Rod(Anode) dipped in 1M Zinc Sulphate solution and Cu Rod(Cathode) dipped in 1M Copper Sulphate solution.

ELECTRODE POTENTIAL

- Electrode Potential (E): The tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions is called electrode potential. Or the electrical potential difference set up between the metal and its ions in the solution is called electrode potential.
- When in the half cell, the electrode is in a solution of 1M conc. and the temperature is at 298K, pressure is at 1 bar then the electrode potential is called standard electrode potential(E^0).
- Electrode potential can be expressed in terms of oxidation potential and Reduction potential. Tendency of an electrode to lose electrons or to get oxidize is called oxidation potential. Tendency of an electrode to gain electrons or to get reduce is called reduction potential.
- Standard oxidation potential and standard reduction potential of an electrode are same in magnitude with opposite in sign.
- According to convention the standard reduction potentials are called standard electrode potentials. Electrode potential depends on the following factors:
 - i) Nature of the electrode. ii) Concentration of the electrolytic solution. iii) Temperature.

ELECTRODE POTENTIAL AND CELL POTENTIAL: MATHEMATICAL EXPRESSION AND NOTATIONS

- The difference between the two electrode potentials of the two electrodes is called cell potential or cell voltage or cell emf when no current is drawn from the cell.

$$E_{Cell} = E_{Cathode} - E_{Anode}$$

Or

$$E_{Cell} = E_{Right} - E_{Left}$$

- The standard cell potential is given as:

$$E_{Cell}^{\circ} = E_{cathode}^{\circ} - E_{Anode}^{\circ}$$

Where E_{Cell}° : Standard Cell Potential

Where $E_{Cathode}^{\circ}$: Standard Reduction Potential of Cathode

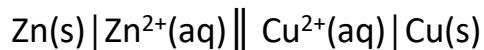
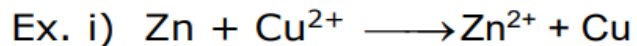
Where E_{Anode}° : Standard Reduction Potential of Anode

➤ At equilibrium, as the electrode potentials of the two half cells remain same so the emf of the cell is zero. But as in standard state the electrode potential of two electrodes are not same so the standard cell potential (E_{Cell}°) of any Galvanic cell never becomes zero.

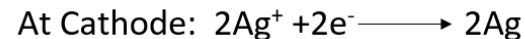
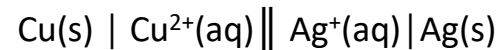
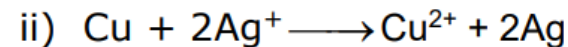
Lecture-02:

Cell Representation, Measurement of Electrode potential:
Standard Hydrogen Electrode

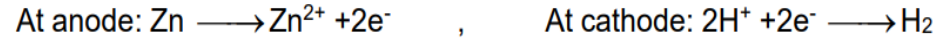
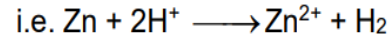
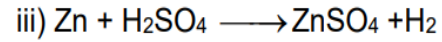
CELL REPRESENTATION OR CELL NOTATION:



$$E_{\text{cell}} = E_{\text{Cu}^{2+} | \text{Cu}} - E_{\text{Zn}^{2+} | \text{Zn}}$$



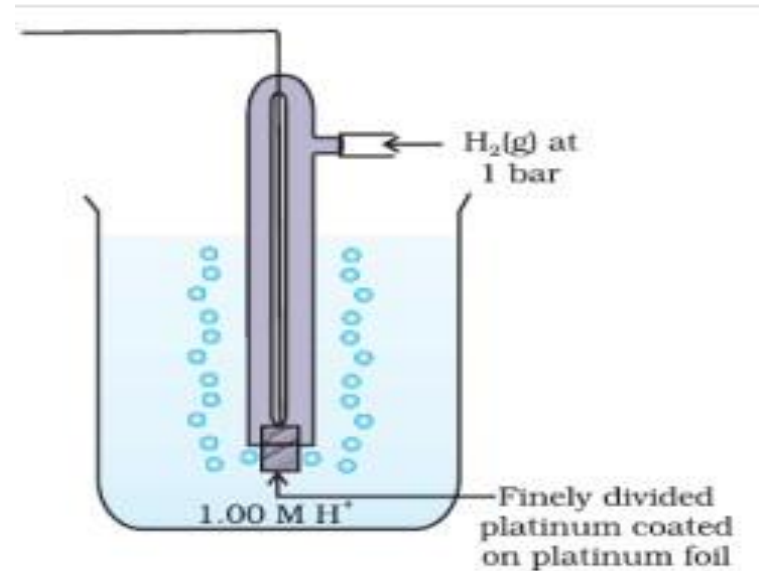
$$E_{\text{cell}} = E_{\text{Ag}^{+} | \text{Ag}} - E_{\text{Cu}^{2+} | \text{Cu}}$$



$$E_{\text{cell}} = E_{\text{H}^+ | \text{H}_2} - E_{\text{Zn}^{2+} | \text{Zn}}$$

Measurement of Electrode potential: Standard Hydrogen Electrode(SHE)

- Represented by $\text{Pt(s),H}_2\text{(g)} \mid \text{H}^+\text{(aq)}$ (if Anode) and $\text{H}^+\text{(aq)} \mid \text{H}_2\text{(g),Pt(s)}$ (if Cathode) and assigned as zero potential at all temperature.
- Reaction involved: $\text{H}^+\text{(aq)} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2\text{(g)}$ (the reaction is for SHE as Cathode. If SHE is Anode the reaction is just the reverse)



- Platinum electrode coated with platinum black is dipped in an acidic solution and pure hydrogen gas bubbled through it.
- The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity and the gas is at 1 bar pressure and 298 K.
- If SHE acts as anode (reference half cell) the other half as cathode and vice-versa.

➤ **Standard cell potential (E°) = $E_{Right}^{\circ} - E_{left}^{\circ}$ (SHE as anode)**

$$= E_{Right}^{\circ} - 0$$

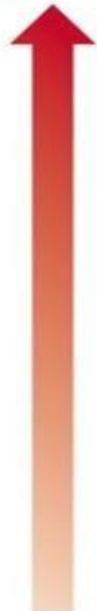
$$= E_{Right}^{\circ}$$

Lecture – 03:Electrochemical Series and its Applications

- The arrangement of all electrodes in the increasing or decreasing order of their standard reduction potential values is called electrochemical series or activity series.
- The -ve value of standard reduction potential indicates the electrode acts as anode when joined with SHE and the +ve value of standard reduction potential indicates the electrode acts as cathode when joined with SHE.

Electrochemical Series

Stronger oxidizing agent



Weaker oxidizing agent

$F_2(g) + 2 e^-$	$\longrightarrow 2 F (aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
$Cl_2(g) + 2 e^-$	$\longrightarrow 2 Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33
$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23
$Br_2(l) + 2 e^-$	$\longrightarrow 2 Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2 H^+(aq) + 2 e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2 e^-$	$\longrightarrow 2 I^-(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^-$	$\longrightarrow 4 OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2 e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2 e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2 H^+(aq) + 2 e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2 e^-$	$\longrightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2 e^-$	$\longrightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2 e^-$	$\longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2 e^-$	$\longrightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2 e^-$	$\longrightarrow Zn(s)$	-0.76
$2 H_2O(l) + 2 e^-$	$\longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3 e^-$	$\longrightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2 e^-$	$\longrightarrow Mg(s)$	-2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04

Weaker reducing agent

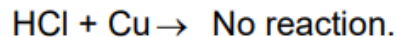
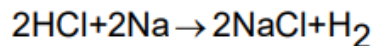


Stronger reducing agent

Application of Electrochemical Series

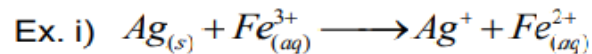
- To compare the relative strength of oxidizing and reducing agent.
- i) The substances which have higher reduction potentials are stronger oxidizing agent and which have lower reduction potentials are weaker oxidizing agent. So F_2 is the strongest oxidizing agent and Li^+ is the weakest oxidizing agent.
- ii) The electrode having higher E^0 value is converted into more stable reduced form. So in activity series F is most stable reduced form and Li is most unstable reduced form.
- iii) The electrode having lower E^0 value acts as stronger reducing agent and having higher E^0 value acts as weaker reducing agent. So Li is the strongest reducing agent and F^- is weakest reducing agent

- i) The electrode having lower E^0 value is converted into more stable oxidized form. So in activity series Li^+ is most stable oxidized form and F_2 is most unstable oxidized form.
- **To predict whether a metal can liberate H_2 from acid or not:**
- i) The metals which have -ve reduction potentials can liberate H_2 from acid and the metals having +ve E^0 value can't liberate H_2 from any acids.
- ii) So Cu doesn't dissolve in HCl as H^+ can't oxidize Cu to Cu^{2+} due to its lower E^0 value. But Cu dissolve in HNO_3 where NO_3^- ion which has higher E^0 value than Cu oxidize Cu to form Cu^{2+} .



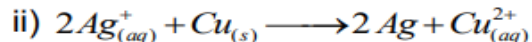
➤ **To predict the feasibility of redox reaction:**

- i. A redox reaction is feasible only if standard EMF of cell is +ve. Otherwise it is not feasible. Or a redox reaction is feasible only if the species which has higher reduction potential is reduced i.e. accepts electrons and the species which has lower reduction potential is oxidized i.e. loses the e^- , otherwise the reaction is not feasible.



$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 0.77 - 0.80 = -0.03V$$

The reaction is not feasible.



$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 0.80 - 0.34 = +0.46V$$

So the reaction is feasible.

To compare the relative activity of metals:

- i) Metals having lower reduction potential value can easily lose electrons and it has greater reactivity. So the metal having lower E^0 value can displace metals with higher E^0 value from their salt solution.
- ii) Ex. $Mg > Zn > Fe > Cu > Ag$

Lecture-04:

Nernst Equation and its application ,Relation between Gibb's free energy and EMF of cell

- Nernst equation gives a relationship between reduction potential of an electrode and conc. of electrolyte in the solution.

Consider an electrode reaction, $M^{n+}(aq) + n e^{-} \rightleftharpoons M(s)$

Nernst Equation is:

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}_{(aq)}]}$$

$$E_{M^{n+}|M} = E^{\circ}_{M^{n+}|M} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}_{(aq)}]}$$

Where

$E_{M^{n+}|M}$ = Electrode potential of the electrode. and

$E^{\circ}_{M^{n+}|M}$ = Standard electrode potential of the electrode.

R = Universal gas Constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. **n** = No of electrons involved in electrode reaction.

F = 1 faraday = 96,500 C $[M]$ = Concentration of Solid atom = 1M. $[M^{n+}_{(aq)}]$ = Concentration of ion of M.

At 25°C, putting the values of above terms, the Nernst equation becomes:

$$E = E^{\circ} - \frac{0.0591}{n} \log \left[\frac{1}{M^{n+}_{(aq)}} \right]$$

Or

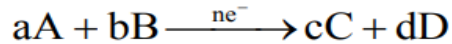
$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}_{(aq)}]$$

Where E = Electrode potential of an electrode

E° = Standard Electrode potential of the electrode

NERNST EQUATION

For a general electrochemical reaction of the type.



The Nernst Equation can be Written as:

$$E_{cell} = E_{cell}^o - \frac{2.303}{nF} RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Converting to Natural Logarithm:

$$E_{cell} = E_{cell}^o - \frac{2.303}{nF} RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Substituting Temperature value as 298K and Value of R and F we get

$$E_{cell} = E_{cell}^o - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

E_{Cell} = Cell potential at the given concentration.

E_{Cell}^o = Standard Cell Potential.

R = Universal gas Constant = 8.314 J K⁻¹ mol⁻¹

T = Temperature in Kelvin.

F = Faraday (F) 1F = 96500 Coulombs.

n = No. of electrons involved in the reaction.

[C] [D], [A], [B] represent concentration of species involved in the reaction in terms of Molarity (moles/L) and c, d, a, b are their respective stoichiometric coefficients.

Application of Nernst Equation to Electrochemical cell

In a Daniel cell :

For cathode : $E_{(\text{Cu}^{2+}|\text{Cu})} = E^0_{(\text{Cu}^{2+}|\text{Cu})} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]}$

For anode : $E_{(\text{Zn}^{2+}|\text{Zn})} = E^0_{(\text{Zn}^{2+}|\text{Zn})} - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]}$

Cell potential : $E_{\text{Cell}} = E_{(\text{Cu}^{2+}|\text{Cu})} - E_{(\text{Zn}^{2+}|\text{Zn})}$
 $= E^0_{(\text{Cu}^{2+}|\text{Cu})} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]} - E^0_{(\text{Zn}^{2+}|\text{Zn})} + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]}$

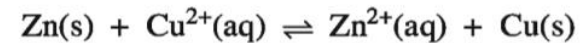
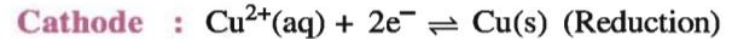
$$= E^0_{(\text{Cu}^{2+}|\text{Cu})} - E^0_{(\text{Zn}^{2+}|\text{Zn})} - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]} + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]}$$

$$\therefore E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

At 25°C the above equation becomes

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Cell reaction :



Relation between Cell Potential and Equilibrium Constant

Consider the Daniell cell: $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

At equilibrium conc. of Cu^{2+} and Zn^{2+} ions don't change and the electrode potentials of the two electrodes remain same.

So $E_{\text{cell}} = 0$ According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Zn}_{(\text{aq})}^{2+}]}{[\text{Cu}_{(\text{aq})}^{2+}]}$$

But $\frac{[\text{Zn}_{(\text{aq})}^{2+}]}{[\text{Cu}_{(\text{aq})}^{2+}]} = K_c$, So $E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log K_c$

For general cell reaction: $E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$

Or, $E_{\text{cell}}^{\circ} = \frac{2.303RT}{nF} \log K_c$, Where $K_c = \text{Equilibrium constant}$

Relation between Cell Potential and Gibb's Free Energy

- The electrical work done by the cell results decrease in free energy of the system and electrical work done on the cell results increase in free energy of the system.

In electrochemical cell,

Electrical work done = Decrease in free energy

= Quantity of electricity flowing X EMF

For 1 mol of electron, quantity of electricity flowing is 1 F

So for n mol of electron, quantity of electricity flowing is nF faraday

So $-\Delta G = nFE_{Cell}$ Or, $\Delta G = -nFE_{Cell}$

In standard state $-\Delta G^0 = nFE_{Cell}^0$ Or, $\Delta G^0 = -nFE_{Cell}^0$

Where ΔG^0 = Standard free energy change

E_{Cell}^0 = Standard emf of cell

Relation between Gibb's Free Energy and Equilibrium Constant

We have
$$E_{cell}^{\theta} = \frac{RT}{nF} \ln K_c$$

So,
$$-\Delta G^{\theta} = nF \frac{RT}{nF} \ln K_c \quad \text{Or, } -\Delta G^{\theta} = RT \ln K_c \quad \text{Or } \Delta G^{\theta} = -2.303 RT \log K_c$$

Or,
$$\ln K_c = \frac{-\Delta G^{\theta}}{RT} \quad , \quad \text{Or, } e^{\ln K_c} = e^{\frac{-\Delta G^{\theta}}{RT}} \quad \text{Or, } K_c = e^{\frac{-\Delta G^{\theta}}{RT}}$$

Or,
$$\log K_c = \frac{-\Delta G^{\theta}}{2.303 RT} \quad \text{Or, } 10^{\log K_c} = 10^{\frac{-\Delta G^{\theta}}{2.303 RT}} \quad \text{Or, } K_c = 10^{\frac{-\Delta G^{\theta}}{2.303 RT}}$$

Lecture-05:

Resistance and Conductance, Electronic and Electrolytic Conductance:

- According to Ohm's law, the resistance of any object is directly proportional to its length(l) and inversely proportional to its area(a) of cross section.
- i.e $R \propto \frac{l}{a}$ or $R = \rho \left(\frac{l}{a} \right)$ Where ρ = specific resistance or resistivity of the conductor.
- Unit of resistivity: ohm.cm (Ω .cm) or, ohm.m (Ω .m). 1Ω .m = 100 Ω .cm
- The conductance is the reciprocal or inverse of resistance. The ability of electrolytic solutions to allow the passage of electric current through them is known as the electrolytic conductance.
- C or $G = \frac{1}{R}$
- Unit of conductance: Ohm⁻¹ or Ω^{-1} or mho or, Siemens(S)(1S = 1 Ω^{-1})

Electronic and Electrolytic Conductance

➤ Conductors are of two types :

(i) Electronic conductors

(ii) Electrolytic conductor

(i) Electronic Conductors:

- These are the metallic conductors in which the conductance is due to movement of electrons. The electronic conductance depends on:
 - The nature and structure of metal
 - The no. of valence electrons per atom
 - Temperature.
 - The electronic conductance decreases with increase in temperature. This is because with increase in temp, the kernels start vibrating which produce hindrance in the flow of electrons.

(ii) **Electrolytic conductance:**

The conductance of electricity by ions present in the solutions is called electrolytic or ionic conductance. The electrolytic conductance depends on:

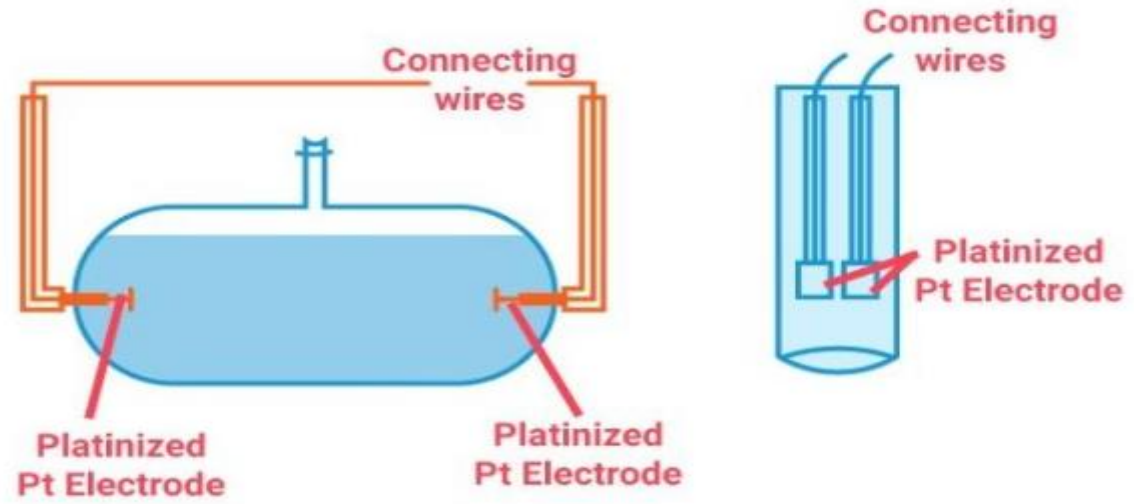
- The nature of the electrolyte.
- Size of ions produced and their solvation.
- The nature of solvent.
- Concentration of the electrolyte.
- Temperature.

The electrolytic conductance increases with the increase in temperature due to increase in dissociation or decrease in ionic attraction.

Measurement of Electrolytic conductance:

- For the measurement of ionic or electrolytic conductance, there are two problems like:
 - Passing direct current changes the composition of solution.
 - The solution can't be connected to bridge like a metallic wire.

- So alternating current is used for ionic conductance to prevent the change in composition of the solution. The conductivity cell is used to connect the solution with the bridge like metallic wire. The conductivity cell consists of two platinum electrodes coated with platinum black.



_Lecture-06: Types of Electrolytic Conductance, Specific Conductance, Molar Conductance, Equivalent Conductance

The electrolytic or ionic conductance is of three types like

- Specific conductance Molar conductance Equivalent conductance

- **Specific conductance or conductivity:**

We know $R = \rho \left(\frac{l}{a} \right) \Rightarrow \frac{1}{R} = \frac{1}{\rho} \left(\frac{a}{l} \right) \Rightarrow C = \kappa \left(\frac{a}{l} \right)$

or $\kappa = C \times \left(\frac{l}{a} \right) \quad \kappa = \frac{1}{\rho}$

Where κ (kappa) is called Conductivity or specific conductance of the electrolyte.

Specific conductance or conductivity(κ):

- l/a is called as Cell constant symbolized by 'G*'. For a given conductivity cell, the cell constant value remains fixed.
- The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, KCl solutions are used whose conductivity is known accurately at various concentrations.
- So, $\kappa = C \times \frac{l}{a} = C \times G^*$ Where $G^* = \frac{l}{a} = \text{Cell Constant}$
 When $l=1\text{cm}$, $a= 1\text{cm}^2$, then $\kappa = C$
- So specific conductance of a solution is defined as the conductance of the solution of 1cm length and having 1 cm² as the area of cross section.
 When $l=1\text{ cm}$, $a = 1\text{cm}^2$, then $V=1\text{cm}^3$ So, $\kappa = C$
- So specific conductance of a solution is defined as the conductance of the solution having volume 1 cm³.
- Unit of κ is: Ohm⁻¹.cm⁻¹ or Ohm⁻¹m⁻¹ or S m⁻¹ or, S. cm⁻¹ 1S.cm⁻¹=100 S. m⁻¹

Measurement of Resistance or Conductivity of any solution

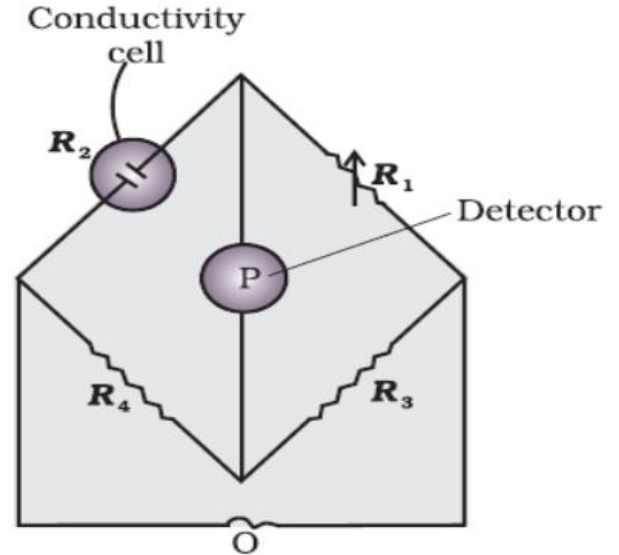
- Once the cell constant is determined using KCl solutions ,it can be used for measuring the resistance or conductivity of any solution.
- The set up for the measurement of the resistance is shown in the Figure to the right(known as wheat-stone bridge). It consists of two resistances R_3 and R_4 (known resistances), a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 . The Wheatstone bridge is fed by an oscillator O (Oscillator O is the source of A.C power.)
- P is a suitable detector (a headphone or other electronic device) and the bridge is balanced when no current passes through the detector. Under these conditions:

- Once the cell constant and the resistance of the solution in the cell is determined, the conductivity of the solution is given by the equation:

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

$$\kappa = \frac{G^*}{R}$$

Arrangement of Wheatstone bridge Circuit to measure Conductivity of a solution



Molar Conductance or Molar Conductivity(Λ_m):

- It is defined as the conductance of a solution containing 1 mole of electrolyte kept between two electrodes which are 1 cm apart from each other.
- Let 1 mole of the electrolyte is present in V ml (cm^3) of solution and κ is its specific conductance.
Conductance of V ml solution = $\kappa \times V$.
- So $\Lambda_m = \kappa \times V$
- Let M be the molarity of the solution, then volume of solution containing 1 mole of electrolyte is $\frac{1000}{M}$
- So, $\Lambda_m = \kappa \times \frac{1000}{M}$
- Unit: $\text{Ohm}^{-1} \text{ cm}^2 \cdot \text{mol}^{-1}$ or, $\text{S cm}^2 \cdot \text{mol}^{-1}$ or, $\text{S m}^2 \cdot \text{mol}^{-1}$. $1 \text{ S m}^2 \text{ mol}^{-1} = 10^4 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
- Limiting Molar Conductance: The molar conductance of an electrolyte at infinite dilution or zero concentration is known as limiting molar conductance. (Λ_m^o)

Equivalent Conductance or Equivalent Conductivity (Λ_{eq}):

- The term 'equivalent conductance' can be defined as the net conductance of every ion that is produced from one gram equivalent of a given substance.
- It can be calculated using the following formula: $\Lambda_{eq} = \kappa \times V$, where V is the volume of the solution containing 1 gram-equivalent of electrolyte.
- Let N be the Normality of the solution, then volume of solution containing 1 gram-equivalent of electrolyte is $\frac{1000}{N}$
- So, $\Lambda_{eq} = \kappa \times \frac{1000}{N}$
- Unit: Ohm⁻¹ cm². equivalent⁻¹ or S cm². equivalent⁻¹
- Equivalent Conductance = $\frac{\text{Molar Conductance}}{n}$ Where $n = \frac{\text{Molecular Mass}}{\text{Equivalent Mass}}$

Lecture-07:

Variation of Conductance or Conductivity with Dilution for Strong and Weak Electrolyte, Debye-Huckel Equation, Kohlrausch's Law and its Applications

- The specific conductance of an electrolyte decreases with dilution. This is because on dilution the ions present per 1 cm^3 volume of the solution decreases.
- It has been found that the decrease in specific conductance on dilution of a solution is more than compensated by increases in its volume.
- For strong electrolytes the molar conductance increases slowly with dilution because for a strong electrolyte the dissociation is complete in solution, so on dilution the no of ions remain constant but with dilution the inter ionic attraction decrease and mobility of ions increases due to which the conductance increases.
- For weak electrolyte, the molar conductance increases steeply with dilution. This is because with dilution the dissociation of electrolyte increases and the no. of ions from 1 mol of electrolyte in total volume of solution increase.

Debye-Huckel Equation

- The variation of molar conductance with concentration (for strong Electrolytes) is given by Debye-Huckel-Onsager equation which is:

$$\Lambda_m^c = \Lambda_m^o - A\sqrt{C}$$

Λ_m^o = Molar conductance at infinite dilution.

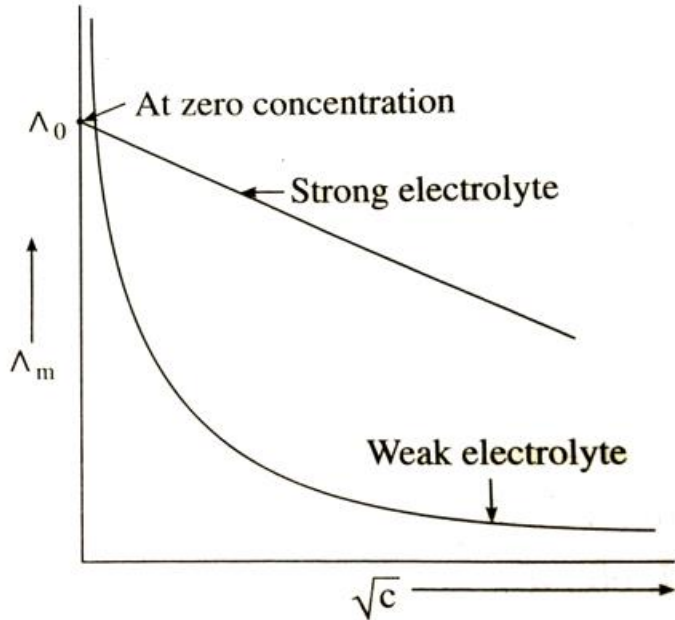
Λ_m^c = Molar conductance at given concentration.

C = Concentration of Electrolyte.

A = Constant depending on the type of electrolyte i.e. on the charges of Cation or anion produced by dissociation of electrolyte.

For NaCl type A = 1-1, For CaCl₂ type A = 2-1.

Variation of Molar conductance with Dilution for Strong and Weak Electrolyte and measurement of limiting molar conductance



- It is possible to determine the molar conductance at infinite dilution in case of strong electrolyte by extrapolation of curve of Λ_m vs \sqrt{C} .
- On contrary, the value of molar conductance of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.
- So molar conductance of weak electrolyte at infinite dilution is determined by infinite dilution.

Variation of Molar conductance with Concentration(Λ_m vs \sqrt{C} graph) for Strong and Weak Electrolyte
(Slope of the graph=- A)

Kohlrausch's law

Kohlrausch's law states that 'The limiting molar conductance of an electrolyte is the sum of individual contributions of the cation and anion of the electrolyte at infinite dilution'.

$$\Lambda_m^o = \nu_+ \Lambda_+^o + \nu_- \Lambda_-^o$$

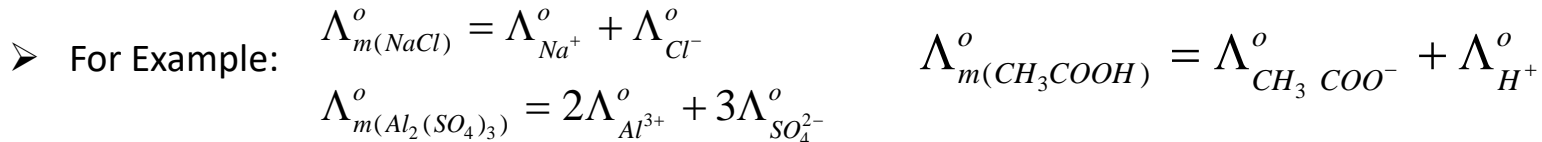
Where Λ_m^o = Limiting molar conductance of an electrolyte.

Λ_+^o = Limiting molar conductance of cation.

Λ_-^o = Limiting molar conductance of Anion.

ν_+ = Number on cations as per the chemical formula of the electrolyte.

ν_- = Number on Anions as per the chemical formula of the electrolyte.



Application of Kohlrausch's law

- (i) **Calculation of limiting molar conductance for weak electrolyte:** The molar conductance of weak electrolyte at infinite dilution can't be obtained experimentally. It can be obtained indirectly by applying Kohlrausch's Law:

For example :molar conductance of CH_3COOH can be determined in the following way;

$$\begin{aligned}
 \Lambda^\circ(\text{CH}_3\text{COOH}) &= \Lambda^\circ(\text{CH}_3\text{COO}^-) + \Lambda^\circ(\text{H}^+) \\
 &= \Lambda^\circ(\text{CH}_3\text{COO}^-) + \Lambda^\circ(\text{Na}^+) + \Lambda^\circ(\text{H}^+) + \Lambda^\circ(\text{Cl}^-) - \Lambda^\circ(\text{Na}^+) - \Lambda^\circ(\text{Cl}^-) \\
 &= [\Lambda^\circ(\text{CH}_3\text{COO}^-) + \Lambda^\circ(\text{Na}^+)] + [\Lambda^\circ(\text{H}^+) + \Lambda^\circ(\text{Cl}^-)] - [\Lambda^\circ(\text{Na}^+) + \Lambda^\circ(\text{Cl}^-)] \\
 &= \Lambda^\circ(\text{CH}_3\text{COONa}) + \Lambda^\circ(\text{HCl}) - \Lambda^\circ(\text{NaCl})
 \end{aligned}$$

(iii) **Calculation of dissociation constant of weak electrolyte (α):** By knowing the value of K_a and Concentration('C'), K_a value can be determined by the following formula:

$$\alpha = \frac{\text{molar conductance at given conc}}{\text{molar conductance at zero conc (infinite dil.)}}$$

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

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

Lecture-08: Electrolysis , Electrolytic Cell, Faraday's Laws of Electrolysis, Predicting Products of Electrolysis

- The device in which electrical energy is used to bring about a non-spontaneous redox reaction is called Electrolytic Cell.
- Two metallic electrodes are kept immersed in an electrolyte. The one connected to +ve terminal of the battery is called anode and the one connected –ve terminal of the battery is called cathode.
- When no electric current is passed the ions of the electrolyte move randomly and due to passage of electric current the ions migrate towards oppositely charge electrodes and get neutralized. This process is called electrolysis.
- Like Galvanic cell here reduction takes place at cathode and oxidation takes place at anode.
- Some important applications of the process of electrolysis are Electroplating, Electro refining etc.
- The metals which have higher reducing power like Na, Mg, Al can be reduced by electrochemical reduction. Copper can be purified by electrolysis method.

FARADAY'S LAWS OF ELECTROLYSIS:

- First Law of Electrolysis: The mass or amount of the substance deposited or liberated at any electrode during electrolysis is directly proportional to the amount of electricity passed through the electrolyte.
- Mathematically, $W \propto Q$ or $W = ZQ$

Where W = amount of substance produced at electrode

Q = quantity of electricity passed through electrolyte

Z = Proportionality constant called electrochemical equivalent of the substance.

When $Q = 1$ C, then $Z = W$

- So electrochemical equivalent (Z) is defined as mass of the substance deposited or liberated by passing 1 coulomb of electricity through the electrolyte.
- Again where I = Current in Amperes and t = Time in seconds

$$\text{So, } Q = I \times t \quad W = Z \times I \times t$$

Some Important points regarding Faraday and Electrochemical Equivalent

Note:

(i) Charge on 1 electron = 1.602×10^{-19}

➤ Charge on 1 mole of Electrons = $1.602 \times 10^{-19} \times 6.022 \times 10^{23} = 96487C \approx 96500C$
= 1Faraday

➤ 1 Faraday is amount of charge in Coulomb carried by 1 mole of electrons.
1 Faraday=96500 Coulomb

(ii) Experimentally it is obtained that 1 F electricity always deposits 1 gm equivalent(E) of substance.

So , 96,500 C deposits E of substance

Then 1 C deposits E /96,500 of substance. Hence, $Z = \frac{E}{96500}$

(iii)So, $W = \frac{E \times I \times t}{96500}$

Since, Equivalent Mass = $\frac{\text{Atomic Mass}(A)}{\text{Valency}(n)}$ Hence $W = \frac{A \times I \times t}{n \times 96500}$

Second Law of Electrolysis:

- When same amount of electric current is passed through different electrolytes connected in series, then masses of the substances produced at the electrodes are directly proportional to their equivalent masses
- Considering two electrolytic solutions like CuSO_4 solution and AgNO_3 solution which are also connected in series.

Suppose	W1: Mass of Cu deposited	E1: Equivalent mass of Cu
	W2: Mass of Ag deposited	E2: Equivalent mass of Ag

By Faradays 2nd Law of electrolysis

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

By Faradays 1st Law of electrolysis : $W_1 = Z_1 \times Q$ and $W_2 = Z_2 \times Q$ $\Rightarrow \frac{W_1}{W_2} = \frac{Z_1}{Z_2}$

- So from all the above equations we finally obtain that : $\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$

Products of electrolysis:

- The product of electrolysis depends on nature of electrodes and nature of electrolyte.
- **When the electrolytic solutions contains more than one same type of ions then the ion having lower discharge potential is liberated at the electrode in preference to other ions.**
- **The potential at which the ion is discharged or deposited on the appropriate electrode is called discharge or deposition potential.**
- **The order of discharge potential among various cations is: $\text{Li}^+ > \text{K}^+ > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Sn}^{2+} > \text{Pb}^{2+} > \text{H}^+ > \text{Cu}^+ > \text{Hg}^{2+} > \text{Ag}^+ > \text{Au}^{3+} > \text{Pt}^{4+}$**
- **The order of discharge potential among various anions is: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$.**

- Higher the value of reduction potential more is its power to get deposited at cathode and Higher the value of oxidation potential more is its power to get discharged at anode.
- During electrolysis of aqueous NaCl following reactions can occur at electrodes:
 - At cathode: i) $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$; $E^0 = -2.71 \text{ V}$
 - ii) $\text{H}^+ + \text{e}^- \longrightarrow 1/2 \text{H}_2$ $E^0 = 0.00\text{V}$
- The reaction with higher E^0 value is preferred and hence H_2 is obtained at cathode.
- The following Reactions can occur at Anode during electrolysis of NaCl
 - At anode: i) $\text{Cl}^- \longrightarrow 1/2 \text{Cl}_2 + \text{e}^-$; $E^0 = +1.36 \text{ V}$
 - ii) $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$; $E^0 = +1.23\text{V}$
- As E^0 value of H_2O is lower so it should be oxidized at anode. But instead of H_2O , the Cl^- ion is oxidized at anode due to over potential of H_2O .

- **Over-Potential:** Some electrode reactions (generally process of liberation of gases) although feasible at their reduction potential value but they are kinetically so slow that at lower potential doesn't seem to take place. To occur these processes some extra voltage is required to that of theoretical value. So over potential is defined as difference between the potential required for the evolution of gas and its standard electrode potential.

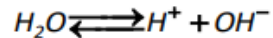
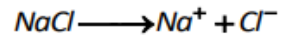
Products of electrolysis: Some Examples

Ex. 1. Electrolysis of molten NaCl

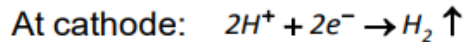


Hence, electrolysis of molten NaCl gives metallic sodium at cathode and can liberate chlorine gas at anode.

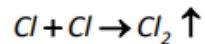
2. Electrolysis of Aqueous NaCl



As the discharge potential of H^+ ion is less than Na^+ ion so H^+ is reduced at cathode in preference to Na^+

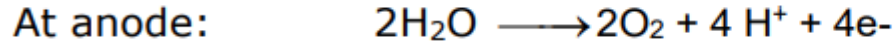
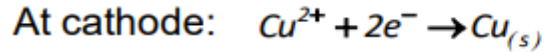
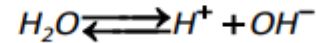
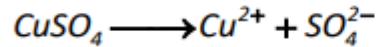


As the discharge potential of Cl^- is less than OH^- so Cl^- is reduced at anode



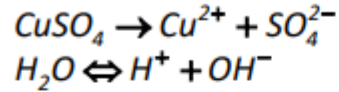
Hence, electrolysis of aqueous NaCl solution can give H_2 gas at cathode and Cl_2 gas anode.

3. Electrolysis of aqueous CuSO₄ solution (using inert Pt electrode)



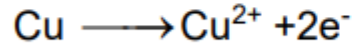
Hence, electrolysis of CuSO₄ solution using inert Pt electrode can liberate O₂ gas at anode, while Cu_(s) is deposited at cathode.

4. Electrolysis of CuSO_4 solution (using attackable copper electrode).



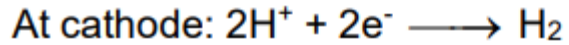
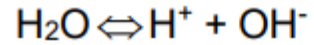
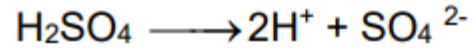
At cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

At anode: Equivalent amount of Cu from anode goes into solution as Cu^{2+} ion



Hence, electrolysis of CuSO_4 solution using attackable Cu electrodes can give copper at cathode and an equivalent amount of Cu^{2+} ions go into the solution from anode.

5. Electrolysis of dil H₂SO₄:



Lecture-09:

Cells and Batteries , Types of Cell , Primary Cell, Secondary Cell, Dry Cell, Mercury Cell, Lead Storage Battery, Ni-Cd Cell, Fuel Cell

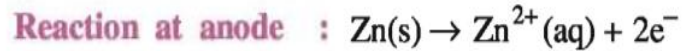
- Cell or Battery: The Galvanic cell which is used as a source of electrical energy from chemical energy of spontaneous redox reaction is called cell or battery.
- The battery may consist of a single cell or a number of cells connected in series.

It is of 2 types like :

- Primary cell
 - Secondary cell
-
- Primary cell: the cell in which the reaction occurs only once and it becomes dead after use over a period of time and can't be reused again is called primary cell. Ex. Dry cell ,Mercury cell etc.
 - Secondary cells are those which can be recharged again and again for multiple uses. e.g. lead storage battery and Nickel – Cadmium Storage Cell.

DRY CELL

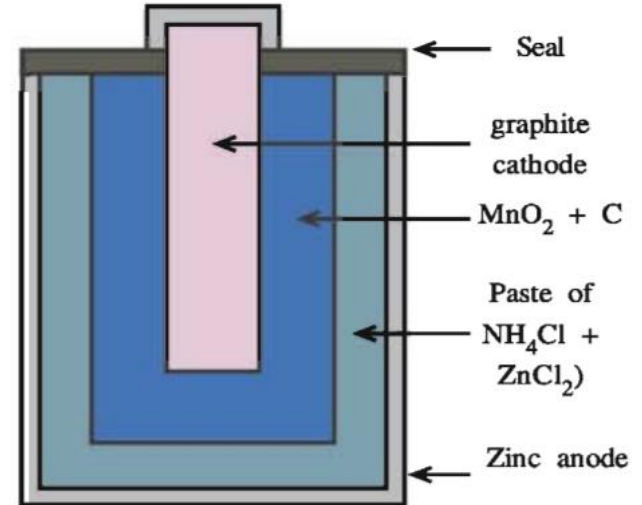
- **Anode** : Zn container
- **Cathode** : Carbon (graphite) rod surrounded by powdered MnO_2 and carbon.
- **Electrolyte** : NH_4Cl and ZnCl_2



Overall Reaction:

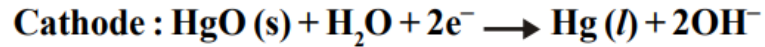
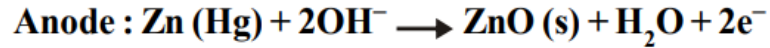


- The standard potential of this cell is 1.5 V and it falls as the cell gets discharged continuously and once used it cannot be recharged.

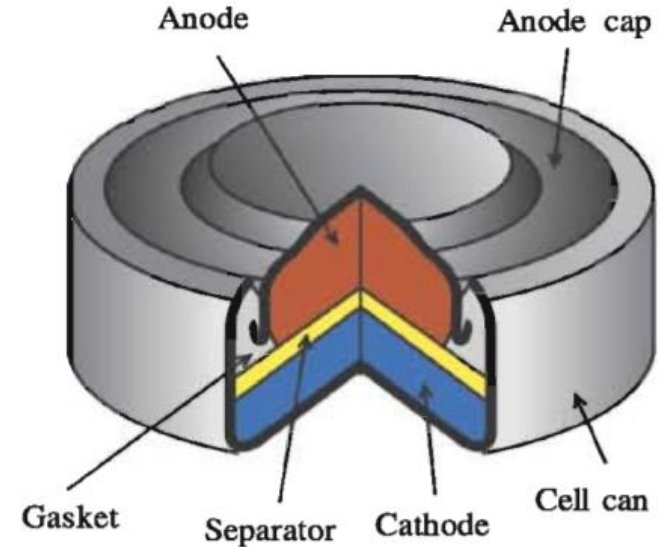


MERCURY CELL

- These are used in small equipments like watches, hearing aids.
- **Anode** : Zn – Hg Amalgam.
- **Cathode** : Paste of HgO and carbon.
- **Electrolyte** : Paste of KOH and ZnO.



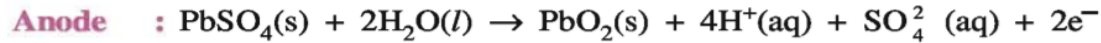
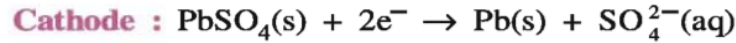
- **Overall Reaction** : $\text{Zn (Hg) + HgO (s) } \longrightarrow \text{ZnO (s) + Hg (l)}$ s constant during its life.



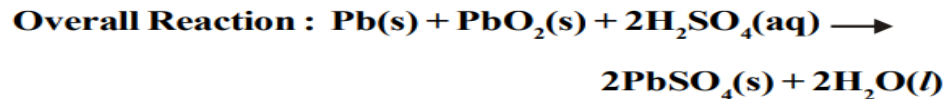
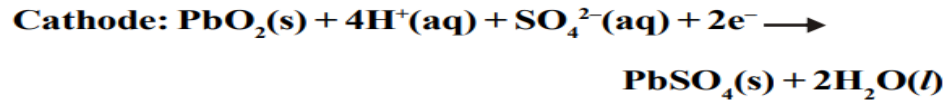
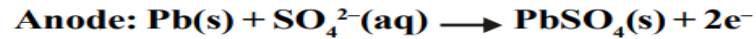
LEAD STORAGE BATTERY

- It consists of 6 cells each producing 2V
- **Anode** : Lead (Pb)
- **Cathode** : Grid of lead packed with lead oxide (PbO₂)
- **Electrolyte** : 38% solution of H₂SO₄

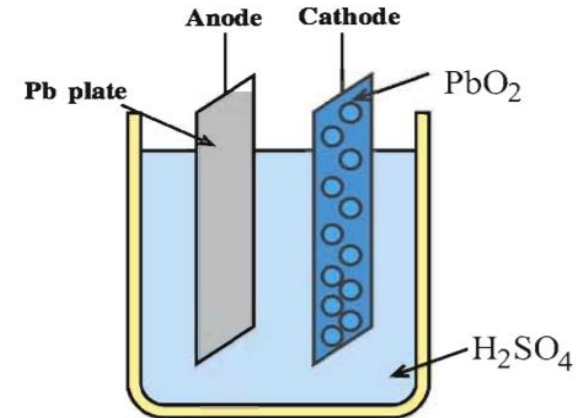
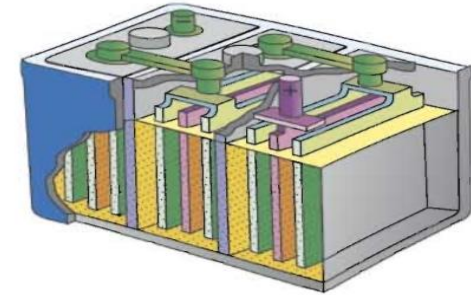
Charging Reactions:



Dis-Charging Reactions:

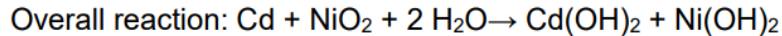
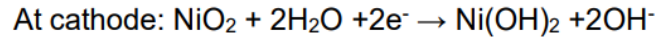
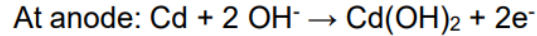


- It is used in automobiles and invertors.

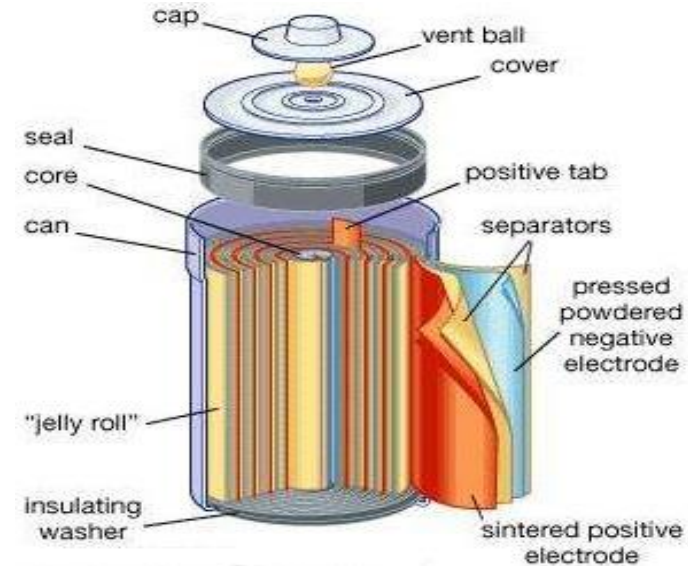


NICKEL-CADMIUM STORAGE CELL

- **Anode:**Cadmium.
- **Cathode:**Metal grid containing NiO_2
- **Electrolyte:**KOH.
- **Cell Reactions:**



- On recharging the above reaction is reversed i. e. Cd(OH)_2 at anode is converted into Cd and Ni(OH)_2 at cathode is converted into NiO_2
- EMF of Ni-Cd cell is 1.4 V and it is used in calculators.



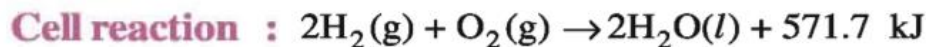
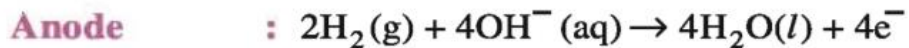
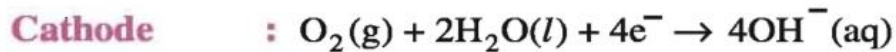
Nickel - Cadmium Cell

Fuel cells:

- The electrochemical cell in which the energy produced from the combustion of fuels like H_2 , CO , CH_4 , CH_3OH etc. is directly converted into electrical energy are called fuel cells

H_2 - O_2 fuel cell:

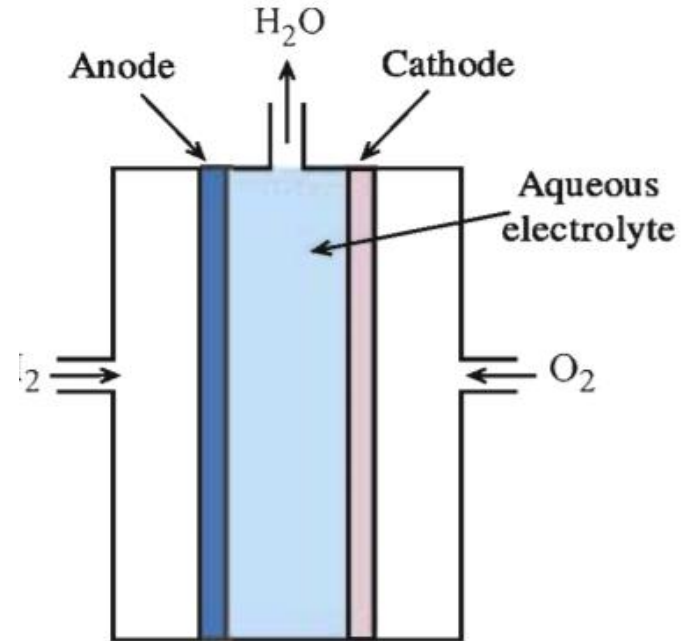
- It has E_{cell} of about 1.23 V.
- It is used as a source of energy in Apollo space programme.
- It consists of porous carbon electrodes containing suitable catalysts like Pt, Pd etc and conc. KOH or NaOH solution as electrolytes.
- H_2 and O_2 are bubbled through the porous electrodes into the NaOH or KOH solution.



FUEL CELLS

Advantages:

- Fuel cells don't cause any pollution.
- They give an efficiency of 70% compared to thermal plants which have efficiency 40%.
- Fuel cells never become dead.



Lecture10:

Corrosion, its Mechanism and its Prevention

Corrosion:

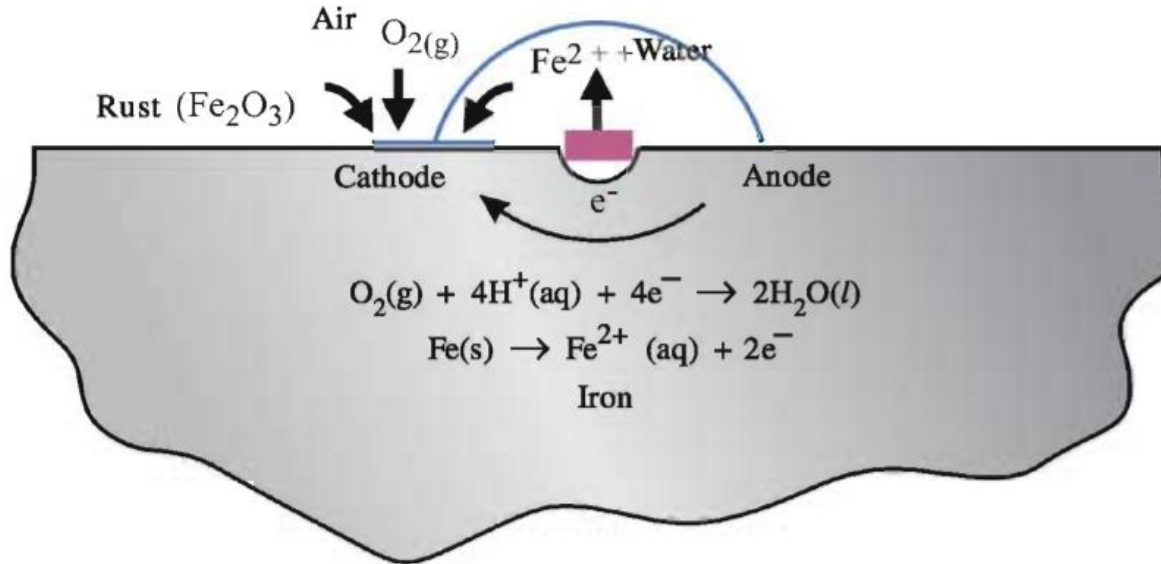
- The process of slowly eating of metal in contact with water and air due to formation of oxides, sulphides and sulphates is called corrosion. Ex. Rusting of iron, tarnishing of silver, development of green coating on copper and bronze etc.
- Rusting of iron: Rusting of iron is an electrochemical phenomenon and the formation of rust involves the following steps:
 - i) The water present on the surface of metal dissolves CO_2 to form H_2CO_3 , which dissociates to small extent to form H^+ ions.

$$\text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{H}_2\text{CO}_3 \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$$
 - ii) At a particular spot of the object made of iron, oxidation takes place in presence of H^+ ion and this spot behaves as anode.
 At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$
 - iii) The electrons lost at anode move through surface of metal and reduce O_2 in presence of H^+ ion at other spot which acts as cathode.
 At cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$
 The overall reaction is: $2\text{Fe} + \text{O}_2 + 4\text{H}^+ \longrightarrow 2\text{Fe}^{2+} + 2\text{H}_2$
 - iv) The Fe^{2+} ions are further oxidized by atmospheric O_2 in H_2O to form Fe_2O_3 .

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}_2\text{O} \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{H}^+$$
 - v) The Fe_2O_3 undergoes hydration to form rust.

$$\text{Fe}_2\text{O}_3 + x\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(\text{Rust})$$

Mechanism of Corrosion



Prevention of Corrosion

Corrosion can be prevented by:

- By covering the surface of metal with paint or by some chemicals like bisphenol.
- By covering the surface of metal with inert or less reactive metals like Sn, Cr, Cu etc.
- By sacrificial protection i.e. the surface of metal is coated with more reactive metals like Mg, Zn which corrodes themselves but saves iron metal.
- The metals whose reduction potential value has higher -ve than Iron are more reactive and hence can be used for sacrificial protection.
- The electroplating of Zn on iron is called Galvanisation. Galvanizing is the process of immersing iron or steel in a bath of molten zinc to produce a corrosion resistant, multi-layered coating of zinc-iron alloy and zinc metal.
- Alkaline medium inhibits the rusting of iron. Rusting of iron decreases with decrease in conc. of H^+ ion on its surface. Alkaline medium prevents the availability of H^+ ion which reduce rate of oxidation of Fe to Fe^{2+} . So rate of rusting process decreases.

THANKING YOU
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