

ELECTROCHEMISTRY

- Electrochemistry: It is the study of production of electricity from energy which is released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.
- A chemical reaction in which e^- are lost by one substance and gained by another is called Redox Reaction.
- There are two types of cell -
 - ① Electrochemical cells
 - ② Electrolytic cells.
- Electrochemical cells.
 - It is a device in which chemical energy of Redox-Reaction is converted into electrical energy.
 - It consists of two metallic electrodes dipping in electrolytic solution. The solutions in two compartments is connected through an inverted U-shaped tube containing a mixture of agar-agar jelly and electrolytes like KCN or KNO₃ or NH₄NO₃ (Inert electrolyte). This tube is called Salt bridge.
- Significance of salt bridge: - connects the half cell hence complete the circuit.
 - It prevents the transference of the solution from one half cell to other.
- In Galvanic cell, Oxidation occurs at anode and it is a Negative plate while Reduction at cathode and it is a positive plate.

→ DANIELL CELL

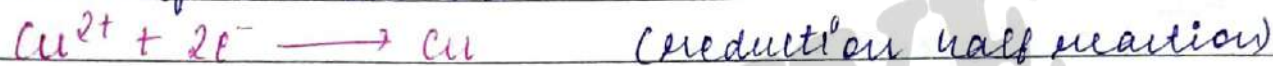
→ Among the galvanic cell when cell is designed in such a manner to make the use of spontaneous reaction between Zinc and Copper. Ion to produce an electric current, that cell is called Daniell cell.

Reaction occurs,



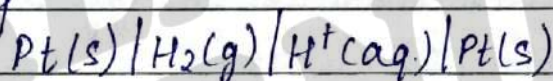
cell is represented as $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$.

→ The two half reactions are.

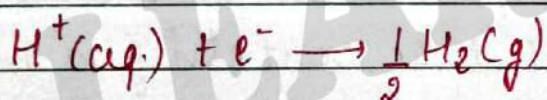


→ STANDARD HYDROGEN electrode (SHE)

It is represented by



→ It is assigned to Zero potential at all the temperature
Reaction



→ Electrode Potential

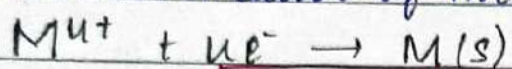
→ Potential difference between the metal and the metal ion in which electrode is dipped is called Electrode potential.

→ In electrochemical cell, the electrodes in diff. half cells have different reduction potential. As the result of this, different flow of e^{-} is seen from the electrode of higher tendency to lose e^{-} this difference in electrode potential is called cell potential or **emf**.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \text{ or } E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}}$$

→ NERST EQUATION

→ It gives the relation between electrode potential, temperature and concentration of Metal ions.



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

$T = 298\text{K}$ & $R = 8.314$
 $F = 96500 \text{ C mol}^{-1}$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

→ Relationship b/w equilibrium const. and standard electrode potential of the cell.

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

At equilibrium $E_{\text{cell}} = 0$

$$E^{\circ}_{\text{cell}} = \frac{0.059}{n} \log K_c \quad (*)$$

→ ELECTROCHEMICAL Series

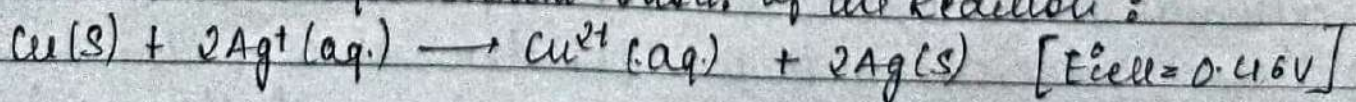
→ The arrangement of metal in decreasing order of tendency to lose e^- is called electrochemical series.

→ Applications of electrochemical series include.

- In comparing reactivity of metals.
- In comparing Oxidising and Reducing behaviour of elements.
- In calculation of emf of the cell.
- In predicting the feasibility of a Reaction.

(*) A Negative E° means that the redox couple is a stronger reducing agent than H^+/H_2 couple and Vice Versa.

Example: Calculate the equilibrium const. of the Reaction:



Solve as at equilibrium, $E_{\text{cell}} = 0$

$$0 = E^{\circ} - \frac{0.059}{n} \log K_c$$

$$\Rightarrow 0.46 = \frac{0.059}{2} \log K_c$$

$$\Rightarrow K_c = 3.92 \times 10^{15}$$

• CONCENTRATION CELL :-

→ If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different conc. and the solⁿ are connected through salt bridge, such cell is known as Concentration cell.



$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

⊛ $E^{\circ}_{\text{cell}} = 0$ (as metal is same in both the half reaction)

• GIBBS ENERGY

→ To obtain maximum work from a galvanic cell, change has to be passed reversibly.

The Reversible Work done by a galvanic cell is equal to decrease in its Gibbs energy.

Therefore, ΔG° gives the maximum work

$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$ - If E° is +ve, $\Delta G = -ve$ and cell will work (spontaneous process)

→ If E° is +ve, the Redox is spontaneous (i.e., do not require any external work) but if E° is -ve, $\Delta G = +ve$ (Non-spontaneous)

→ H^+ can't oxidise Cu as it has positive value of standard electrode potential, that's the reason Cu can't dissolve in HCl.

example What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

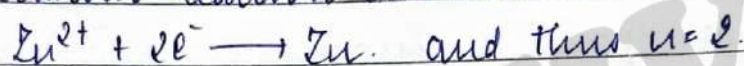
→ The chemical reaction of the cell is reversed and current flows in opposite direction when opposing emf is slightly greater than that of cell.

example A zinc rod is dipped in 0.1 M solution of ZnSO_4 .

(2012) The salt is 95% dissociated at this dilution at 298 K.

calculate the electrode potential [$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$]

Solve The electrode reaction involved is



By using Nernst equation we get,

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ - \frac{0.059}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

Given that 0.1 M ZnSO_4 solution is 95% dissociated that means

$$[\text{Zn}^{2+}] = \frac{95 \times 0.1}{100} = 0.095 \text{ M}.$$

$$\therefore E_{\text{Zn}^{2+}/\text{Zn}} = -0.76 - \frac{0.059}{2} \log \frac{1}{[0.095]}$$

$$[E_{\text{Zn}^{2+}/\text{Zn}} = -0.790 \text{ V}]$$

(2010)

example Given that, the standard electrode potential (E°) of metals

$$\text{K}^+/\text{K} = -2.93 \text{ V}$$

$$\text{Ag}^+/\text{Ag} = 0.80 \text{ V}$$

$$\text{Cu}^{2+}/\text{Cu} = 0.34 \text{ V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.37 \text{ V}$$

$$\text{Cu}^{3+}/\text{Cu} = -0.74 \text{ V}$$

$$\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$$

Arrange these metals in an increasing order of their reducing power.

Solve

$$\text{Reduction power} \propto \frac{1}{\text{Reduction pot.}}$$

$$\text{Order: } \text{Ag} < \text{Cu} < \text{Fe} < \text{Cu} < \text{Mg} < \text{K}.$$

(more Negative E° means that the redox couple is a stronger reducing agent)

→ CONDUCTANCE

→ Every substance offers resistance to the flow of electricity to a small or large extent.

Resistance, $R = V/I$ where V is voltage and I is current
SI unit of Resistance is ohm (Ω).

→ The electrical resistance (R) of any object is directly proportional to its length (l) and inversely to its area of cross section.

i.e.,

$$R \propto \frac{l}{A} \text{ and } R \propto l \Rightarrow R = \frac{\rho l}{A} \quad \begin{array}{l} \rho = \text{Resistivity} \\ \text{(unit ohm cm)} \end{array}$$

→ ρ is also known as Specific Resistance.

→ It is the property of material and independent of A or l .

→ Conductance: The ease with which current flows through a conductor.

(G)

- It is inverse of resistance i.e., conductance.

$$G = \frac{1}{R} = \frac{A}{\rho l} = \frac{K A}{l} \quad K = \text{conductivity}$$

- SI unit of conductance is Siemens (S) or ohm⁻¹.

- The Quantity l/A is known as Cell Constant (G^*)

→ Conductivity: The inverse of resistivity (ρ)

(K)

- also known as specific conductance

$$K = \frac{1}{\rho}$$

SI unit is Sm⁻¹, but quite often it is Scm⁻¹.

(*) - It always decreases with decrease in concentration for weak and strong electrolytes.

conductivity of Ag = 6.2×10^3 (Best conductor)

conductivity of Cu = 5.9×10^3

Types of Conductors

① Metallic or Electronic Conductors.

- In Metallic conductors, the flow of electricity takes place due to the flow of electrons only.
- It Depends on: (i) the Nature and Structure of metal.
 - (ii) the Number of Valence e^- per atom.
 - (iii) Temperature (conductance \downarrow es with \uparrow in temperature)

② Electrolytic conductors.

- In Electrolytic conductors, the flow of electricity takes place due to the flow of Ion (charges).
- It Depends on: (i) The Nature of electrolyte added and its concentration.
 - (ii) The size of the ions produced and their solvation
 - (iii) The Nature of the solvent and its viscosity.
 - (iv) Temperature (It \uparrow es with \uparrow in temperature)

NOTE: Superconductors have zero Resistivity or infinite conductivity.

MOLAR CONDUCTIVITY

- It is defined as the conductance of that volume of solution which contains one mole of the electrolyte such that, entire solution is in b/w the two electrodes kept 1 cm apart and have large 'A', so as to contain the electrolyte. Thus, Molar conductance.

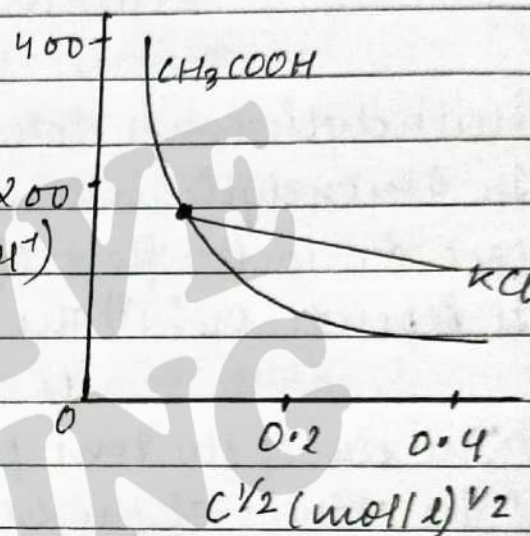
$$\lambda_m = \frac{K \times 1000}{\text{Molarity}} \quad \text{or } \lambda_m = K'V$$

- It increases with decrease in concentration (or increase on dilution). Its unit is $\text{Sm}^2\text{mol}^{-1}$ or $\text{Scm}^2\text{mol}^{-1}$.

- When $C \rightarrow 0$, $\lambda_m \rightarrow \lambda_m^\circ$. i.e., when concentration approaches zero, the molar conductivity reaches a limiting value known as limiting molar conductivity (λ_m°)
- The variation in λ_m with concentration is different for strong and weak electrolyte.
- Such variation for KCl (strong electrolyte)
 CH_3COOH (weak electrolyte)

- For strong electrolytes λ_m increases slowly with dilution and can be represented by the λ_m equation, Debye-Huckel - Onsager equation.

$$\lambda_m = \lambda_m^\circ - AC^{1/2}$$



→ KOHLRAUSCH'S Law of Independent Migration.

- This law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cations of the electrolyte.
- If an electrolyte on dissociation gives ν_+ cations and ν_- anion then its limiting molar conductivity is given

$$\lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$
 where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and ν_+ and ν_- are the No. of cations and anions respectively at infinite dilution.
- A weak electrolyte is not completely dissociated at all conc. With dilution, the degree of dissociation α increases, resulting in \uparrow in the No. of ions.

→ The Ratio of molar conductivity at a specific concⁿ to the molar conductivity at ∞ dilution is known as degree of dissociation (α) i.e., $\alpha = \frac{\lambda_m}{\lambda_m^0}$

→ For a weak electrolyte, if K_a is dissociation constt,

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

→ Application of Kohlrausch's law.

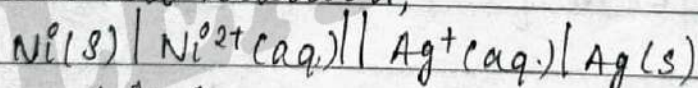
- The molar conductivity of weak electrolytes at infinite dilution can be calculated by using Kohlrausch law.

- Degree of dissociation of a weak electrolyte (like CH_3COOH) at a given concⁿ can be calculated.

- knowing the Degree of Diss. (α) the dissociation constt. (K) of the weak electrolyte at a given concⁿ of the solution, can be calculated.

2015

Example for the cell reaction,



Calculate the equilibrium constant at 25°C.

How much maximum work would be obtained by operation of this cell? ($E_{\text{Ni}^{2+}/\text{Ni}}^0 = 0.25\text{V}$ and $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80\text{V}$)

Solve Given $E_{\text{Ni}^{2+}/\text{Ni}}^0 = 0.25$ and $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80\text{V}$

At anode $\text{Ni}(s) \rightarrow \text{Ni}^{2+} + 2e^-$

at cathode $[\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag}(s)] \times 2$

$$E_{\text{cell}}^0 = E_{\text{cathode}} - E_{\text{anode}} = 0.80 - 0.25 = 0.55\text{V}$$

Equilibrium constant

$$\text{antilog} \left(\frac{nE^0}{0.059} \right) = \text{antilog} \left(\frac{2 \times 0.55}{0.059} \right) \quad K = 4 \times 10^{18}$$

$$\text{Maximum Work } (\Delta G) = -nFE^\circ$$

$$= -2 \times 96500 \times 0.55 = -106150 \text{ J mol}^{-1}$$

→ ELECTROLYSIS

→ The cell which converts electrical energy to chemical energy are c/d electrolytic cells.

★ In this Oxidation occurs at anode and it is a positive plate while reduction occurs at Cathode and it is a Negative plate.

→ In electrolytic cells, electrical energy is used to carry out non-spontaneous chemical reactions and the process which takes place in a electrolytic cell is c/d electrolysis

→ FARADAY'S Law of Electrolysis :- Ist Law.

- The amount of chemical reaction which occurs at any electrode during electrolysis by passing current is proportional to the quantity of electricity passing through electrolyte

- Thus, 'm' gms of the substance get deposit on passing Q coulomb of electricity

$$m \propto Q \text{ or } Q = z \cdot m \text{ (z = prop. constt)}$$

$$\text{★ } m = z \cdot i \cdot t$$

where Q = Quantity of electricity, I = current (in Ampere)

t = time (s)

z = electrochemical equivalent.

- IInd Law.

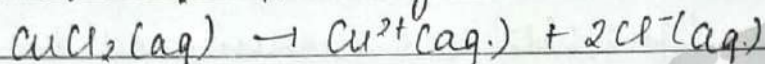
- The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solutions are proportional to their chemical equivalent

$$\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3} = \dots$$

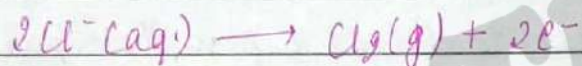
→ Products of Electrolysis

- The products of electrolysis depends upon the nature of electrolyte being electrolysed and the nature of electrodes.
- If electrodes are inert like Pt or Au, they do not take part in reaction.
- The product of electrolysis also depends upon the electrode potential of oxidising and reducing species.

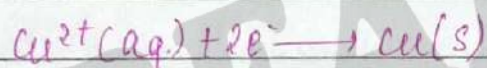
(P) Electrolysis of $\text{CuCl}_2(\text{aq})$ using Pt electrode.



At anode.

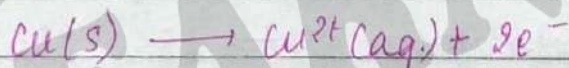


At cathode.

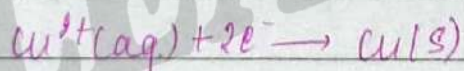


(PP) Electrolysis of CuCl_2 using Cu electrode.

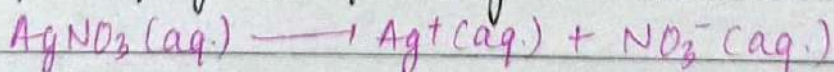
At anode



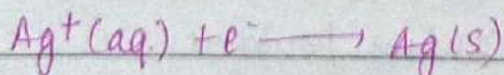
At cathode



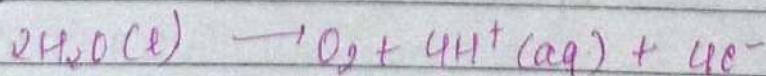
(PPP) Electrolysis of $\text{AgNO}_3(\text{aq})$ using Pt electrode



At cathode

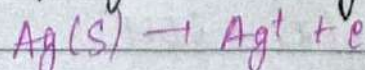


At anode.

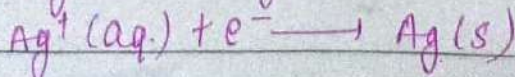


(PV) Electrolysis of AgNO_3 using Ag electrode,

At anode,



At cathode,



→ PRIMARY CELLS

- The device which provides the electrical energy is called cell.
It can be primary or secondary.

→ The cell in which products can't be changed back into reactants is called primary cell.

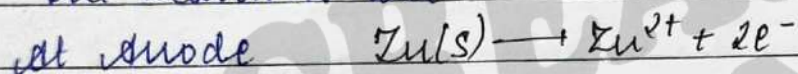
eg) Daniell cell, Mercury cell, dry cell etc.

→ Dry cell (Leclanche cell)

- It consists of a zinc container which acts as anode and cathode is carbon (graphite) rod surrounded by powdered Manganese Dioxide and Carbon.

- The space b/w the electrodes is filled by moist paste of NH_4Cl and ZnCl_2 .

- The reactions are.



At cathode



- At cathode, Mn is reduced from +4 \rightarrow +3

Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$.

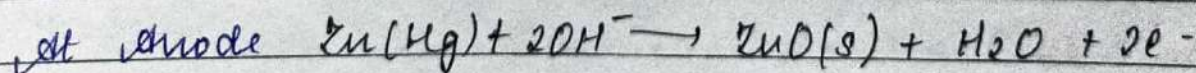
- The cell has a potential of nearly 1.5V, decreases with time.

→ Mercury cell.

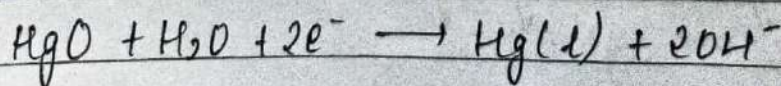
- It consists of Zn-Hg amalgam as anode the cathode is paste of mercuric oxide (HgO) and carbon powder.

- The electrolyte is a paste of KOH and ZnO .

- The reactions are



At cathode



The Overall reaction



- The cell potential is approx. 1.035 V and remains constant during its life.

→ SECONDARY CELL

- A secondary cell is capable of being charged after discharge again and again, eg) lead storage battery
Nickel-Cadmium battery.

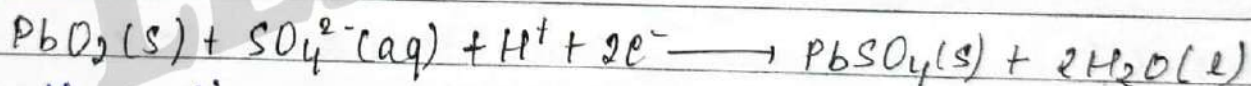
→ Lead storage battery

- It consists of lead anode and a grid of lead packed with lead dioxide as cathode.
- A 38% solution of H_2SO_4 as an electrolyte.

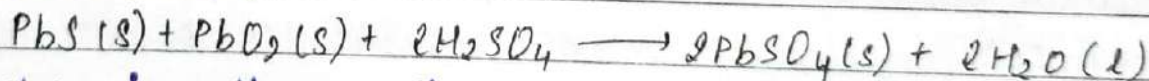
→ When battery in use (Discharging), the reactions are,
At anode,



At cathode,



The Overall reaction,



→ During charging, the reactions are reversed.

→ Nickel-Cadmium cell

- The Overall cell reaction of Ni-Cd cell during discharging is
$$\text{Cd(s)} + 2\text{Ni(OH)}_2(\text{s}) \longrightarrow \text{CdO(s)} + 2\text{Ni(OH)}_2 + \text{H}_2\text{O}$$

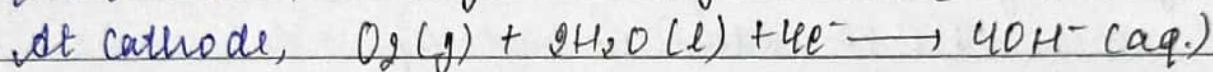
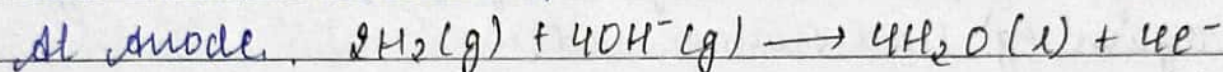
- It is another important secondary cell.

→ FUEL CELL

- They are galvanic cell that are designed to convert the energy of combustion of fuels like H_2 , CH_4 , CH_3OH directly into electrical energy.

eg) H_2 - O_2 fuel cell, in which H_2 and O_2 are bubbled through porous carbon electrodes into conc. KOH soln.

- Chemical reactions are,



- The overall reaction,



$$\text{Efficiency of a cell} = \frac{\Delta G}{\Delta H} = \frac{\text{Useful work}}{\text{Total work}}$$

→ Uses of above cells.

Cells	Uses.
- Dry cell (Leclanche cell)	Transistors and Clock
- Mercury cell	Low current devices like hearing aids, watches etc.
- Lead storage Battery	Automobiles and invertors
* - Fuel cells	Electrical power in Apollo space programme.

→ CORROSION

- It is basically an electrochemical phenomenon

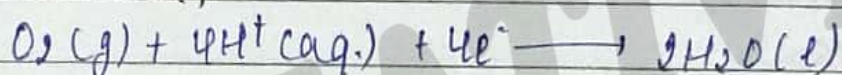
- In this metal oxide or other salt of the metal forms a coating on the metal surface
eg) Tarnishing of silver
Rusting in iron.

→ Rusting of iron.

- Oxidation of Fe, acts as anode
- Reduction of O_2 into H_2O , acts as a cathode.

Oxidation at anode, $2Fe(s) \rightarrow 2Fe^{2+}(aq.) + 4e^-$

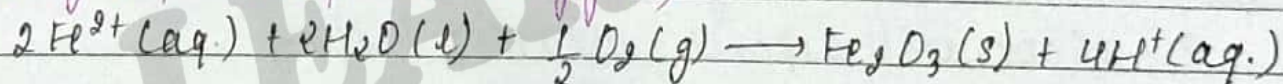
Reduction at cathode,



The Overall Reaction,



- Atmospheric Oxidation (when Fe^{2+} ion are further oxidising by atmospheric Oxygen)



→ Methods Used for Prevention of corrosion

- There is an electrochemical method which provides a sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes itself but saves the object

★ Sacrificial metal should be more electropositive than iron.

- Other methods include by covering surface with paint or by some chemical (eg. kresphenol)

example How many moles of mercury will be produced by electrolysis 10M $Hg(NO_3)_2$ solution with a current of 2000 A for three hours? [$Hg(NO_3)_2 = 200.6 g mol^{-1}$]

(2011)

Solve Given current = 2A,

Time = 3hr = $3 \times 60 \times 60$ sec

$$m = \frac{E}{96500} \times It \Rightarrow m = \frac{200.6 \times 2 \times 3 \times 60 \times 60}{2 \times 96500} = 22.45 \text{ gm}$$

$$\text{No. of moles} = \frac{22.45}{200.6} = 0.112 \text{ mol.}$$

example calculate the mass of Ag deposited at cathode when a current of 2A was passed through a solution of AgNO_3 for 15 min. (Given: Molar mass of Ag = 108 gm mol⁻¹, $1F = 96500 \text{ C mol}^{-1}$)

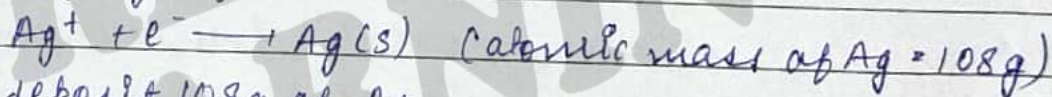
Solve Given current (I) = 2A

Time (t) = 15 min

Quantity of electricity passed will be

$$Q = It = 2 \times 15 \times 60 = 1800 \text{ C}$$

Electrolysis of AgNO_3



As, 96500 C deposit 108 g of Ag

$$\therefore 1800 \text{ C will deposit} = \frac{108 \times 1800}{96500} \text{ g of Ag}$$

$$= 2.014 \text{ gm of Ag.}$$

2014

example Resistance of a conductive cell filled with 0.1 mol l⁻¹ KCl solⁿ is 100 Ω . If the Resistance of the same cell when filled with 0.02 mol l⁻¹ KCl solⁿ is 520 Ω , calc. the conductivity and molar conductivity of 0.02 mol l⁻¹ KCl solⁿ. The conductivity of 0.1 mol l⁻¹ KCl solⁿ is $1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$.

Solve Cell constant, $G^* = \text{conductivity} \times \text{Resistance} = 1.29 \times 100 = 129 \text{ cm}^{-1}$

- Conductivity of 0.02 M KCl solⁿ $\Rightarrow K = \frac{\text{cell const.}}{\text{Resistance}} = \frac{1.29 \text{ cm}^{-1}}{520 \Omega} = 2.48 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$

- Molar conductivity $\Rightarrow \lambda_m = \frac{K \times 1000}{M} = \frac{2.48 \times 10^{-3} \times 1000}{0.02} = 124 \text{ S cm}^2 \text{ mol}^{-1}$