

Flow from the electrode

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

• Standard EMF

— Single Electrode Potential

A single electrode or half cell develops a definite electrode potential due to the spontaneous oxidⁿ and/or redⁿ half rxn occurring at it.

— Origin of SEP

• Consider Zn/ZnSO₄,

A

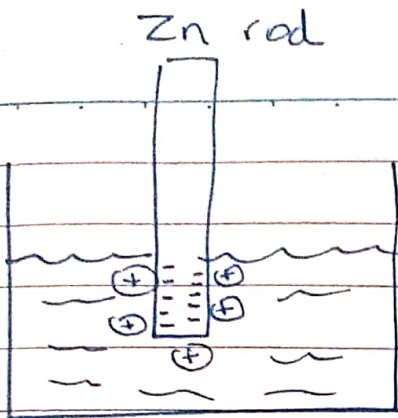
Anodic Process: $\text{Zn}^{2+}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq})$

Cathodic Process: $\text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{s})$

• At equilibrium: $\text{Zn}^{2+}(\text{s}) \rightleftharpoons \text{Zn}^{2+}$

(as e^- 's are getting deposited on the rod as Zn^{2+} are leaving the rod)

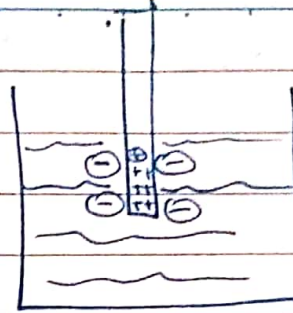
• Metal has net negative charge and solution has equal positive charge leading to the formation of an Helmholtz electrical Double Layer.



Zn SO_4 solⁿ

Zinc ions moves into solⁿ
leaving behind e^- making
it e^- rich

Cu Rod



Cu SO_4 solⁿ

Copper ions gets deposited as
copper leaving behind free -ve
charged sulfate ions in solⁿ
makes the electrode e^- poor

($\sim 30\text{nm}$)

Note: • Diffused e^- layer in the solution, whereas in
the electrode, the layer is thinner (0.01nm)

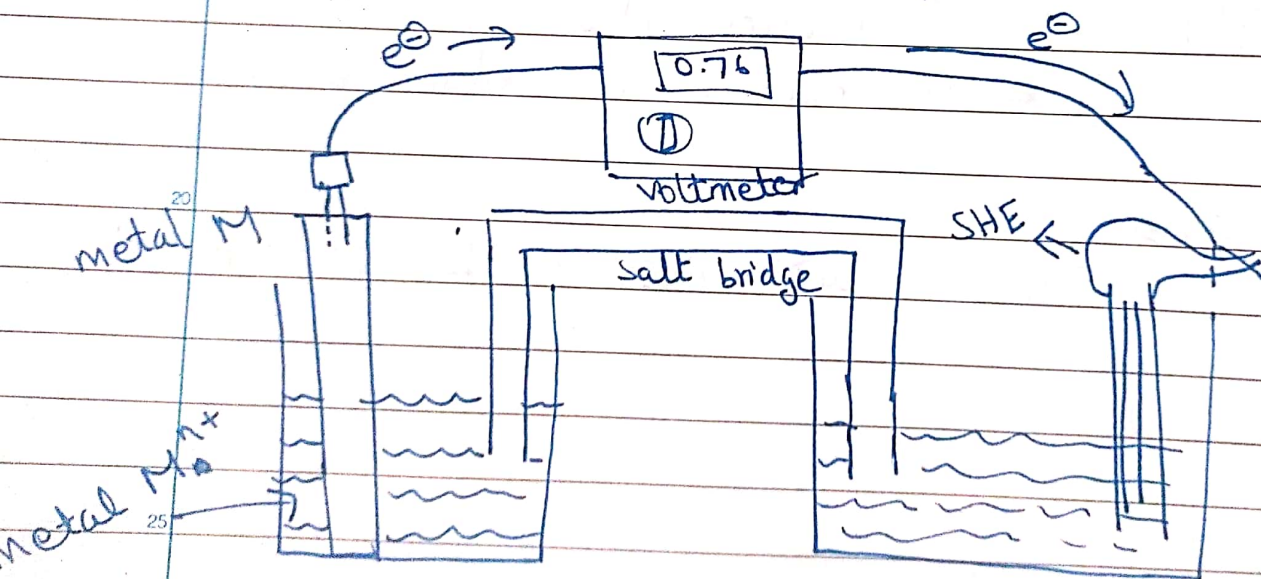
- This process occurs due to metal's
tendency to oxidise or reduce itself

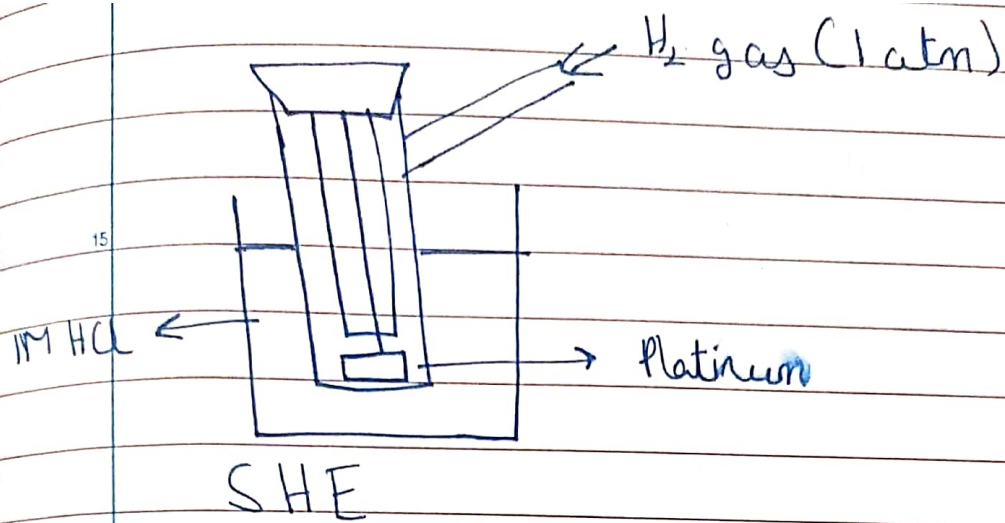
The difference

The double layer occurs due to the difference of

Measurement of Electrode Potential

- It is impossible to determine the absolute half cell potential.
- We can only measure the difference in potential b/w 2 electrodes potentiometrically, by combining them to form a complete cell.

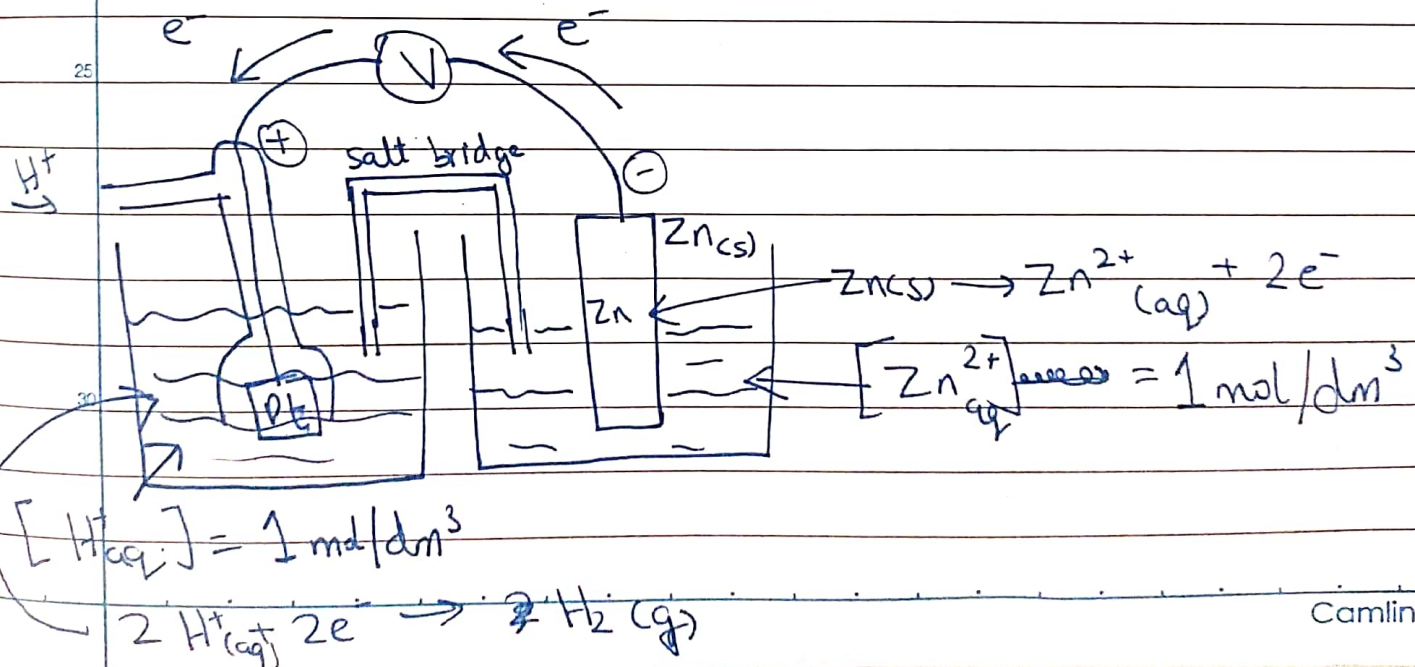




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~~Measurement of Electrode potential~~

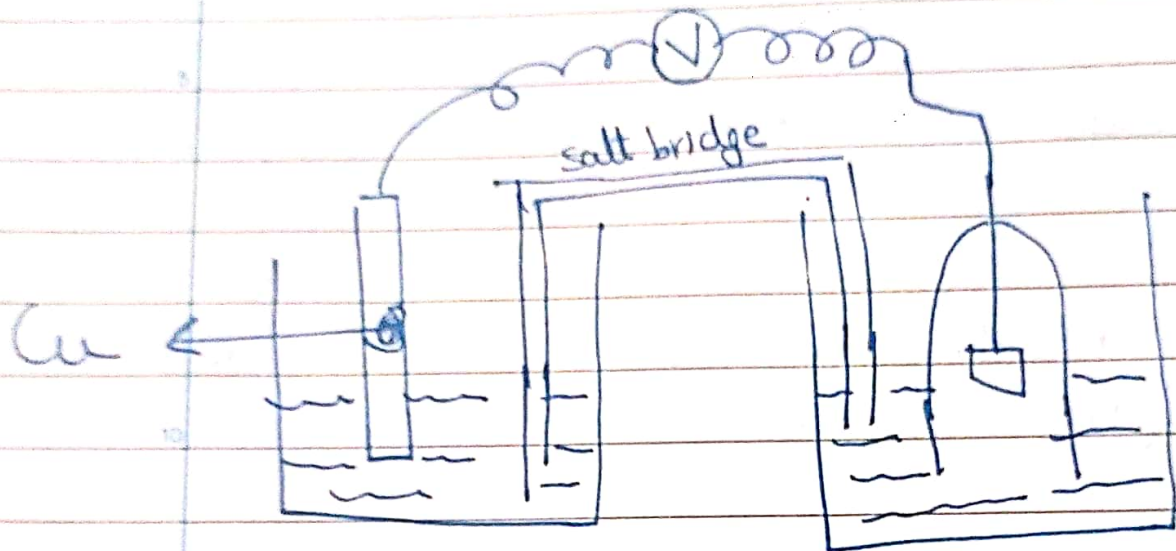
Zn Electrode



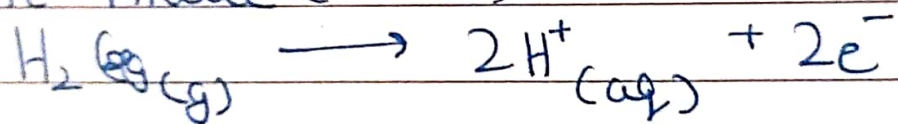
Camlin

Cu Electrode

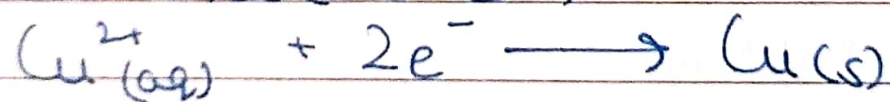
At Anode (Oxidⁿ):



At Anode (Oxidⁿ)



At Cathode (Redⁿ)



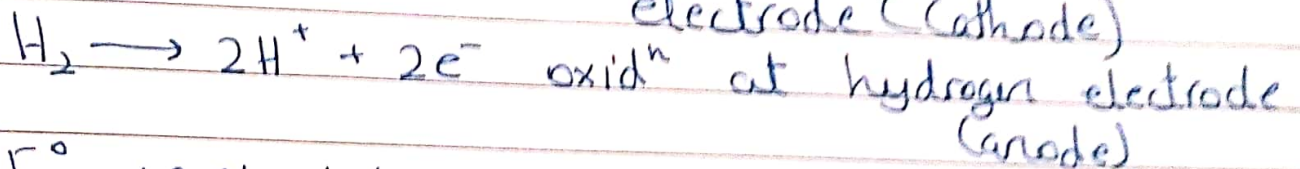
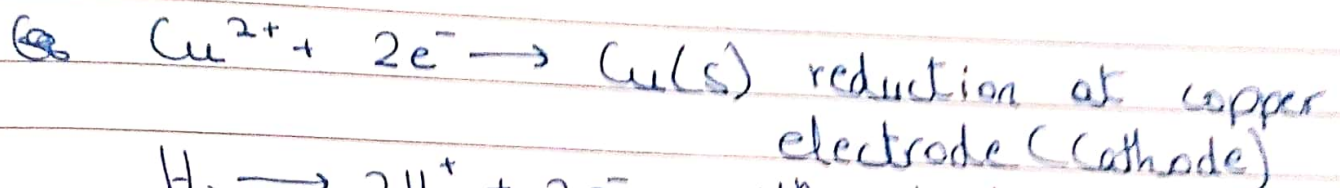
Overall Rxn



Sign of Electrode Potential

- When an electrode is coupled with a SHE, if reduction occurs then EP is given a +ve sign.

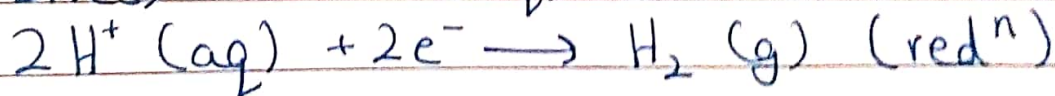
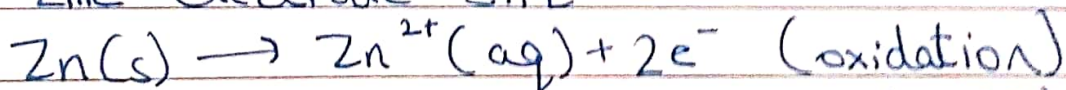
eg. Copper Electrode + SHE



$$E^\circ = +0.34 \text{ Volt}$$

- When an electrode is coupled with a SHE, if oxidⁿ occurs then EP is given a -ve sign.

eg. Zinc electrode + SHE



$$E^\circ = -0.76 \text{ V}$$

Where is SALT BRIDGE

- The liquid junction potential can be reduced (to about 1-2 mV) by joining the electrolyte compartments through a salt bridge

LIQUID JUNCTION POTENTIAL

- Diff. b/w the electric potentials developed in the 2 solutions across their int interface.

$$E_j = \phi_{\text{soln}, R} - \phi_{\text{soln}, L}$$

- eg. Contact b/w 2 different electrolytes ($\text{ZnSO}_4 / \text{CuSO}_4$)

$$E_{j.p.} = \left[(t_-) - (t_+) \right] \frac{RT}{F} \ln \left(\frac{a_2}{a_1} \right)$$

t = transference Number
 a = activity

Note: Why is KCl chosen?

- It is because mobility of K^+ and Cl^- is almost same.