

Electrochemistry

Area of chemistry which is concerned with interconversion of chemical and electrical Energy.

Electric conduction :-

(A) Metallic conduction :- Conduction through metal involves a direct flow of electron from one point to the other

Outermost e^- are from conduction bond. and e^- are free to move.

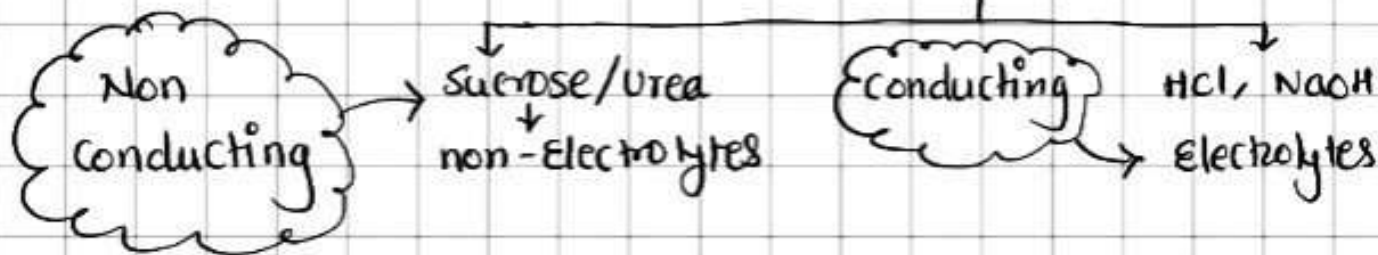
(B) Electrolytic or Ionic conduction :- conduction of electric current by the movements of ion of the electrolyte.

The movement of ion through molten electrolytes or aq. solution of electrolytes

eg:- Ionic salts, Strong / weak electrolytes.

Information provided by measurement of conductivities of Solution

① conducting or non-conducting \rightarrow by conductivity of solⁿ
Nature of Solution



② On the basis of high or low electrical conductivity Electrolytes are classified as

→ Strong electrolyte
→ weak electrolyte

Electrical conductance of the solution

According to the ohm's law

$$V = IR$$

$$\therefore R = \frac{V}{I}$$

$$\Omega = \frac{\text{Volt}}{\text{Ampere}}$$

V = potential difference

I = electric current

R = Resistance

$$\Omega = VA^{-1}$$

G is electric conductance

$$\therefore G = \frac{1}{R}$$

SI unit of G Siemens (S)

$$\therefore S = \Omega^{-1} = A V^{-1}$$

$$C = AS$$

$$\therefore S = CV^{-1}S^{-1}$$

$$R \propto \frac{l}{a}$$

length
cross section

$$R = \rho \frac{l}{a}$$

where ρ = resistivity

conductivity

$$G = \frac{1}{R}$$

$$\text{So } G \propto \frac{a}{l}$$

$$G = k \frac{a}{l}$$

k = conductivity

Conductivity of solution of electrolyte is called electrolytic conductivity

k is conductance of unit volume = 1 cm^3 or 1 m^3

$$k = G \frac{l}{a} = \frac{1}{R} \frac{l}{a}$$

$$\therefore k = \frac{1}{\rho} \leftarrow \text{resistivity}$$

Molar conductivity

(Λ lambda)

$$\Lambda = \frac{k}{C}$$

where C = molar concentration

SI units

$$k = S m^{-1}$$

$$C = \text{mol } m^{-3}$$

$$\therefore \Lambda = S m^2 \text{ mol}^{-1}$$

also

$$\Lambda = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda = \frac{S m^{-1}}{\text{mol } m^{-3}}$$

Significance of molar conductivity

Molar conductivity

→ Electrical conductance generated by all the ion in 1 mol of the electrolyte

Relation between K & Λ

K = ele. conductance of 1cm^3 of solⁿ

Λ = Volume V in cm^3 containing 1 mol Electrolyte show Electric conductance Λ

$$\Lambda = KV$$

→ K is 1cm^3 conductance in total volume V

∴ total conductance is KV which is molar conductance

Concentration of solution

$$= C \text{ mol L}^{-1}$$

$$= \frac{C \text{ mol L}^{-1}}{1000 \text{ cm}^3 \text{ L}^{-1}} = \frac{C}{1000} \text{ mol cm}^{-3}$$

$$V = \frac{1}{C} \quad \therefore V = \frac{1000}{C} \text{ cm}^3 \text{ mol}^{-1}$$

$$\Lambda = \frac{1000}{C} \times K = \frac{1000K}{C}$$

Variation of conductivity with concentration

⇒ conductivity depends on no. current carrying ions present in unit volume

⇒ on dil. no. of ion increase & degree of dissociation

⇒ dil. decrease con. so conductivity decrease

Variation of molar conductivity with concentration

⇒ molar conductivity is the electrical conductance

of 1 mol of an electrolyte in given volume

⇒ increase in no. of moles will increase molar conductivity

variation of molar conductivity with concentration

(a) Strong Electrolytes:- The molar conductivity of solution of Strong Electrolyte increase rapidly with dilution.

Molar conductivity at zero concentration OR Infinite dilution
 $[\Lambda_0]$

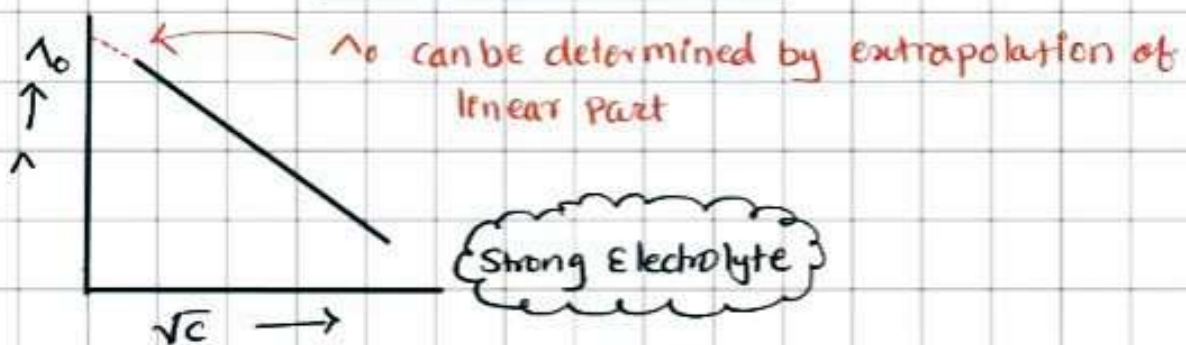
(the limiting value 0.001M to 0.0001M)

means no change in conductivity on further dilution

⇒ Molar conductivity of strong electrolyte varies linearly with sq. root of concentration

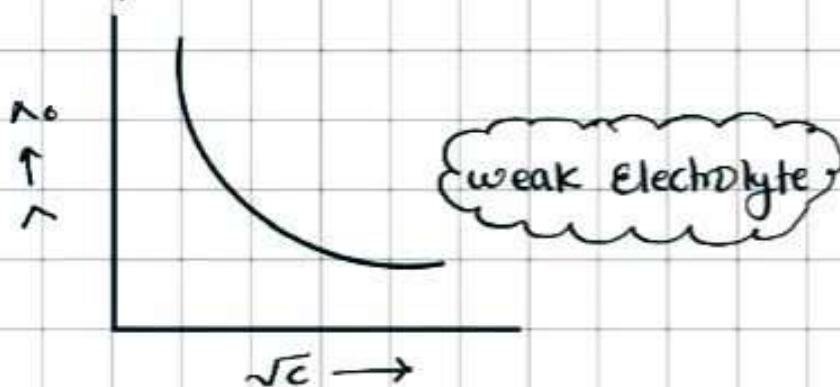
$$\Lambda = \Lambda_0 - a\sqrt{c}$$

where : $a \Rightarrow$ constant



(b) Weak Electrolytes:- The molar conductivity of weak Electrolyte increase rapidly on dilution
⇒ The value of Λ is lower than Λ_0

Graph Λ vs \sqrt{c} (concentration)



Kohlrausch law of Independent migration of ion

at infinite dilution each ion migrates independent of co-ion & contribute to total molar conductivity of electrolyte & not on nature of other ion.

$$\Lambda_0 = n_{+} \lambda_{+}^{\circ} + n_{-} \lambda_{-}^{\circ}$$

λ_{+}°
 λ_{-}° } Molar conductivity of cation & anion

n_{+}
 n_{-} } No. of moles of cation & anion

Applications of Kohlrausch theory

⇒ to calculate molar conductivity of an electrolyte at Zero Concentration

eg:- $\Lambda_0(\text{KCl}) = \lambda_{\text{K}^{+}}^{\circ} + \lambda_{\text{Cl}^{-}}^{\circ}$

$\Lambda_0[\text{Ba}(\text{OH})_2] = \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{OH}^{-}}^{\circ}$

⇒ calculation of weak electrolytes from strong electrolyte

eg:- $\Lambda^{\circ}(\text{CH}_3\text{COOH})$

we have HCl NaCl CH_3COONa
 └ Strong electrolytes ┘

$$\begin{aligned} & \Lambda_0(\text{HCl}) + \Lambda_0(\text{CH}_3\text{COONa}) - \Lambda_0(\text{NaCl}) \\ &= \underbrace{\lambda_{\text{H}^{+}}^{\circ} + \lambda_{\text{Cl}^{-}}^{\circ}}_{\text{HCl}} + \underbrace{\lambda_{\text{CH}_3\text{COO}^{-}}^{\circ} + \lambda_{\text{Na}^{+}}^{\circ}}_{\text{CH}_3\text{COOH}} - \underbrace{\lambda_{\text{Na}^{+}}^{\circ} + \lambda_{\text{Cl}^{-}}^{\circ}}_{\text{NaCl}} \\ &= \lambda_{\text{CH}_3\text{COO}^{-}}^{\circ} + \lambda_{\text{H}^{+}}^{\circ} \\ &= (\Lambda^{\circ} \text{CH}_3\text{COOH}) \end{aligned}$$

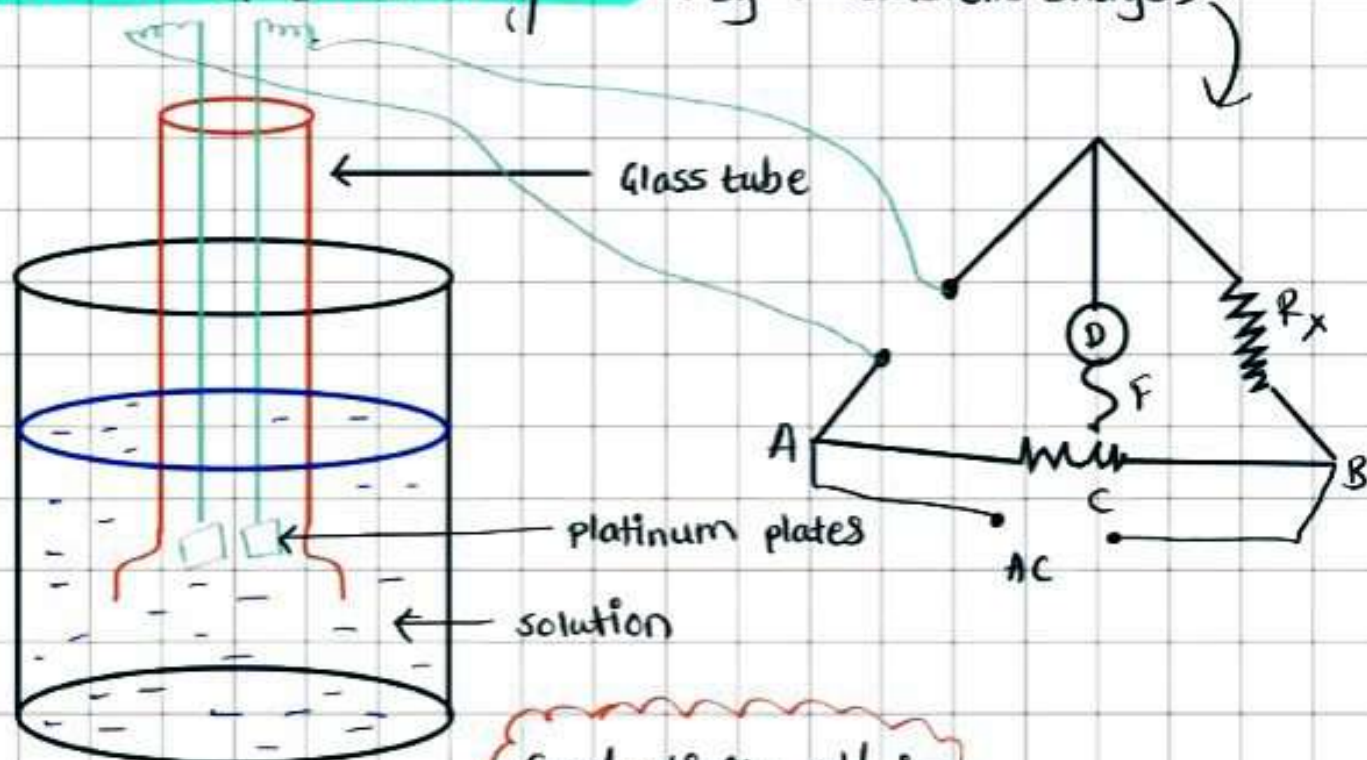
Solve problems

Molar conductivity and degree of dissociation of weak electrolyte

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

Λ_c = molar conductivity of weak electrolyte at conc. 'c'

Measurement of conductivity # (By wheatstone bridge)



Conductivity cell :-

Cell constant :-

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

$$\text{Cell constant} = \frac{l}{A}$$

SI unit $\text{m}^{-1}/\text{cm}^{-1}$

$$K = \frac{\text{cell constant}}{R}$$

→ Determination of cell constant ←

According to wheatstone bridge

$$\frac{R_{\text{solution}}}{l(AC)} = \frac{R_x}{l(BC)}$$

$$\therefore R_{\text{solution}} = \frac{l(AC)}{l(BC)} \times R_x$$

$$\boxed{\text{Cell constant} = K_{\text{KCl}} \times R_{\text{solution}}}$$

② Determination of conductivity of given solution

$$K = \frac{\text{Cell constant}}{R_{\text{solution}}}$$

③ calculation of molar conductivity

$$\Lambda = \frac{1000K}{C}$$

Electrochemical reaction

- ⇒ chemical reaction occurring in electrochemical cell
- ⇒ involves transfer of electron
- ⇒ It is redox reaction

Electrodes

- (A) cathode :- Electrode at which reduction takes place
- (B) Anode :- Electrode at which oxidation takes place

Types of electrochemical cell

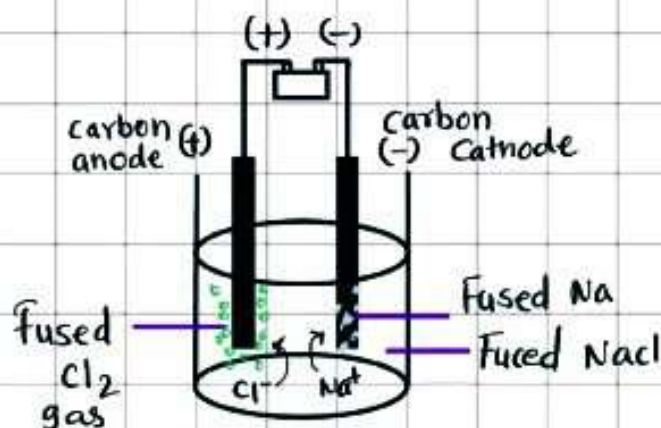
- (A) Electrolytic cell :- Non-spontaneous reaction (Electrolysis)
 - ⇒ convert Electrical Energy → Chemical Energy.
 - ⇒ Anode (+) Cathode (-)

- (B) Galvanic or voltaic cell :- Spontaneous chemical reaction produce Electricity.
 - ⇒ Chemical Energy → Electrical Energy
 - ⇒ Anode (-) Cathode (+)

Electrolytic cell

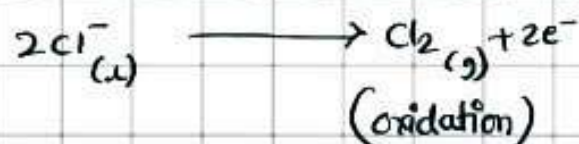
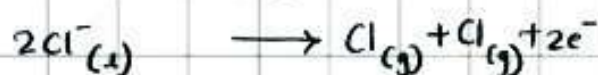
① Electrolysis of Molten NaCl

④ Construction of cell -

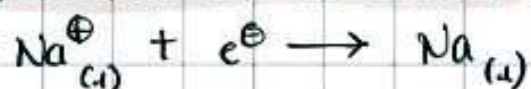


⑥ Cell Reaction :-

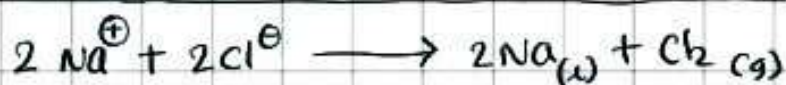
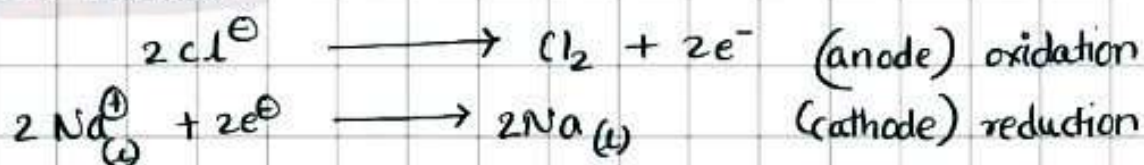
oxidation half reaction
at anode



Reduction half at cathode :



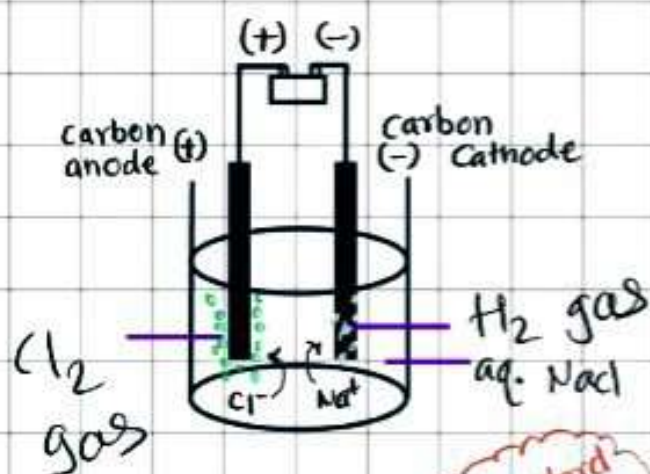
Net cell reaction



Results of Electrolysis of molten NaCl

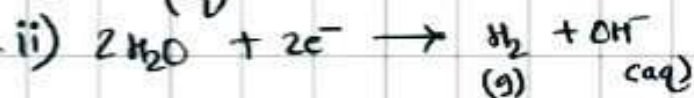
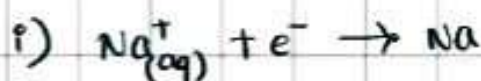
- (i) pale green Cl_2 gas released at anode
- (ii) Molten silvery-white sodium is formed at cathode

Electrolysis of aqueous NaCl



Cell reaction :

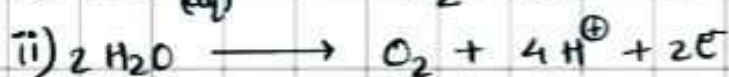
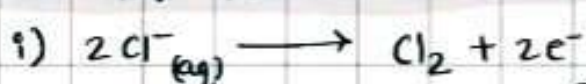
Reduction half at cathode



Standard Reduction Potential

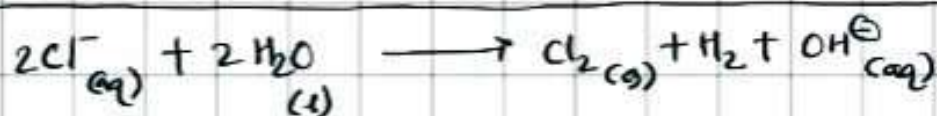
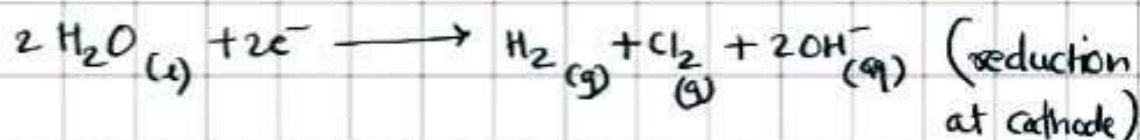
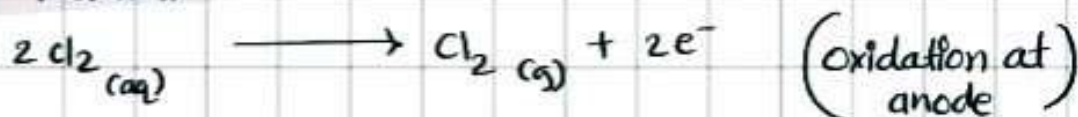
SRP of water is higher than Na^+
 \therefore there is redⁿ of H_2O at cathode

Oxidation half reaction at anode



Cl^- greater tendency to get oxidised

Overall cell reaction



Results of electrolysis of aq NaCl

- (i) H_2 gas liberated at cathode
- (ii) Cl_2 gas released at anode
- (iii) Na^+ ions and OH^- ions remain unreacted
 \therefore solution become alkaline (NaOH)

Quantitative aspects of electrolysis

(i) calculation of quantity of electricity passed

$$Q = I \times t$$

$$\begin{array}{c} \text{units} \rightarrow C = AS \rightarrow \text{Seconds} \\ \downarrow \quad \quad \downarrow \\ \text{Coulomb} \quad \text{Ampere} \end{array}$$

(ii) calculation of moles of Electrons passed

$$= \frac{Q \text{ (C)}}{96500 \text{ (C/mol } e^-)}$$

(iii) calculation of moles of product formed

$$\begin{aligned} &= \frac{Q}{96500} \times \text{mole ratio} \\ &= \frac{I \times t}{9600} \times \text{mole ratio} \end{aligned}$$

$$\begin{aligned} &\text{mole ratio} \\ &= \frac{\text{moles of product formed}}{\text{moles of } e^- \text{ required}} \end{aligned}$$

(iv) calculation of mass of product

Mass of product

$$(w) = \text{Moles of product} \times \text{Molar mass of product}$$

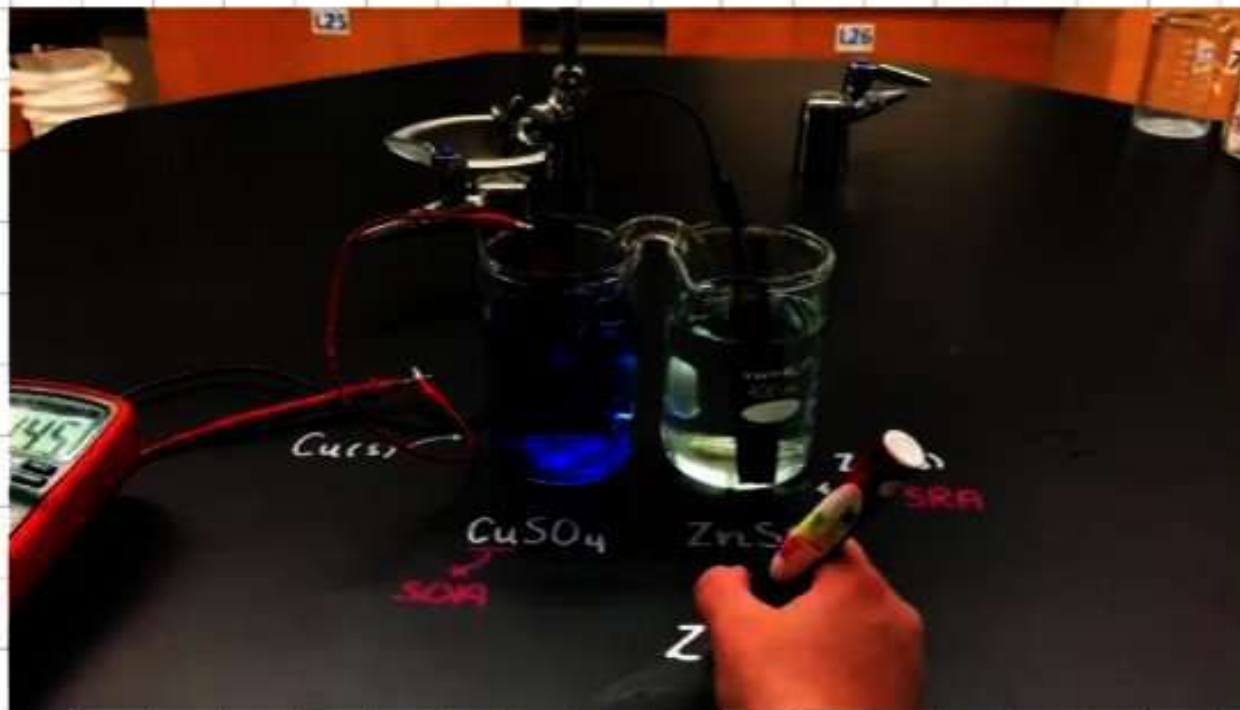
∴

$$= \frac{I \times t}{96500} \times \text{mole ratio} \times \text{Molar Mass of product}$$

⇒ Electrolytes are connected in series

$$\frac{w_1}{(\text{mole ratio})_1 \times M_1} = \frac{w_2}{(\text{mole ratio})_2 \times M_2}$$

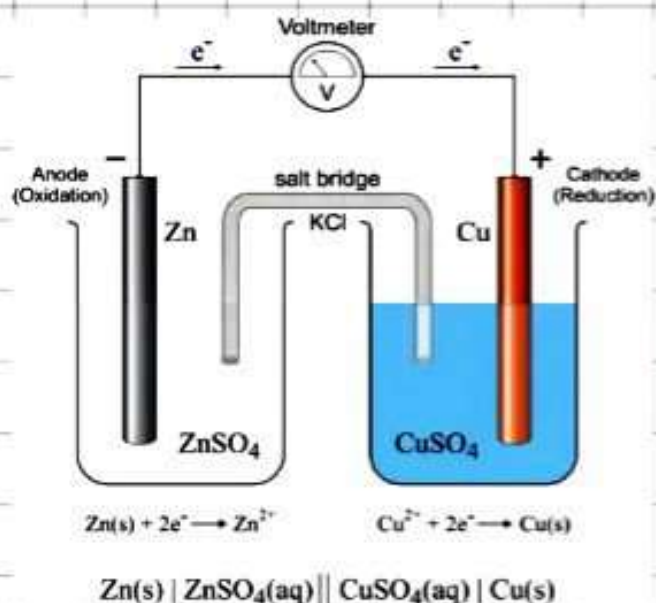
Galvanic or Voltaic cell



Salt bridge:- It is a U-shape tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 & 5% agar solution

Function of the salt bridge

- i) It provides an electrical contact between two solutions & complete the electrical circuit
- ii) It prevents mixing of two solutions
- iii) It maintains electrical neutrality in both the solutions by transfer of ions

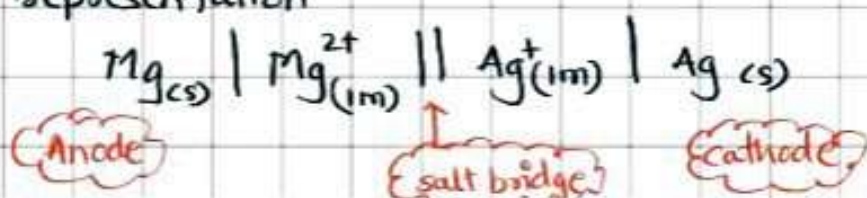


Formation or short notation of galvanic cell

- ① The metal electrode or the inert electrodes are denoted by vertical lines placed at the end of the formula or short notation
 \leftarrow extreme left $\left[\text{Anode} \right] (-)$ extreme Right \rightarrow $(\text{cathode}) (+)$
- ② The insoluble species or gases are placed in the interior position adjacent to the metal electrode.
- ③ The aq solⁿ of ions placed at the middle of the cell formula.
- ④ A single vertical line between two phases indicates the phase boundary. It indicates the direct contact between them.
- ⑤ A double vertical line betⁿ two solⁿ indicates that they are connected by salt bridge.
- ⑥ The additional information such as concentration, phases etc also given.
- ⑦ Single half cell is written in the order
 \rightarrow aq solⁿ of Pn 1st then solide electrode
 eg:- $\text{Zn}^{2+} (1\text{M}) \mid \text{Zn} (s)$

eg:- of short notation of galvanic cell

- ① two half cells are a) $\text{Mg}^{2+} (1\text{M}) \mid \text{Mg} (s)$ b) $\text{Ag}^{+} (1\text{M}) \mid \text{Ag} (s)$
 cell representation



writing of cell reaction

best with examples

Electrode potential & cell potential

Electrode potential - potential difference established due to electrode half reaction occurring at the electrode surface, is the electrode potential.

Overall cell potential (E_{mf}) (Electromotive Force)
the contribution of each electrode or
algebraic sum of the electrode potential

$$E_{cell} = E_{(oxi)}^{anode} + E_{(Red)}^{cathode}$$

Standard potential [E°]

Standard condition 1 M concentration
1 atm pressure

$$E_{cell}^\circ = E_{(anode)}^{oxi} + E_{(cathode)}^{red}$$

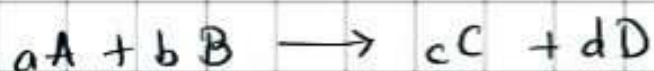
According to the IUPAC Standard Electrode potential is taken as Standard Reduction potential [SRP]

$$\therefore E_{cell}^\circ = -E_{anode}^\circ + E_{cathode}^\circ$$

$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$

This formula is used
to calculate cell potential
[emf] of standard cell.

Dependence of cell potential on concentration # (Nernst equation)



The cell voltage is given by

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$
$$= E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

at 25°C

$$\frac{2.303 RT}{F} = 0.0592$$

$F = \text{Faraday} = 96500 \text{ C}$

$R = \text{gas const} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$T = \text{temp in } ^{\circ}\text{K} \text{ i.e. in } ^{\circ}\text{C} + 273$

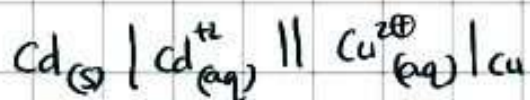
$n = \text{no. of moles of } e^{-}$

$$\therefore E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

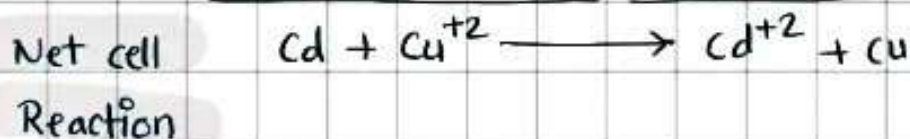
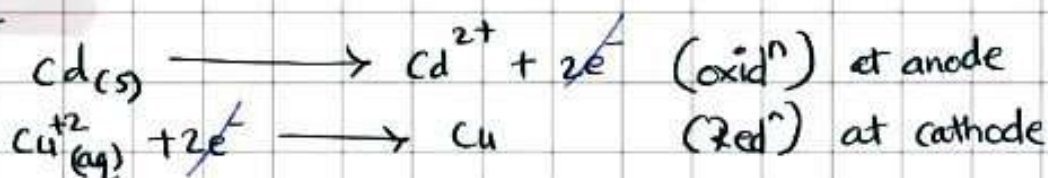
If con. of reactant and product is (1 M) then,
 $E_{\text{cell}} = E_{\text{cell}}^{\circ}$

If con is not standard then
Emf of cell can be calculated
by Nernst equation

(i) Calculation of cell potential



cell reaction



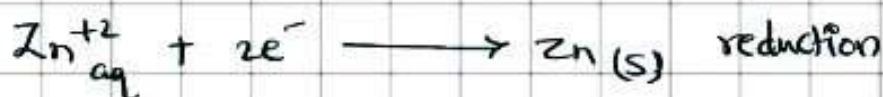
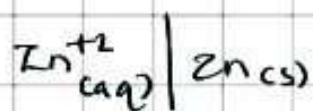
$$n = 2$$

\therefore

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{2} \log_{10} \frac{[\text{Cd}^{2+}]}{[\text{Cu}^{2+}]}$$

Concentration of solid & pure liq.
are taken to be unity (1)

(ii) calculation of Electrode potential



$$E_{\text{Zn}} = E^{\circ}_{\text{Zn}} - \frac{0.0592}{2} \log_{10} \frac{1}{[\text{Zn}^{2+}]}$$

$$= E^{\circ}_{\text{Zn}} + \frac{0.0592}{2} \log_{10} [\text{Zn}^{2+}]$$

Thermodynamics of galvanic cell

Gibbs energy of cell reaction and cell potential

Electrical work = amount of charge passed \times cell potential $[E_{\text{cell}}]$

$$\text{charge passed} = nF \quad \therefore = nF E_{\text{cell}}$$

But

$$\text{Electrical Energy} = -\Delta G$$

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

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

at standard $\Delta G^\circ = -nF E_{\text{cell}}^\circ$

extensive

intensive

Standard cell potential & equilibrium constant

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

$$\text{But } \Delta G = -RT \ln K$$

$$\therefore -nF E_{\text{cell}}^\circ = -RT \ln K$$

$$nF E_{\text{cell}}^\circ = RT \ln K$$

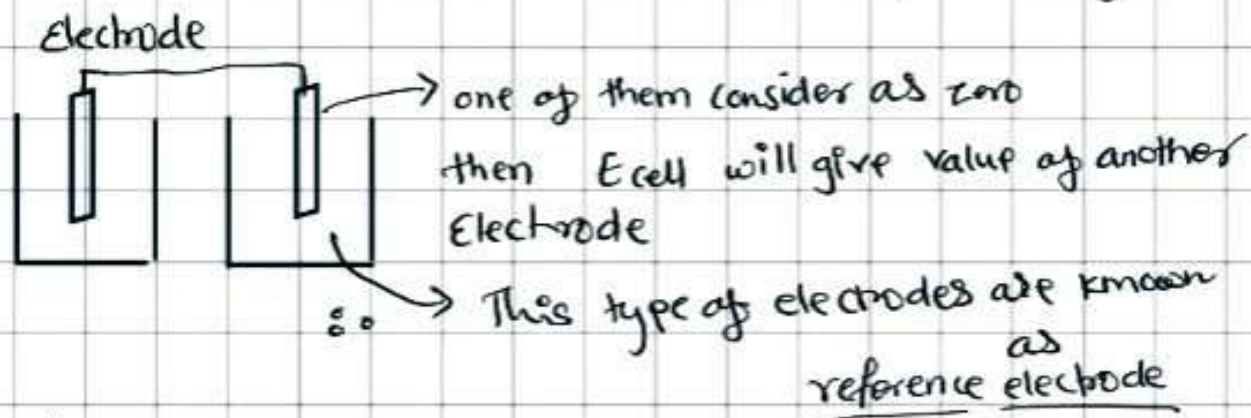
$$E_{\text{cell}}^\circ = \frac{RT}{nF} \ln K$$

$$= \frac{2.303 RT}{nF} \log_{10} K \quad \text{But } \frac{2.303 RT}{F} = 0.0592$$

$$\therefore E_{\text{cell}}^\circ = \frac{0.0592}{n} \log_{10} K$$

Reference Electrode

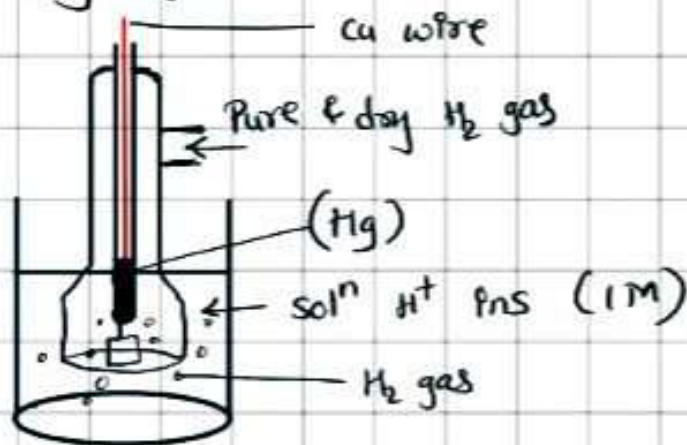
it is used to calculate the potential of the



eg \rightarrow

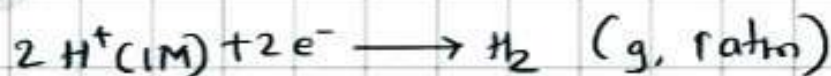
① Standard Hydrogen Electrode (SHE)

Construction



Formulation $H^+(1M) | H_2(g)(1atm) | Pt$

Electrode reaction

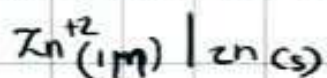


$$E^{\circ}_{H_2} = 0.000V$$

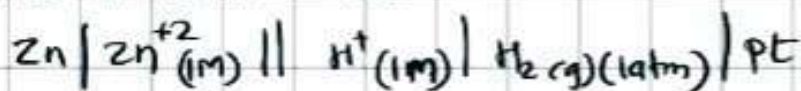
Application of SHE

SHE is used as a reference electrode

For eg:- determine the standard potential of



combine it with SHE

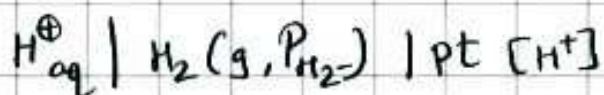


$$E^{\circ}_{\text{cell}} = E^{\circ}_{H_2} - E^{\circ}_{Zn} \quad \text{But } E^{\circ}_{H_2} = 0 \quad \therefore E^{\circ}_{\text{cell}} = -E^{\circ}_{Zn}$$

Difficulties

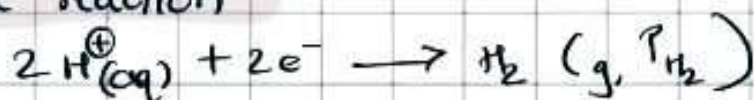
- ① difficult to obtain pure & dry Hydrogen
- ② pressure cannot be maintain 1 atm
- ③ con. of solⁿ cannot be exactly 1 M

Hydrogen gas Electrode



$P_{\text{H}_2} \rightarrow$ Pressure of Hydrogen gas P_{H_2} not ① which means it is not standard.

Electrode reaction



$$E_{\text{H}_2} = E^\circ_{\text{H}_2} - \frac{0.0592}{2} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$
$$= 0 - \frac{0.0592}{2} \log_{10} \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

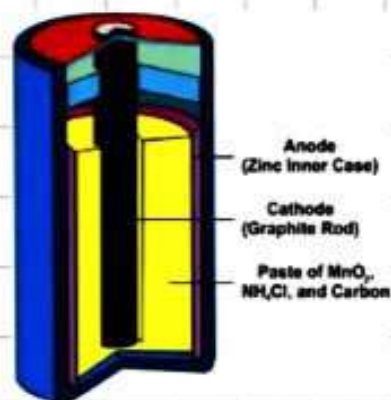
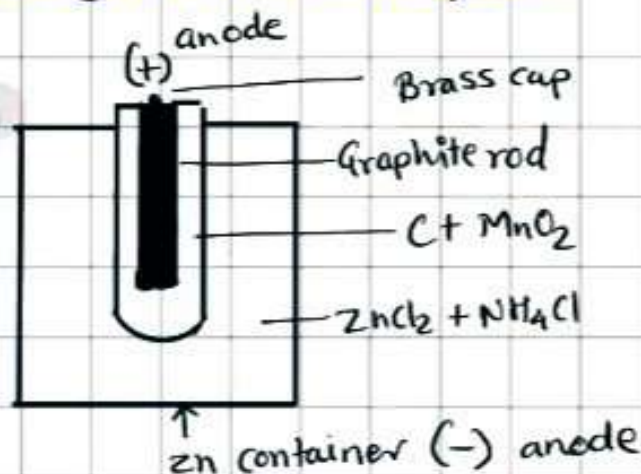
$$E^\circ_{\text{H}_2} = 0 \text{ V}$$

Galvanic cells useful in day to day life

- Types
- ① primary voltaic cell :- cannot be recharged
eg- dry cell
 - ② Secondary voltaic cell :- can be recharged
while recharge they will act as Electrolytic cell

① Dry cell (Leclanche' cell)

Construction

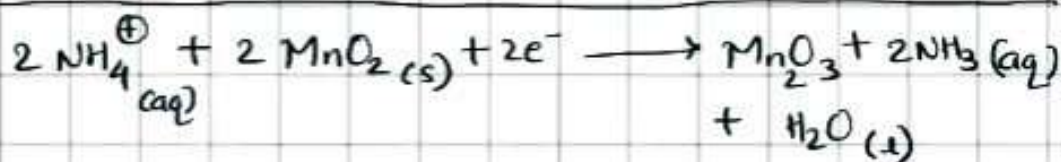
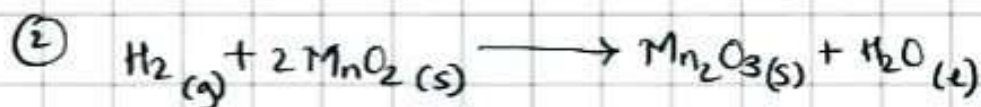
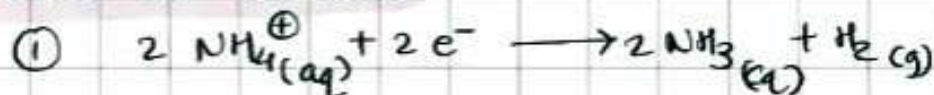


Cell reaction

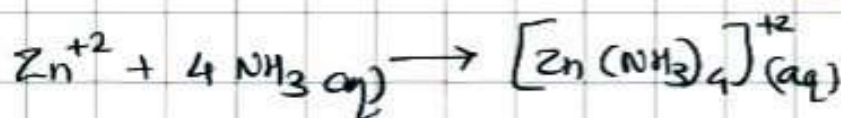
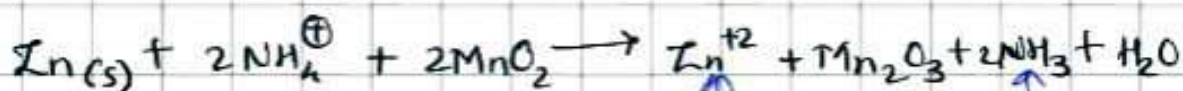
(A) oxidation at anode



(B) Reaction at cathode



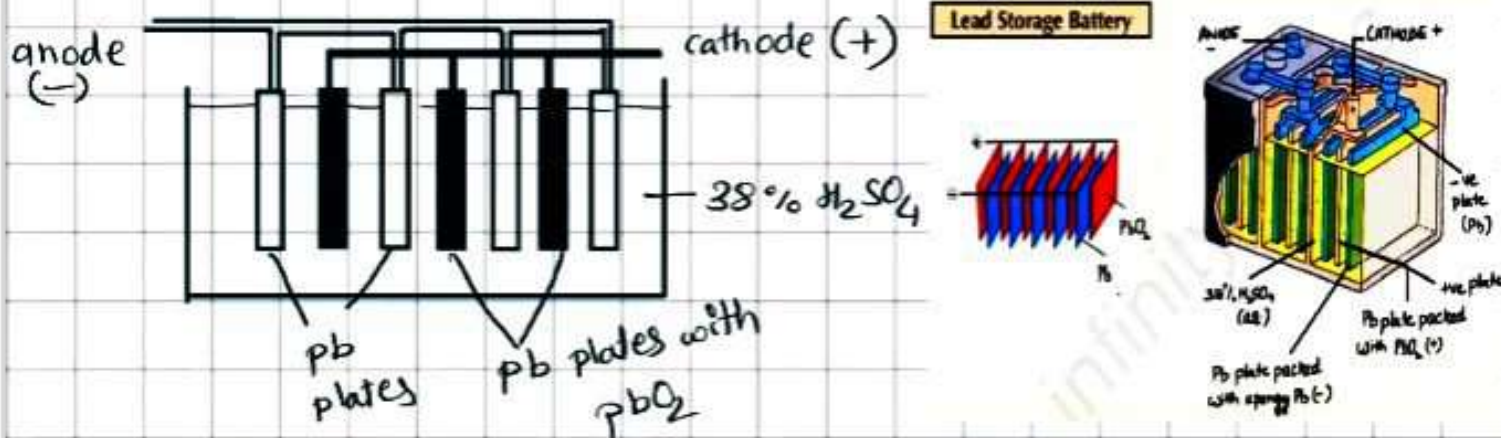
(C) Net cell reaction



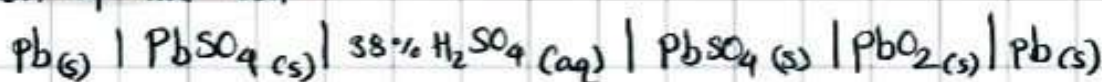
use of dry cell :-

Source of power in flashlight, portable radio tape recorders etc.

Lead storage battery (lead accumulator)

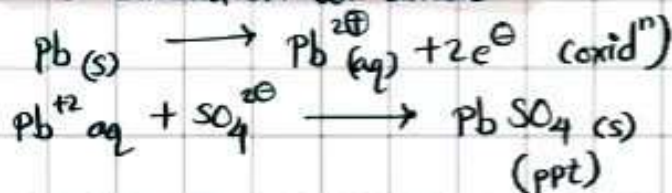


Notation of the cell

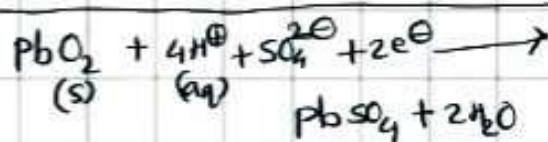
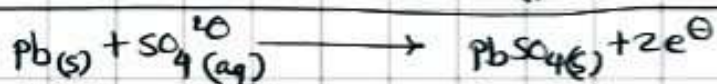
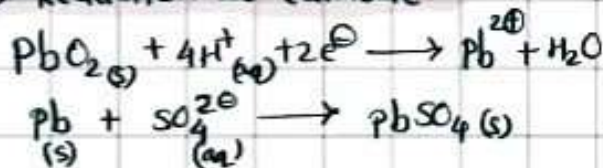


(A) Cell reaction during discharge

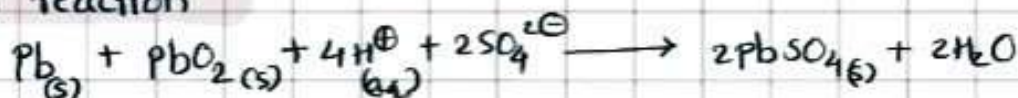
a) oxidation at anode



b) Reduction at cathode



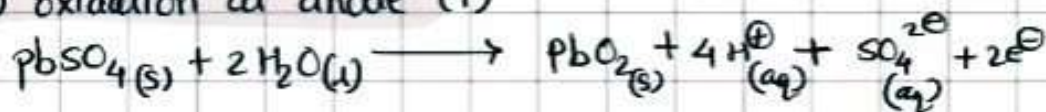
Net cell reaction



(B) Cell Reaction during recharge

During recharge cell function as electrolytic cell

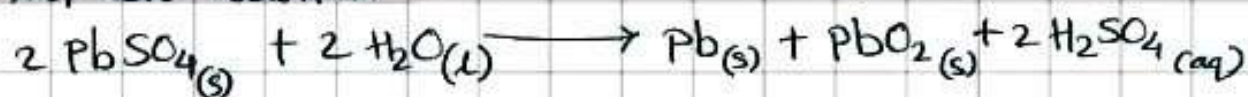
(a) oxidation at anode (+)



(b) Reduction at cathode (-)



(c) Net cell reaction



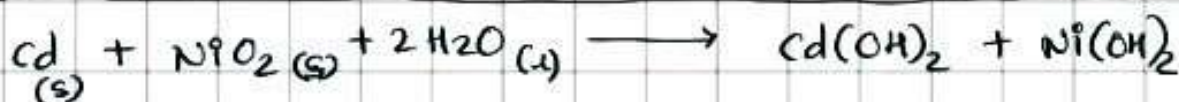
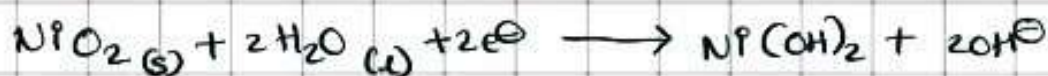
Applications of lead accumulator

- 1) used as source of direct current in the laboratory
- 2) a 12V lead storage battery constructed by connecting six 2V cells in series is used in automobiles & inverters

Nickel-Cadmium or NICAD storage cell

⇒ it is secondary cell ⇒ cathode is Ni(IV) oxide
Anode is Cd-metal

Cell Reaction



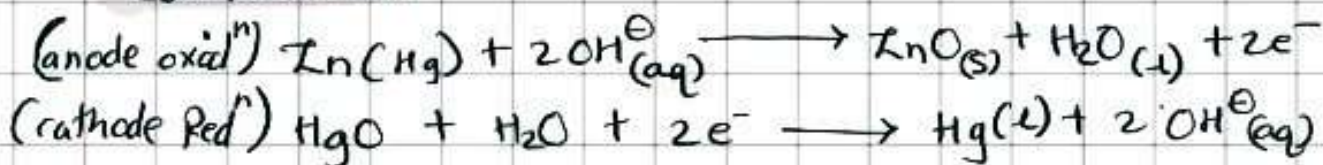
uses: - longer life than other dry cell
used in watches, calculators etc.

Mercury battery

⇒ secondary cell

⇒ zinc (Zn) anode
Carbon + Hg Cathode

Cell Reaction



Fuel cell

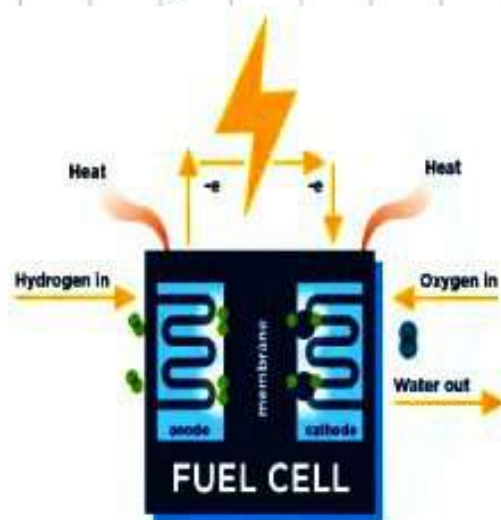
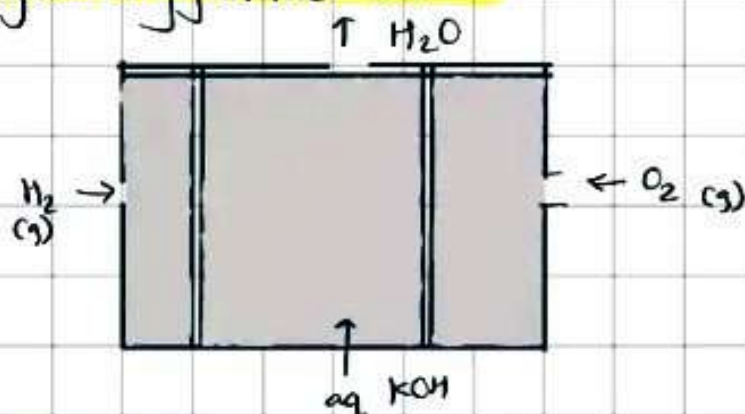
Function is based on combustion reaction are redox type & can be used to generate electricity.

⇒ one of the reactant is fuel & other is reactant such as O_2 , is oxidant

eg:- Hydrogen-oxygen fuel cell

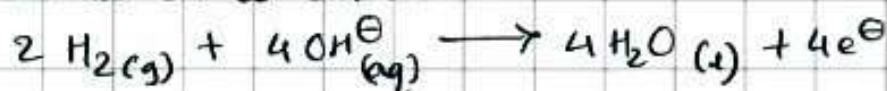
⇒ fuel is hydrogen (H_2) gas.

Hydrogen-oxygen fuel cell

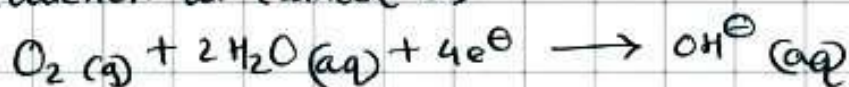


Cell Reaction

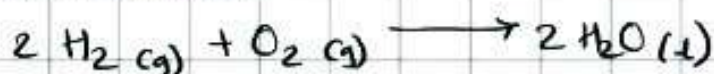
(i) oxidation at anode (-)



(ii) Reduction at cathode (+)



(iii) Net cell reaction



Advantages of fuel cell

- (1) they are nonpolluting as the only reaction product is H_2O
- (2) provides electricity with high efficiency (70%)

- (3) the reacting substance is continuously supplied
 ∴ not have to be discarded on consuming of chemicals

Drawbacks of fuel cell

H_2 gas is hazardous & preparation cost is high

- Applications :- ① experimental basis in automobiles
 ② For electrical power in space programme

Electrochemical series

Sr. No.	Electrode	Reduction Half reaction Oxidising agent → Reducing agent	E^0 (volts) At 25
1	$F^- F_2 Pt$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87
2	$Au^+ Au$	$Au^+ + e^- \rightarrow Au$	+1.68
3	$Ce^{4+}, Ce^{3+} Pt$	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
4	$Au^{3+} Au$	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
5	$Cl^- Cl_2 Pt$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
6	$Pt^{2+} Pt$	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20
7	$Br^- Br_2 Pt$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
8	$Hg^{2+} Hg$	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.854
9	$Ag^+ Ag$	$Ag^+ + e^- \rightarrow Ag$	+0.799
10	$Hg_2^{2+} Hg$	$Hg_2^{2+} + 2e^- \rightarrow Hg_2$	+0.790
11	$Fe^{3+}, Fe^{2+} Pt$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771
12	$I^- I_2(s) Pt$	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
13	$Cu^{2+} Cu$	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
14	$Pt Hg Hg_2Cl_2 Cl^-$	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.242
15	$Ag AgCl(s) Cl^-$	$AgCl + e^- \rightarrow Ag + Cl^-$	+0.222
16	$Cu^{2+} Cu^+$	$Cu^{2+} + e^- \rightarrow Cu^+$	+0.153
17	$Sn^{4+}, Sn^{2+} Pt$	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	-0.15
18	$H^+ H_2 Pt$	$2H^+ + 2e^- \rightarrow H_{2(g)}$	0.0 (Definition)
19	$Pb^{2+} Pb$	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
20	$Sn^{2+} Sn$	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.136
21	$Ni^{2+} Ni$	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.257
22	$Co^{2+} Co$	$Co^{2+} + 2e^- \rightarrow Co$	-0.280
23	$Cd^{2+} Cd$	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
24	$Fe^{2+} Fe$	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.440