Electrochemistry.

→ It is the branch of chemistry which deals with the study of reactions carried out with the help of electric current or electrical changes carried out by chemical reaction.

Types of electrochemical cell :-

① Electrolytic cell.

→ Cell which can convert electrical energy into chemical energy is called as electrolytic cell.

② Galvanic/voltaic cell

→ Electrochemical cell which can convert chemical energy into electrical energy is called as voltaic cell.

⊛ Single electrode potential.

→ When metal rod is dipped in it's salt sol^n (electrolytic sol^n), metal ion will collide with electrode (metal). After collision between metal ion and metal electrode as

i) Nothing will happen

ii) Metal ion may gain electron from metal surface and reduced to metal atom. During this process, +ve charge is developed on metal electrode.

iii) Metal atom from surface of electrode may lose electron and oxidized to metal ion.

and metal atom become -ve charged.

$M \longrightarrow M^+ + e^-$

i.e. when metal electrode is dipped in electrolytic soln, charge is developed on electrode due to oxidation or reduction.

- Charged electrode is surrounded by oppositely charged ion. Thus potential difference is developed in electrode soln interface which is called as electrode potential.

- There are two types of electrode potential and they are :-

(i) Oxidation potential

- Tendency of element to be oxidized is called as oxidation potential.

(ii) Reduction potential.

- Tendency of element to be reduced is called as reduction potential.

- For an element, oxidation and reduction potential are equal but opposite in sign.

eg. $Zn \longrightarrow Zn^{2+} + 2e^-$: $E^\circ = 0.76V$

$Zn^{2+} + 2e^- \longrightarrow Zn$: $E^\circ = -0.76V$

- Generally reduction potential is used as electrode potential.

(*) Standard electrode potential (E°).

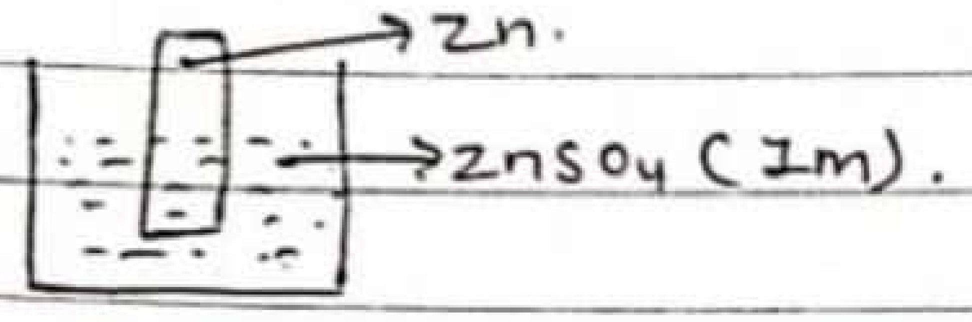
→ Electrode potential determined at 25°C temp., 1atm pressure and 1 M concentration (standard condition) is called as Standard electrode potential.

→ It is denoted by E°.

eg. $E^\circ_{Zn^{++}/Zn} = -0.76$ V.

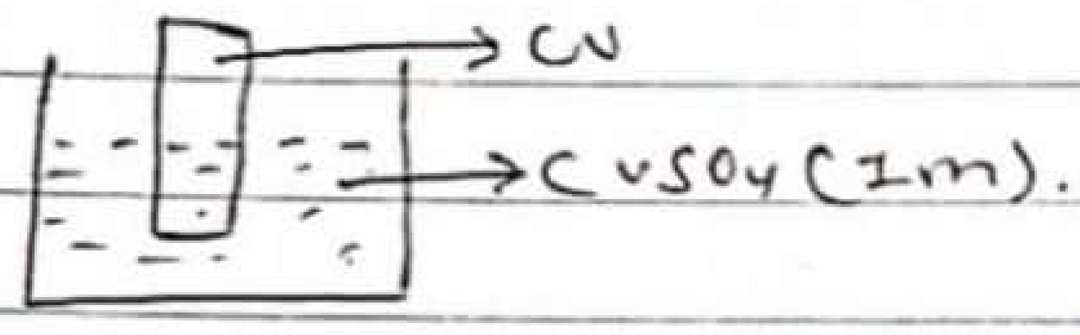
$E^\circ_{Cu^{++}/Cu} = 0.34$ V.

- Electrode in combination with electrolytic solⁿ is called as electrode half cell.
- In cathode half cell, always reduction occurs and rxⁿ is called cathodic rxⁿ.
- In anode half cell, always oxidation occurs and rxⁿ is called anodic rxⁿ.



Anode

$Zn \longrightarrow Zn^{++} + 2e^-$



Cathode.

$Cu^{++} + 2e^- \longrightarrow Cu.$

(*) Notation.

Reactant | product.

$Zn(s) \longrightarrow Zn^{++} + 2e^-$

$Zn \mid Zn^{++}(1M).$

$Cu^{++} + 2e^- \longrightarrow Cu(s).$

$Cu^{++}(1M) \mid Cu(s)$

$H_2(g) \longrightarrow 2H^+ + 2e^-$

$H_2(g) \mid H^+$

Factors Affecting electrode potential.

1). Nature of Metal
→ Metal which can be easily oxidized posses smaller value of electrode potential. whereas metal which can be easily reduced posses higher value of electrode potential.

2). Concentration.
→ Electrode potential of metal decreases with increase in conc. of electrolytic soln.

3). Temperature.
→ Electrode potential increases with increase in Temp.

Nernst Equation:
→ Variation of electrode potential with temp. and pressure is given by Nernst Equation.
Mathematically, it is written as,

$$E = E^\circ - \frac{2.303RT}{nf} \log K$$

E = electrode potential.
E° = Standard " "
R = 8.314 $JK^{-1} mol^{-1}$
T = Temp. in 'K'
n = no. of electron.
f = 96500 C
K = equilibrium constant.

At 25°C, T = 298 K.

$$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} . \log K$$

$$\therefore \quad E = E^\circ - \frac{0.0591}{n} \log K$$

Refrence Electrode.

- Electrode whose standard electrode potential is known and used to determine standard electrode potential of other electrode is called as reference electrode.
- Reference electrode can acts as both cathode and anode according to the condition.
- There are two types of reference electrode. They are:-

① primary reference electrode.

- Reference electrode whose electrode potential is arbitarily fixed is called as 1° reference electrode.

Eg. Normal or standard Hydrogen electrode (NHE/SHE).

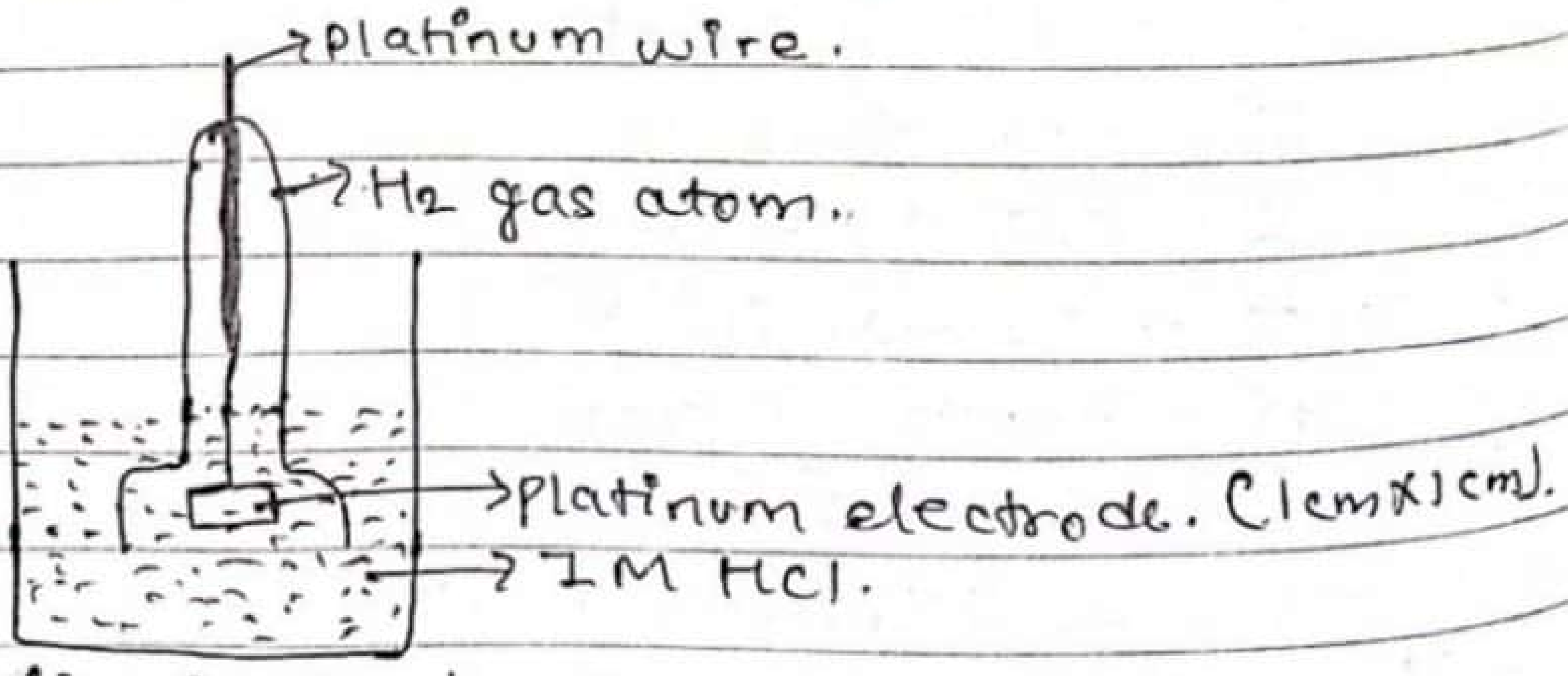


fig: SHE at 25°C

- Standard Hydrogen electrode consist platinum electrode dipped in 1M HCl solution at 25°C.
- platinum electrode is connected with platinum wire. Hydrogen gas at 1atm pressure is continuously bubbled in.
- According to condition, SHE can act as both cathode and anode

If SHE acts as cathode,
cathodic rxn becomes,

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2$$

Notation :- $H^+(1M) \mid H_2(g, 1atm), Pt$

If SHE acts as anode,
Anodic reaction becomes,

$$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$$

$Pt, H_2(g, 1atm) \mid H^+(1M)$.

- Standard electrode potential of Hydrogen is fixed as 0V.
i.e. $E^\circ_{H^+/H_2} = 0V$

② Secondary reference Electrode.
- Reference electrode whose standard electrode potential is determined with help of Primary reference electrode is called as secondary reference electrode.
Eg. Calomel electrode.

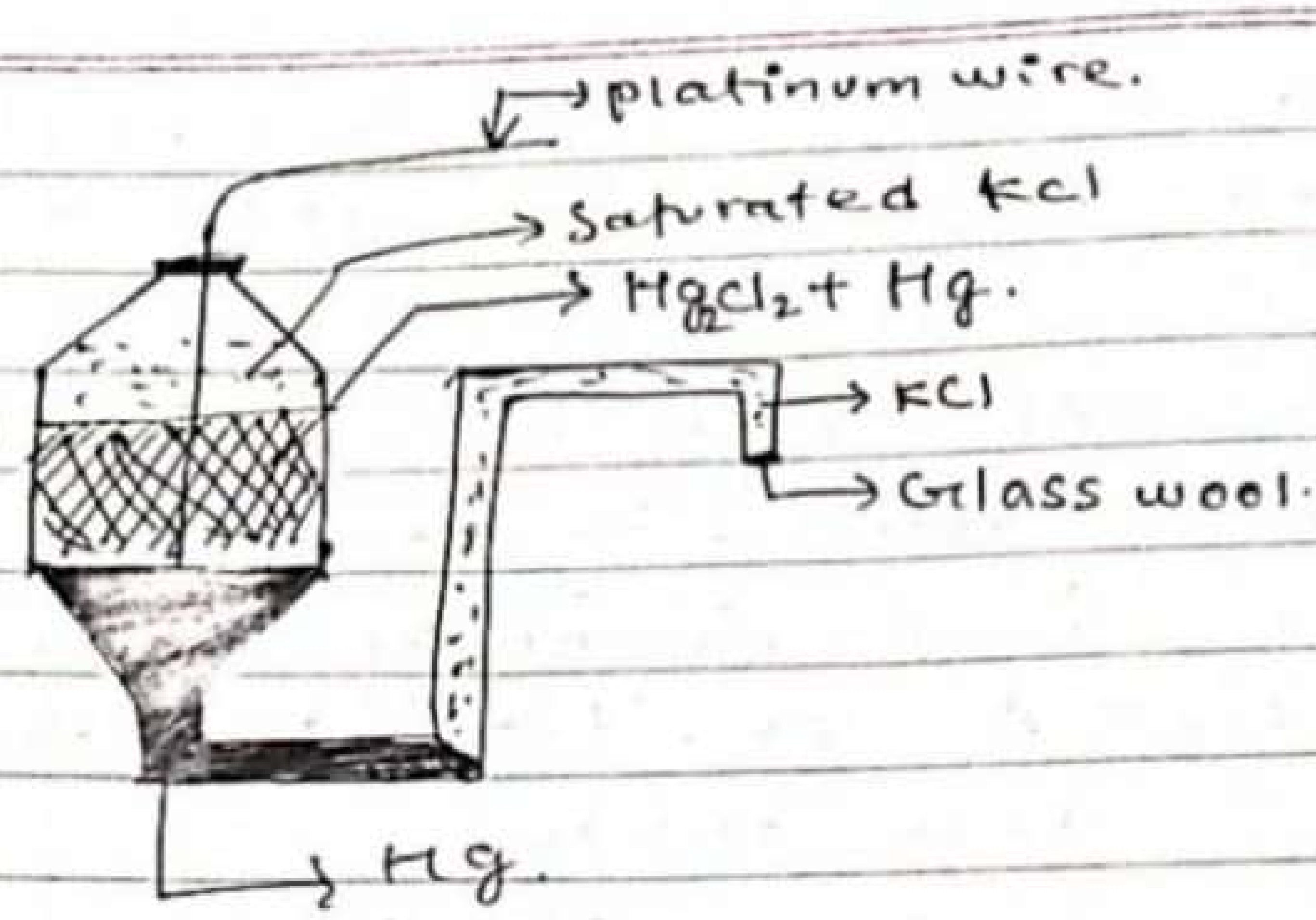


fig: Calomel electrode.

Notation:

cathode:- $Cl^- | Hg_2Cl_2(s) | Hg(l), Pt$

Anode: $Pt, Hg(l) | Hg_2Cl_2(s) | Cl^-$

- Calomel electrode is 2° reference electrode.
- It consist of three layers.
- Bottom layer is occupied by mercury, above mercury paste of calomel and mercury is placed.
- Upper layer is occupied by solⁿ of potassium chloride.
- platinum wire is dipped upto mercury.
- It consist of side tube which acts as salt bridge
- According to condition, calomel electrode can act as cathode and anode.
- Standard electrode potential of calomel electrode depends upon concentration of potassium chloride solution.

$E^{\circ}_{Hg_2Cl_2|Hg} = 0.33334$ V. (0.1M, KCl sol^n)

$E^{\circ}_{Hg_2Cl_2|Hg} = 0.281$ V (1M, KCl sol^n).

$E^{\circ}_{Hg_2Cl_2|Hg} = 0.247$ V (Saturated KCl sol^n)

Galvanic cell.

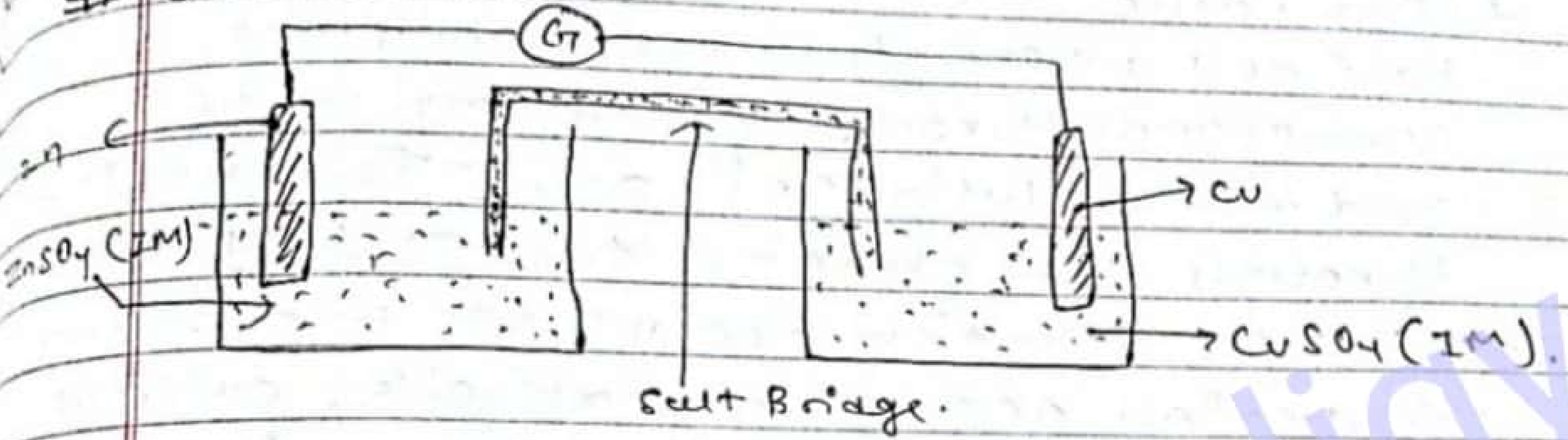


fig: Galvanic cell.

<u>Anodic Reaction:</u>

$Zn \longrightarrow Zn^{++} + 2e^-$

Anode Half cell:- $Zn(s) | Zn^{++}(1M)$.

<u>Cathodic Reaction:-</u>

$Cu^{++} + 2e^- \longrightarrow Cu$

Cathode Half cell:- $Cu^{++}(1M) | Cu(s)$.

<u>Net cell Rxn:</u>

$Zn \longrightarrow Zn^{++} + 2e^-$

$Cu^{++} + 2e^- \longrightarrow Cu$

$Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$

$E^\circ_{Hg_2Cl_2|Hg} = 0.3334\ V$. (0.1M, KCl soln)

$E^\circ_{Hg_2Cl_2|Hg} = 0.281\ V$ (1M, KCl soln).

$E^\circ_{Hg_2Cl_2|Hg} = 0.247\ V$ (Saturated KCl soln).

Galvanic cell.

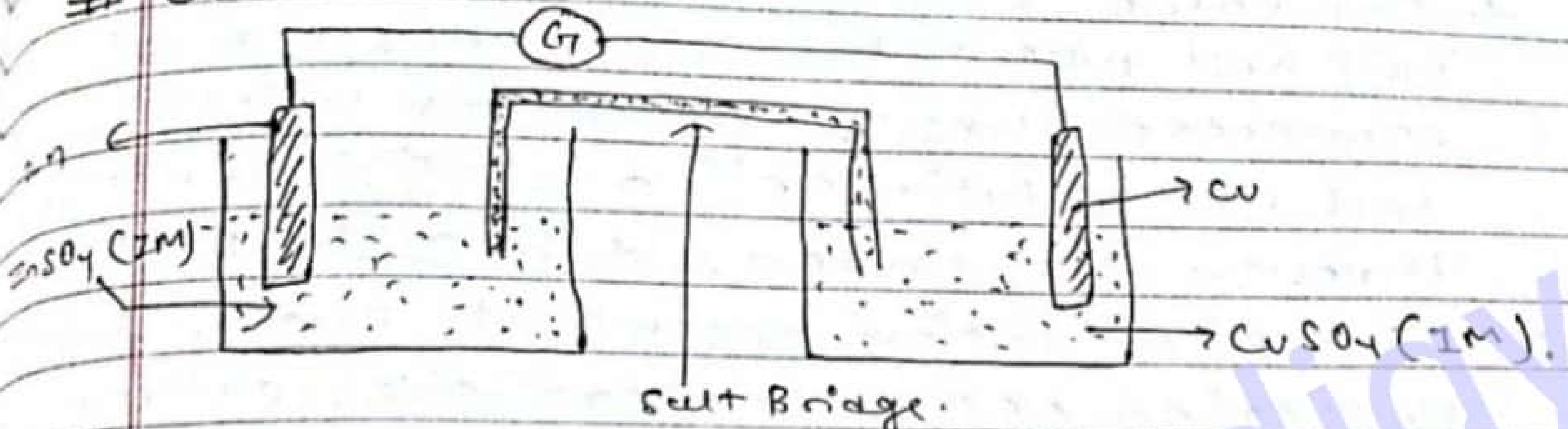


fig: Galvanic cell.

Anodic Reaction:

$Zn \longrightarrow Zn^{++} + 2e^-$

Anode Half cell:- $Zn(s)|Zn^{++}(1M)$.

Cathodic Reaction:-

$Cu^{++} + 2e^- \longrightarrow Cu$

Cathode Half cell:- $Cu^{++}(1M)|Cu(s)$.

Net cell Rxn:

$Zn \longrightarrow Zn^{++} + 2e^-$

$Cu^{++} + 2e^- \longrightarrow Cu$

$Zn + Cu^{++} \longrightarrow Cu + Zn^{++}$

Cell Notation:-

Anode half cell || cathode Half cell.

$Zn(s) | Zn^{++}(1M) || Cu^{++}(1M) | Cu(s)$.

- Electrochemical cell which convert chemical energy into electrical energy.
- Galvanic cell consist of two electrode half cell where two electrodes are connected through conductor wire and electrolytic sol^n are connected through U-shaped tube/salt bridge. (called as)
- Always oxidation occurs at Anode and Reduction occurs at cathode, cathode is +vely charged and anode is -vely charged.

(*) Salt Bridge

- Salt bridge is U-shaped tube filled with electrolytic sol^n supported by Agar Agar gel.
- Generally, KCl, KNO_3, NH_4NO_3 are used in salt bridge.
- Salt bridge completes the ~~electroly~~ circuit in galvanic cell and prevents intermixing of two electrolytic sol^n.

Cell potential (EMF of cell).

- Cell potential / EMF of cell is defined as the difference of electrode potential between two electrode half cell.
- Cell potential is given by

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

Q. $Zn + Cu^{++}(1M) \rightleftharpoons Zn^{++}(1M) + Cu$

Write cell notation for given redox rx^n and calculate standard cell potential

[Given $E^{\circ}_{Zn^{++}/Zn} = -0.76$ and $E^{\circ}_{Cu^{++}/Cu} = 0.74\,V$]

Sol^n:- cell notation : $Zn|Zn^{++}(1M)||Cu^{++}(1M)|Cu$

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{Anode}$

$= E^{\circ}_{Cu^{++}/Cu} - E^{\circ}_{Zn^{++}/Zn}$

$= 0.74V + 0.76\,V$

$\therefore E^{\circ}_{cell} = 1.5\,V$

Spontaneity of rx^n.

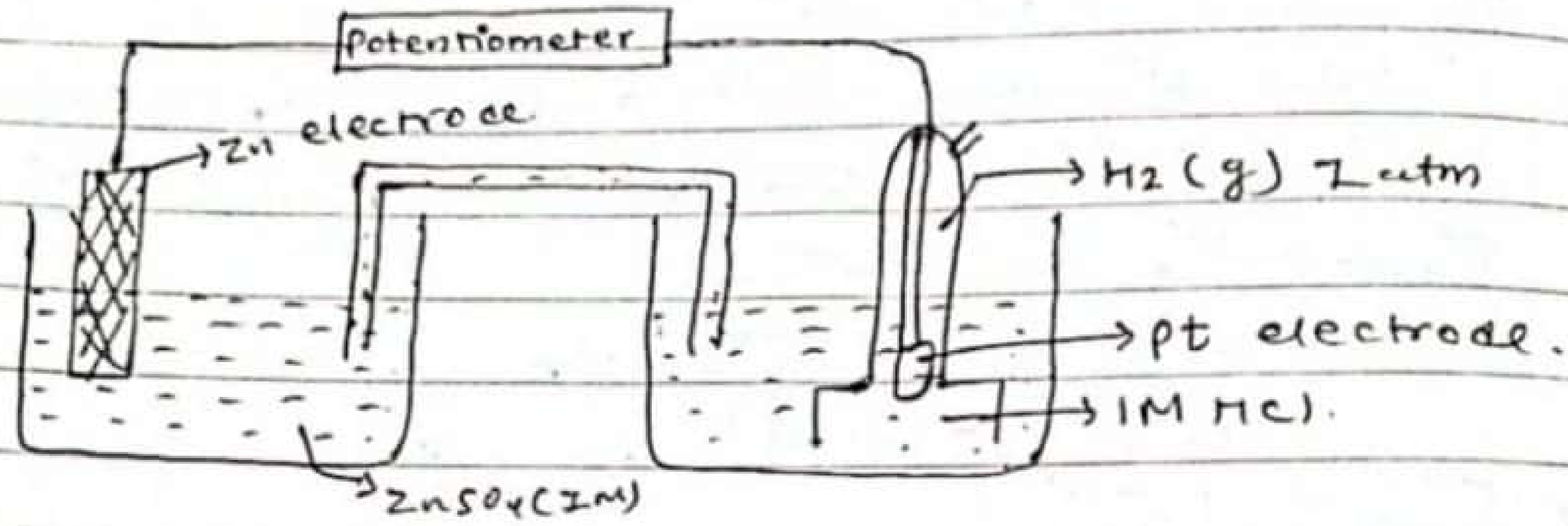
① If cell potential is +ve, given reaction is spontaneous.

② If cell potential is -ve, given redox rx^n is non-spontaneous.

③ If cell potential is 0, given redox rx^n is in equilibrium.

... reaction is

(*) Determination of standard electrode potential of zinc by using NHE.



Anodic Rxn :-

$Zn \longrightarrow Zn^{++} + 2e^-$

Anode half cell

$Zn | Zn^{++} (1M)$.

Cathodic Rxn :-

$2H^+ + 2e^- \longrightarrow H_2$

Cathode half cell

$H^+ (1M) | H_2 (g, 1 atm), pt$

Net cell Rxn:

$Zn \longrightarrow Zn^{++} + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$

$Zn + 2H^+ \longrightarrow Zn^{++} + H_2$

Cell notation :-

$Zn | Zn^{++} (1M) || H^+ (1M) | H_2 (g, 1 atm), pt$

(*) ~~SDo~~

→ In order to determine standard electrode potential of zinc, a galvanic cell is set up by using electrode half cell obtained by dipping zinc rod in 1M $ZnSO_4$ solⁿ.

and Standard Hydrogen electrode at 25°C.

Standard cell potential of constructed galvanic cell is found to be 0.76 volt.

standard cell potential.

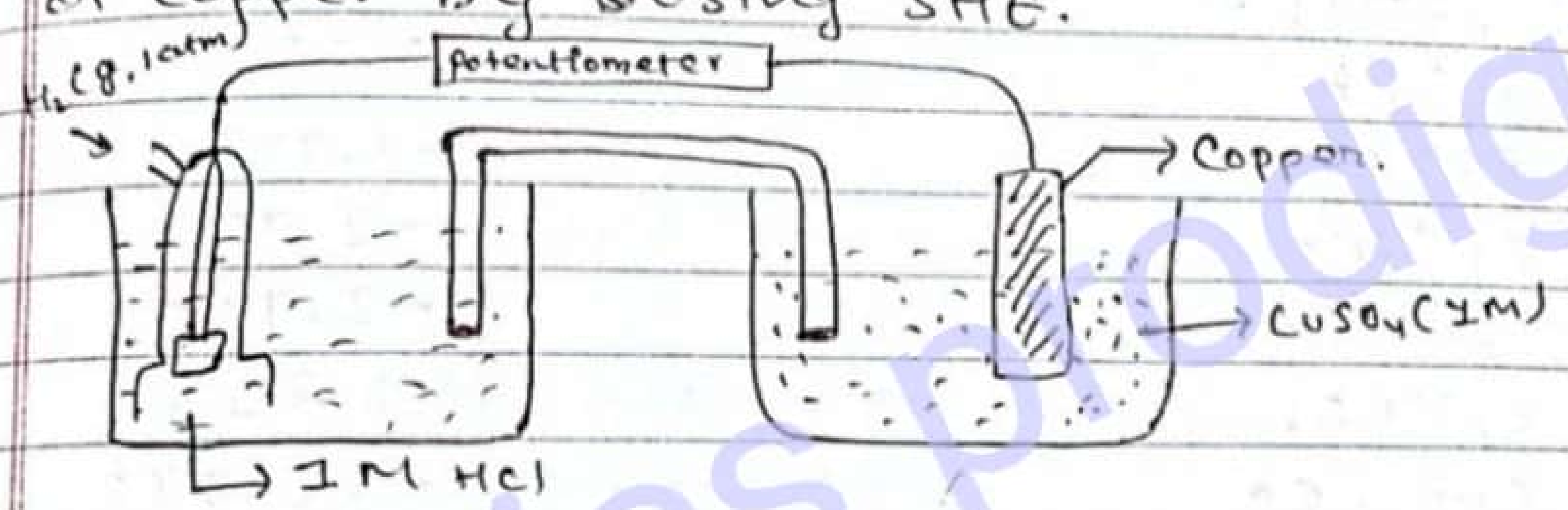
$E^\circ_{cell} = 0.76\ V$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$0.76 = 0 - E^\circ_{Zn^{++}/Zn}$

$\therefore E^\circ_{Zn^{++}/Zn} = -0.76\ V$

* Determination of standard electrode potential of copper by using SHE.



Anodic Rx^n :-

$H_2 \longrightarrow 2H^+ + 2e^-$

Anode Half cell.

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

cathodic Rx^n :-

$Cu^{++} + 2e^- \longrightarrow Cu$

Cathode half cell.

Cu^{++}(1M) | Cu

Net cell rxn :-

$H_2 \longrightarrow 2H^+ + \cancel{2e^-}$

$Cu^{++} + \cancel{2e^-} \longrightarrow Cu$

$H_2 + Cu^{++} \longrightarrow 2H^+ + Cu$

Cell Notation:-

$Pt, H_2(g, 1 atm) / H^+(1M) || Cu^{++}(1M) | Cu$

Electrochemical series.

→ When elements are arranged according to increase in their standard electrode potential, a series of elements is obtained which is called as electrochemical series.

Uses of electrochemical ~~cell~~ series :-

i) Used to compare oxidizing and reducing action of eleoments.

→ Element having smaller electrode potential is good reducing agent.

→ Element having larger standard electrode potential is good oxidizing agent.

ii) Used to select cathode and anode in galvanic cell.

→ Element having smaller value of standard electrode potential is used as anode and

→ element having higher value of E° is used as cathode.

iii) To predict whether given metal displaces hydrogen from dilute acid.

→ Element whose standard electrode potential is smaller than that of hydrogen can displace hydrogen from dilute acid.

iv) To predict whether given metal displaces another metal from it's compound

→ Metal having smaller value of E° can displace metal having higher value of standard electrode potential from it's compound.

V) To predict spontaneity of redox rxn.

→ Only those redox rxns are spontaneous in which 'E°_{cell}' of rxn is +ve.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}.$$

Types of Galvanic Cell.

① Primary cell.

→ Galvanic cell which cannot be recharged is called as primary cell.

→ Primary cell cannot be recharged because it's cell reaction cannot be reversed.

Eg. Dry cell

(*) Dry cell / Lechlanche cell.

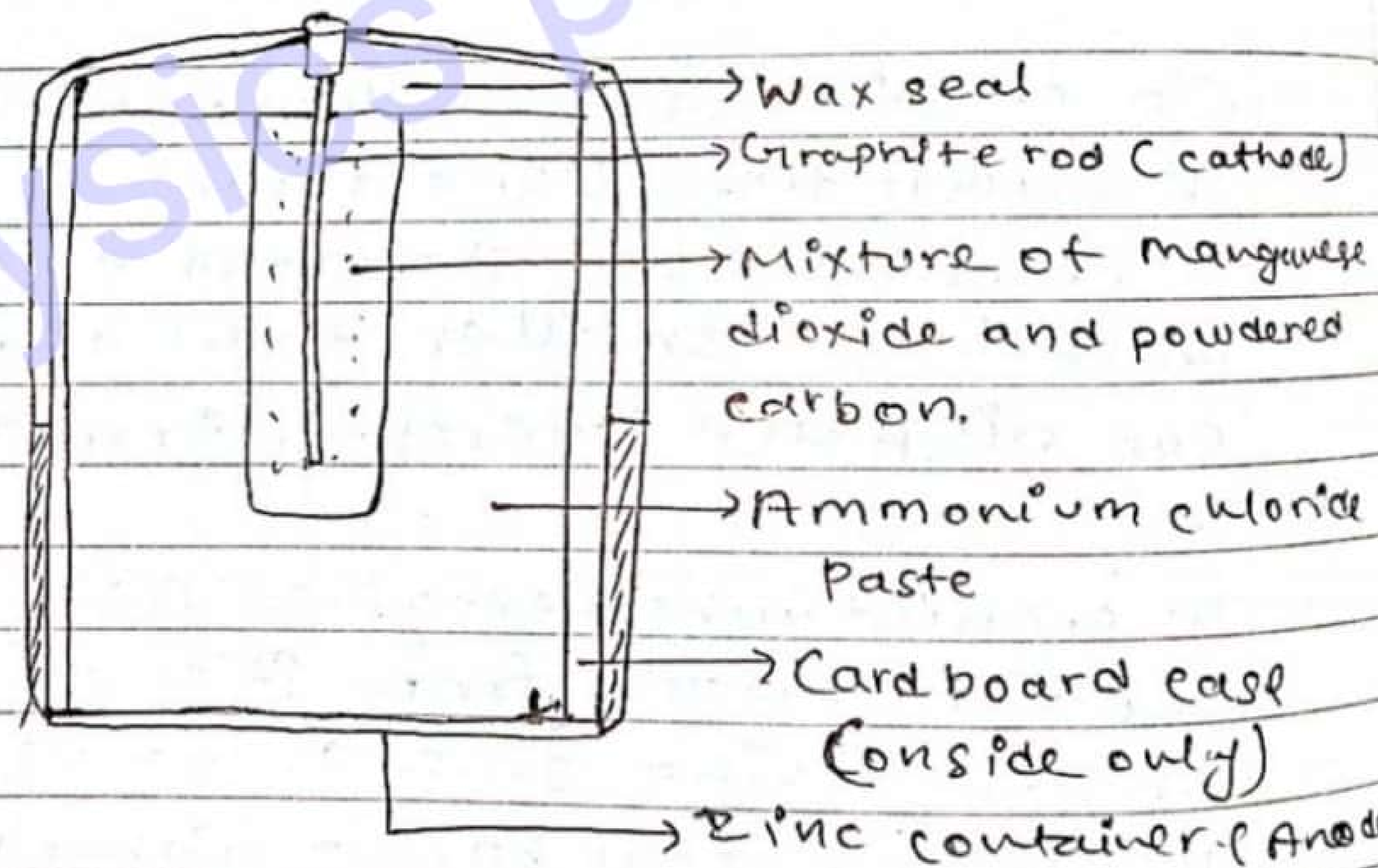


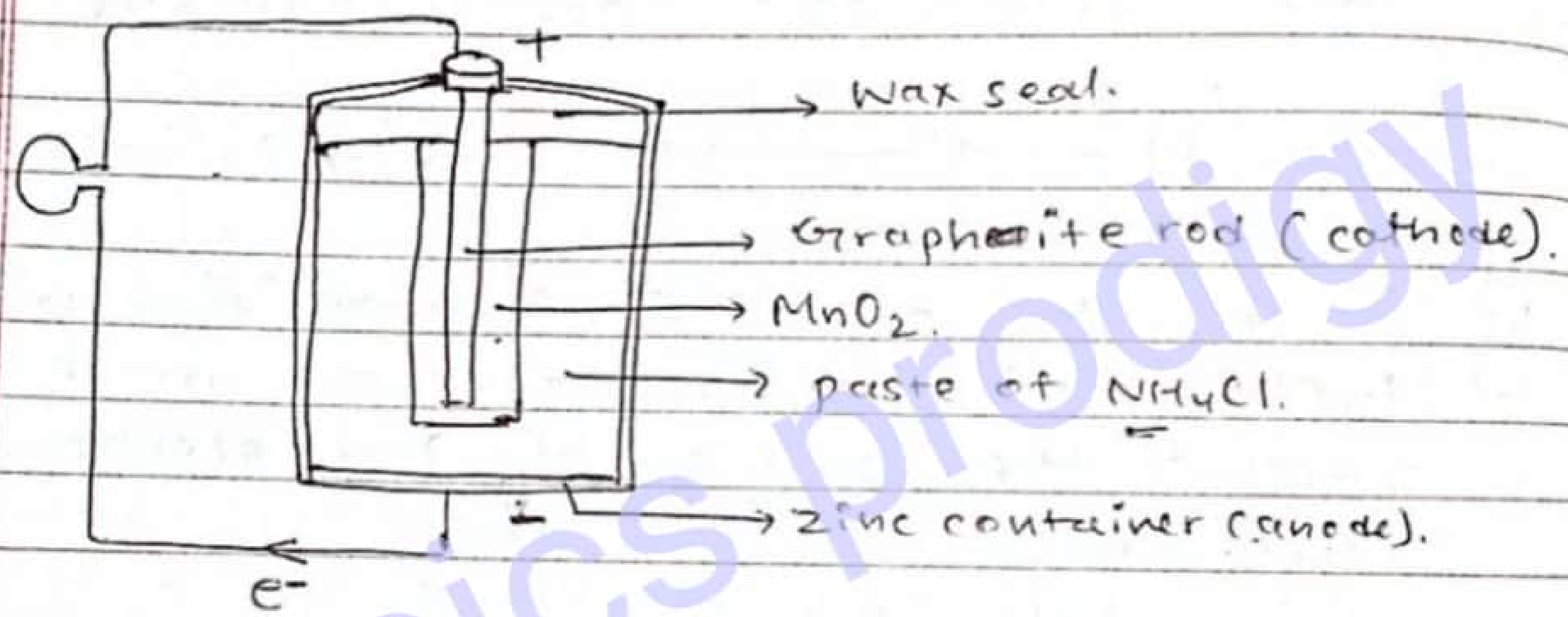
fig: Lechlanche cell

They are of two types :-

① Primary batteries.

- They cannot be recharged.
- Once these have been used, they must be discarded and net cell rxn cannot be reversed.

Dry cell / Leclanche cell.



- It consist of a negative zinc electrode, a positive graphite electrode. surrounded by MnO_2 and paste of ammonium chloride.

At anode :- $Zn \longrightarrow Zn^{2+} + 2e^-$

At cathode :-

$$2MnO_2(s) + H_2O(l) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-$$

overall rxn :-

$$Zn + 2MnO_2(s) + H_2O(l) \longrightarrow Zn^{++} + MnO_2(s) + 2OH^-$$

Secondary rxns :-

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

$Cl^- + Zn^{2+} + NH_3 \longrightarrow Zn(NH_3)_2Cl_2\ (s)$

- These rxns do not contribute in emf of cell.

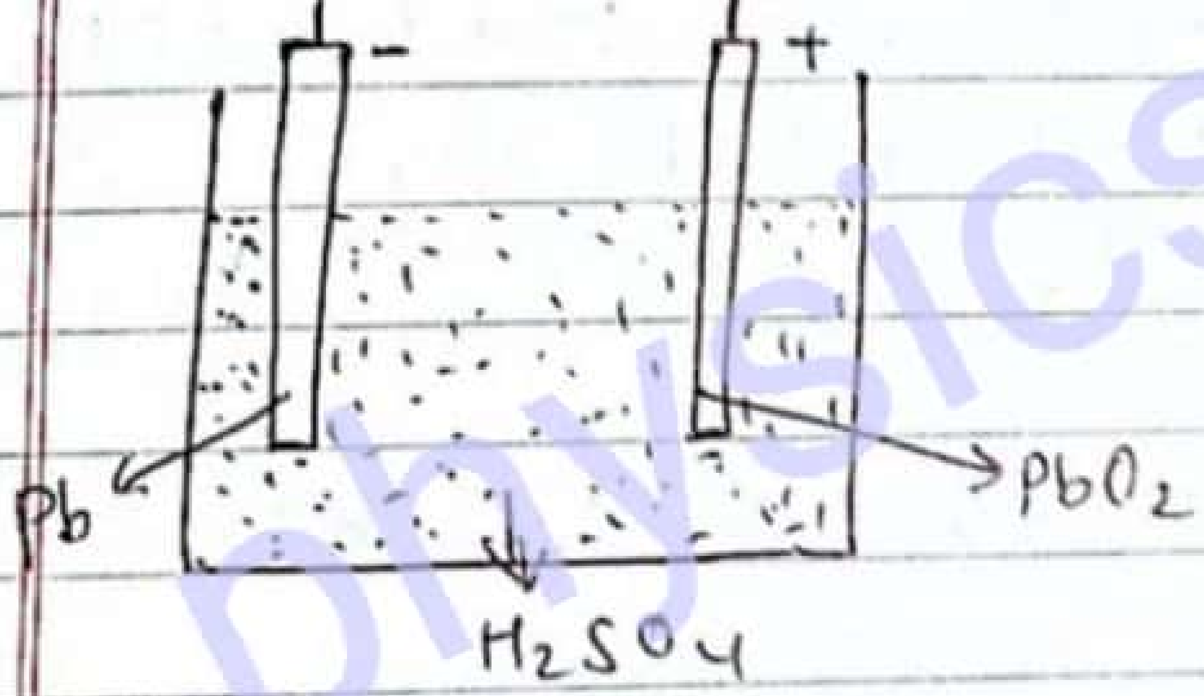
- The emf of cell come out to be 1.5V.

2) Secondary Batteries.

- The batteries which can be ~~reversible~~ recharged is called secondary batteries.
- The net cell reaction is reversible.

Lead Storage cell:

- In this cell, negative terminal (anode) is lead and positive terminal (cathode) is lead oxide.
- 30% conc. H_2SO_4 is used as electrolyte.



At anode:-

$Pb \longrightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode:-

$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{++} + 2H_2O$

$Pb^{++} + SO_4^{--} \longrightarrow PbSO_4$

$PbO_2 + 4H^+ + 2e^- + SO_4^{--} \longrightarrow PbSO_4 + 2H_2O$

net cell rxn:-

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

- The potential of the cell depends only upon the activity of H_2SO_4 soln.
  At 250°C,
  7.4% of $H_2SO_4 \longrightarrow 1.90V$
  21.4% of $H_2SO_4 \longrightarrow 2.00V$
  39.2 of $H_2SO_4 \longrightarrow 2.14V$.

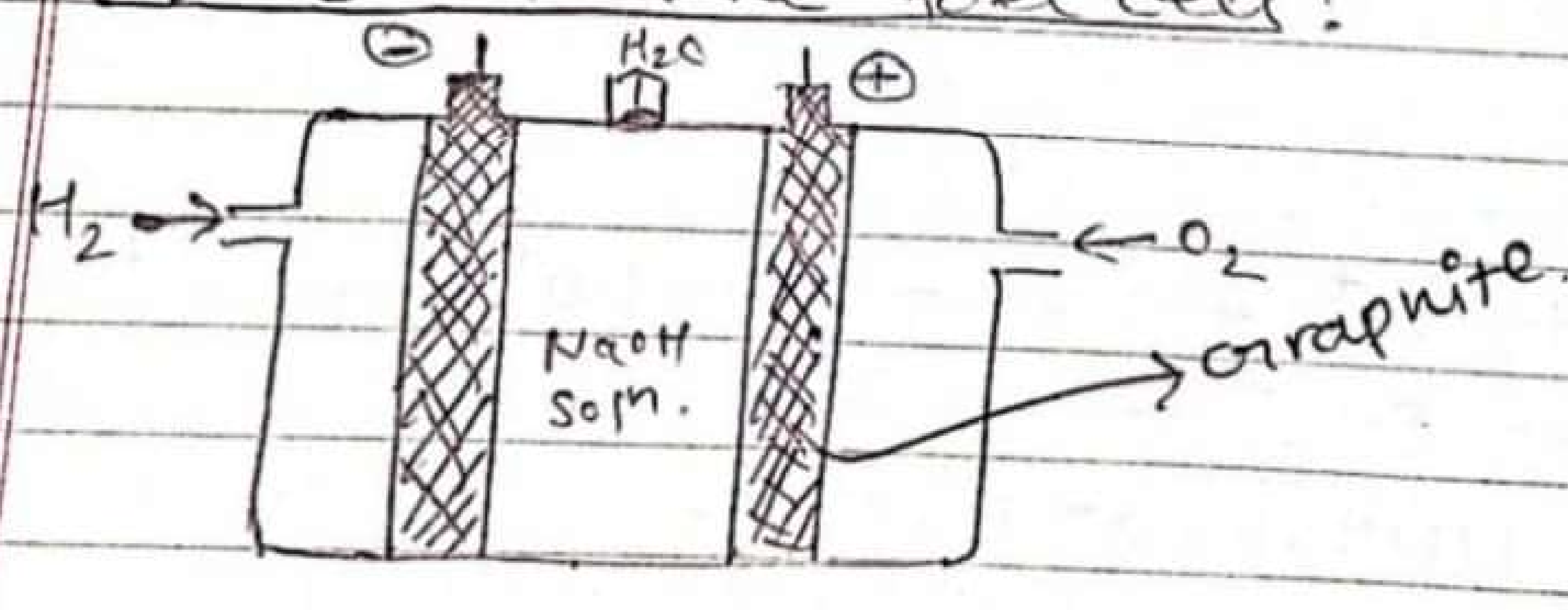
- To recharge the cell, net cell reaction must be reversed. For this, potential higher than that of the cell must be applied externally.
- When done so, electrolysis occur. Lead is deposited at anode and lead oxide is deposited at cathode while H_2SO_4 is regenerated in cell.

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$

Fuel cells

- Primary cell in which reactant are continuously supplied to the cell from outside.

H₂-O₂ alkaline fuel cell:



- It consists two porous graphite electrodes at 60°c – 80°c.
- Electrolyte is KOH / NaOH. H_2 is flushed into anode compartment and O_2 is flushed into cathode compartment.

At anode :-

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

At ~~anode~~ cathode :-

$$2e^- + \frac{1}{2}O_2 + H_2O \longrightarrow 2OH^-$$

net rxn :

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

- It generates potential of 1.15V.
- It is used in space mission.

~~Hydrogen~~ Relation between Gibb's free energy change and cell potential.

- Maximum work done by cell potential is given by $W_{max} = nFE$ ..... (i)

  n = no. of electrons
  F = faraday
  E = cell potential

- Maximum work done by a reaction is equal to decrease in Gibb's Free energy.

  $W_{max} = -\Delta G$ —— (ii)

  from eqn (i) and (ii), we get,

  $\Delta G = -nFE$ —— (iii)

$\Rightarrow$ $\Delta G^\circ = -nFE^\circ$ —— (iv)

  ΔG° = standard Gibb' free energy
  ΔE° = standard cell potential.