***Chapter : 02**

classmate
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# electrochemistry

* **Cell :**

a) Electrochemical cell.
(chemical energy ⟶ electric energy)

b) Electrolytic cell.
( electrical energy ⟶ chemical energy)

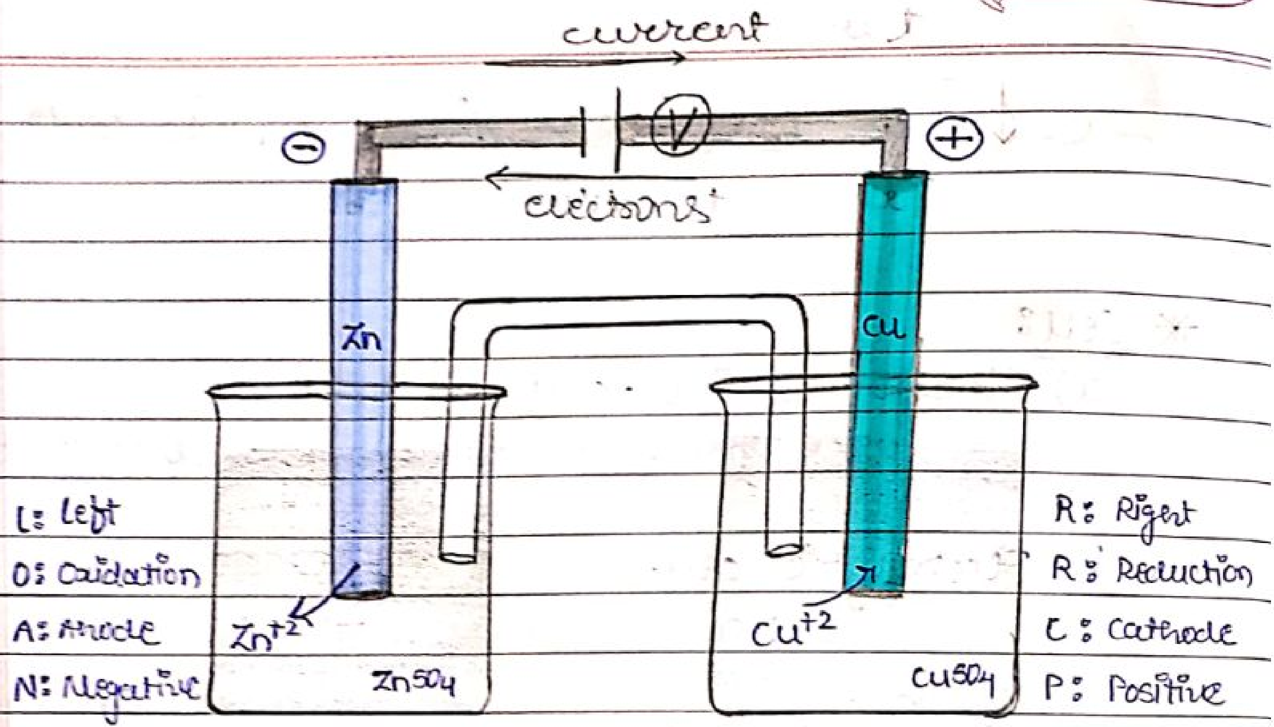
## *(A.) ELECTROCHEMICAL CELL :

- device in which chemical energy of a redox reaction is converted to electrical energy.

- simplest electrochemical cell is Daniel cell or Galvanic cell or Voltaic cell. (Zn & Cu.)

- electrode at which oxidation occurs is called Anode and is negatively charged.
- electrode at which reduction takes place is called Cathode and is positively charged.

- transfer of electrons takes place from anode to cathode so the flow of current is from cathode to anode.



⟹ Net Cell Reaction:

- Reaction at Anode:

$$Zn_{(s)} \xrightarrow{oxidation} Zn^{+2}_{(aq)} + 2e^-$$

- Reaction at Cathode:

$$Cu^{+2}_{(aq)} + 2e^- \xrightarrow{reduction} Cu_{(s)}$$

(from $CuSO_4$).

- Net cell reaction:

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

('n factor' = 02).

⟹ Salt bridge:

- U-shaped tube filled with inert electrolyte solution like Sodium sulphate ($Na_2SO_4$); Potassium Nitrate ($K_2NO_3$); Sodium Chloride ($NaCl$)
- electrolytes used in salt bridge who will not be interfering in the redox reaction.

- agar-agar jellies filled in the salt bridge for ions continous flow.

→ Significance of salt bridge:

a.) maintain electrical neutrality.

b.) complete inner circuit without mixing of solutions.

c.) minimize liquid-liquid junction potential.

⇒ **Electrode Potential:**

- electrical potential difference developed between metal and its solution is called electrode potential.
- It can also be defined as tendency of an electrode in a half cell to gain or lose electrons

⇒ **Oxidation Potential:**

- tendency of an electrode to lose electrons or to get oxidised. ~~and reductio~~

⇒ **Reduction potential:**

- tendency of an electrode to gain electrons or to get reduced.

Electrode Potential → Oxidation Potential. ($E_{anode}$)

Electrode Potential → Reduction Potential ($E_{cathode}$

## * Cell Potential: (Ecell)

- difference between two electrode potentials of two half cells.
- measured in Volts.

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

RP = reduction potential

$$E_{cell} = E_{right} - E_{left}.$$

$$\boxed{E_{cell} = \underset{(RP\ value)}{E_{cathode}} - \underset{(RP\ value)}{E_{anode}}}$$

$$\boxed{E_{cell} = \underset{(cathode)}{E_{m^+/m}} - \underset{(anode)}{E_{m^+/m}}}$$

## * Standard cell Potential: ($E^\circ_{cell}$)

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

## * Standard electrode Potential: ($E^\circ$)

- may be defined as electrode potential of an electrode (half cell) determined relative to standard hydrogen electrode under standard condition.
- denoted as $E^\circ$.
- Standard electrode potential of hydrogen electrode is 0.00 volts.

- Standard conditions are:

I) 1 Molar ion concentration in each solution.
II) 298K temperature } of each gas
II) 1 bar pressure }

SRP → standard reduction potential
SHE → standard hydrogen electrode

- negative $E^\circ$ value means that redox couple is a stronger reducing agent than $H^+/H_2$. couple.
- positive $E^\circ$ value means that redox couple is a weaker reducing agent than $H^+/H_2$ couple.

## * Standard Hydrogen Electrode (SHE):

- it is a reference electrode use for reference on all half-cell potential reactions.
- value of standard electrode potential is zero volt at all temperature.

- SHE consist of platinum electrode coated with platinum black.
- Platinum is used because it is inert and does not react much with hydrogen.

- electrode is dipped in an acidic solution having 1.0 M concentration of $H^+$ ions.
- during reaction, pure hydrogen gas at 1 bar pressure is continously bubbled through solution at 298K temperature.
- hydrogen electrode can act both ways - as a anode or as a cathode.

→ Act as anode

(oxi. takes place) $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$

→ Act as cathode

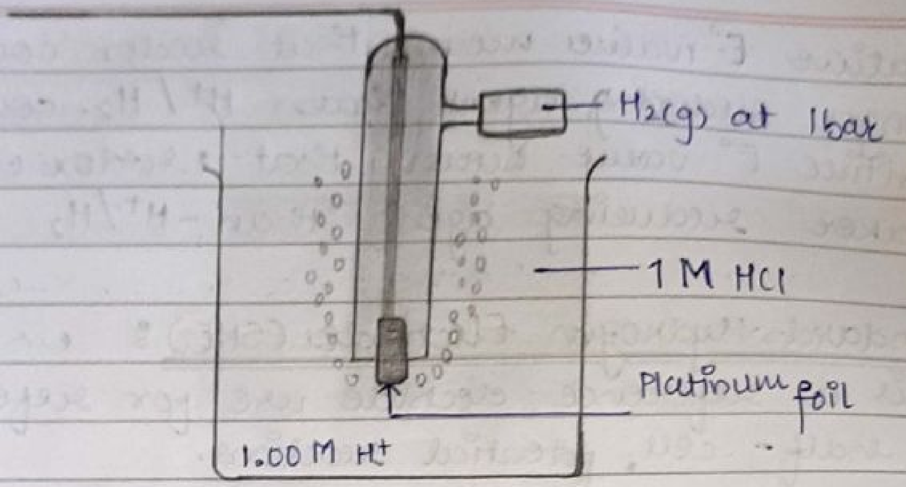
(red. takes place) $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

→ Representation of SHE:

$$Pt_{(s)} \,|\, H_{(g)}\ (1\text{bar}) \,|\, H^+_{(aq)}\ (1M)$$

SOP → std oxid. poten

SRP → std. red. poten



## * Cell diagram or representation of cell:

A B C

$Zn_{(s)} \mid Zn^{+2}_{(aq)} (0.1M) \parallel Cu^{+2}_{(aq)} (0.01M) \mid Cu_{(s)}$

salt bridge

Q801. $\underset{\text{ANODE}}{Cr_{(s)} \mid Cr^{+3}_{(aq)}} \parallel \underset{\text{CATHODE}}{Fe^{2+}_{(aq)} \mid Fe_{(S)}}$

Given: $E^{\circ}_{Fe/Fe^{+2}} \rightarrow -0.55$ volt (SOP) (cathode) → SRP $E^{\circ}_{Cr^{3+}/Cr} \longrightarrow -0.85$ volt. → reductive value

(SRP) → (SOP). i.e. usne oxidⁿ kiya anode↑

Find: (a) write net cell rxn.

(b) find n-factor.

(c) find SCP ($E^{\circ}cell$).

$\Delta G^{\circ} = -nFE^{\circ}cell$ (d) find $\underbrace{\text{usefull work}}_{\text{Gibb's free energy}}$ by electrochemical cell.

→

(a) $Cr \longrightarrow Cr^{+3} + 3e^{-}$ }×2

$Fe^{+2} + 2e^{-} \longrightarrow Fe$ }×3

SOP convert to SRP

$2Cr + 3Fe^{+2} \longrightarrow 2Cr^{+3} + 3Fe$.

(b) n-factor = 6.

(c) $Ecell = E_{cath} - E_{anod} \longrightarrow +(0.55) - (-0.85)$

$= \underline{1.4}$.

F= faraday const → 96500 c/mole

(d) $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

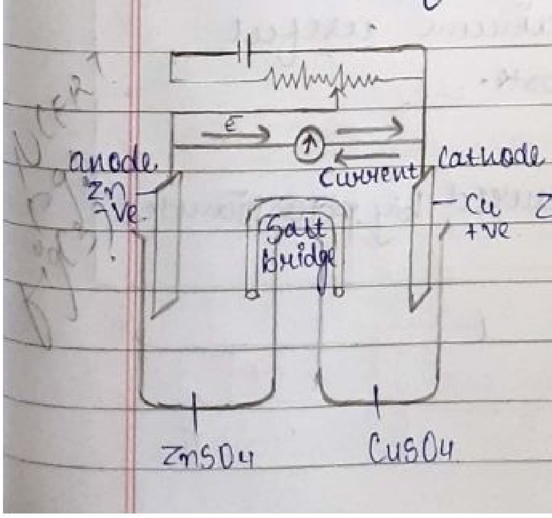
$= -(6)(96500)(1.4).$

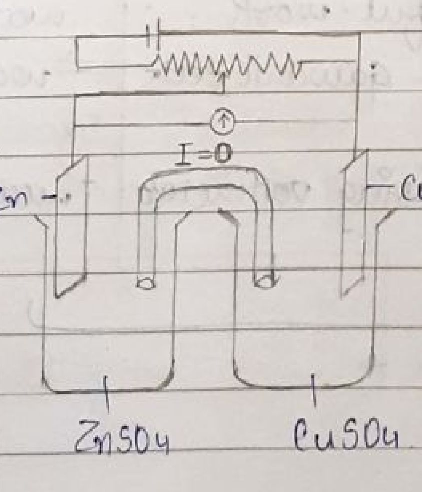
$= -(8.4)(96500) \longrightarrow -810600$ J.

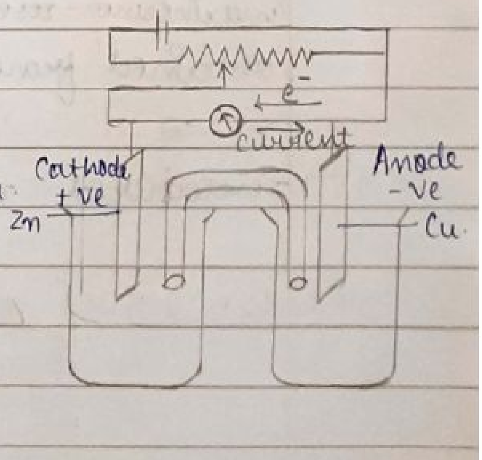
∴ Fe is at cathode cell, ishkee $(Fe^{2+} \rightarrow Fe)$ ($e^-$ gain) reduction ho rahee hai ushkai oxidation vali value di hai ∴ SOP → SRP ∴ value +ve.

## * Reversibility of Danielcell:

- when external voltage is 1.10 V, electrons flow from Zn to cu but current flows from Cu to Zn, i.e., in opposite direction.
- Zinc dissolves at anode and copper deposites at cathode.
- when external voltage applied is less than 1.10V. and is increased slowly, it is observed that reaction continues to take place till external voltage attains value 1.10 V. when this is so, reaction stops altogether and no current flows.
- when value of external voltage exceeds voltage of Daniel cell, reaction takes place in opposite dir. i.e. cell functions like electrolytic cell.







X nernst eqn

fig. (a) (I) electrons flow from Zn rod to Cu rod hence, current flows from Cu to Zn.
$E_{ext} < 1.1V$ (II) Zn dissolves at anode and Cu deposit at cathode

fig. (b) (I) no flow of electrons or current.
$E_{ext} = 1.1V$ (II) no chemical reaction.

fig. (c) (I) electrons flow from Cu to Zn and current flows from Zn to Cu.
$E_{ext} > 1.1V$ (II) Zn is deposited at Zn electrode and Cu dissolves at copper electrodes.

## * Difference b/w Cell Potential & Electromotive Force (EMF):

| Cell Potential | Electromotive Force. |
|---|---|
| - measure potential difference of two half cells when electric current flow thr. cell. | - potential difference b/w two electrodes, when no current is flowing in circuit. |
| - it is always less than the max. voltage obtained from cell. | - it is maximum voltage obtain from cell. |
| - it does not correspond to maximum useful work obtained from Galvanic cell. | - it corresponds to the maximum useful work. |
| - measured using voltmeter | - measured by potentiometer |

Kc = equilib. const.

*** NOTE:**

SRP↑ SOP↓ Oxidising Strength ↑

SRP↓ SOP↑ Reducing Strength ↑

## * Electrochemical cell and Gibb's free energy:

- work done by an electrochemical cell is equal to decrease in Gibb's free energy (useful work).

$$\boxed{\Delta G = -nFE_{cell}}$$

- if concentration of all reacting specie is unite, then $E_{cell} = E^\circ_{cell}$.

- where $E_{cell}$ is cell Potential and $E^\circ_{cell}$ is Std cell Potential

$$\Delta G = -nFE^\circ_{cell}$$

n = number of $e^-$ exchanged F = faraday const. (96500 C/mol)

- from fundamental thermo. eqⁿ;

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -2.303\ RT \log K$$

$$\cancel{-}nFE^\circ_{cell} = \cancel{-}2.303 \cdot RT \log K$$

$$E^\circ_{cell} = \frac{2.303}{nF} \cdot \log K$$

K = equilibrium constant T = temp. in K = 298K. R = gas constant = 8.314 J/K mol.

$$\boxed{E^\circ_{cell} = \frac{0.0591}{n} \log Kc} \text{ or } \frac{0.06}{n} \log Kc$$