18/10/21

ANODE: $Cd_{(s)} \longrightarrow Cd^{2+} + 2e^-$

CATHODE: $Hg_2^{2+} + 2e^- \longrightarrow 2Hg$

Reaction: $Cd + Hg_2SO_4 \longrightarrow 2Hg + CdSO_4$

Cell representation:

$Cd\text{-}Hg/Cd^{2+}$; Hg_2SO_4/Hg

→ Single Electrode Potential:

A single electrode or half cell develops a definite electric potential due to the spontaneous oxidation or reduction half reaction occuring at it.

Origin of single electrode potential

- Consider $Zn_{(s)}/ZnSO_4$

Anodic process: $Zn^{2+}_{(s)} \longrightarrow Zn^{2+}(aq)$

Cathodic process: $Zn^{2+}(aq) \longrightarrow Zn^{2+}(s)$

- At equilibrium: $Zn^{2+}(s) \rightleftharpoons Zn^{2+}(aq)$

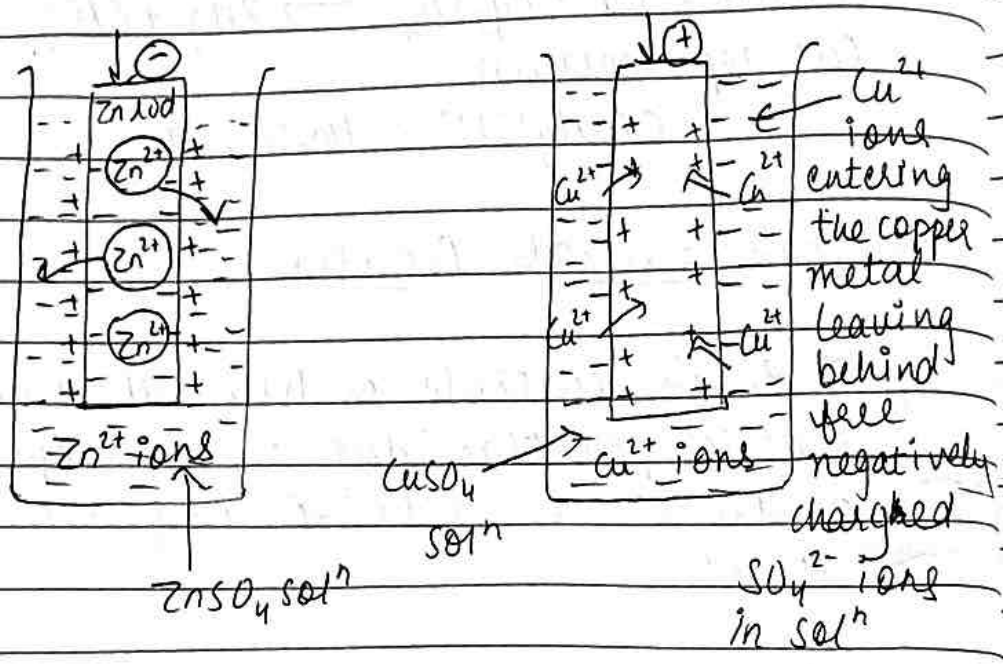
Metal has net negative charge and solution has equal positive charge leading to the formation of an Helmholtz electrical double layer.

(first Zn^{2+} leaves the metal rod into the aq. soln; after the rate decreases, Zn^{2+} goes from aq to (s), but no completely)

21/10/21

$\phi_M - \phi_{aq}$ responsible for electrode potential.

- Helmholtz electrical double layer



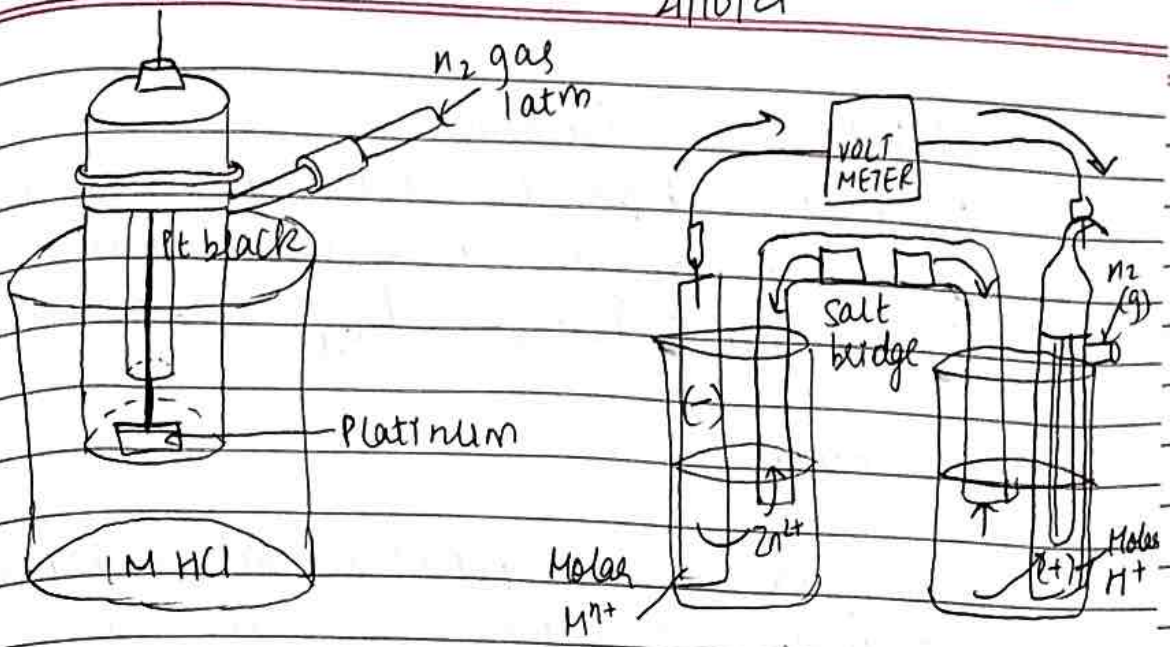
The rate of the reaction depends on:

- nature of metal
- temperature
- Concentration of the metal ions in the solution.

→ Measurement of electrode potential:

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

21/10/21



→ Sign of electrode potential:

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

e.g: Copper electrode + SHE

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ reduction at copper electrode (cathode)

$H_2(g) \rightarrow 2H^+(aq) + 2e^-$ oxidation at hydrogen electrode (anode)

$E^\circ = +0.34\ V$

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

e.g: Zinc electrode + SHE

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation)

$2H^+(aq) + 2e^- \rightarrow H_2(g)$ (reduction)

$E^\circ = -0.76\ V$

21/10/21

→ Liquid Junction Potential

• Difference between the electric potentials developed in the two solutions across their interface.

$E_j = \phi_{soln,R} - \phi_{soln,L}$ $\quad E_{ljp} = (t_- - t_+)\frac{RT}{F}\ln\left(\frac{a_2}{a_1}\right)$

→ Salt Bridge.

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