* Nernst equation:

- Nernst gave an equation for finding out electrode potential and cell potential at any condition of temperature, pressure and concentration of electroly

- for general electrode reduction potential

$$M^{+n}_{(aq)} + e^- \longrightarrow M_{(s)}$$

$$E_{M^{+n}/M} = E^0_{M^{+n}/M} - \frac{0.0591}{n} \log Qc.$$

$$\boxed{E_{M^{+n}/M} = E^0_{M^{+n}/M} - \frac{0.0591}{n} \log \frac{[M]}{[M^{+n}]}}$$

∴, Concⁿ of Solid: 01. $[M]=1$

★. $$\boxed{E_{M^{+n}/M} = E^0_{M^{+n}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{+n}]}}$$ at 298K.

$$\boxed{E_{M^{+n}/M} = E^0_{M^{+n}/M} - \frac{RT}{nF} \log \frac{1}{[M^{+n}]}}$$ at any temp

$$\boxed{E_{M^{+n}/M} = E^0_{M^{+n}/M} - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{+n}]}}$$

for a general redox rexn;

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{cell} = E^0_{cell} - \frac{2.303\,RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

at 298K temp;

$$\boxed{E_{cell} = E_{cell} - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}}$$

10^{-1} 10^{-3}

Q:02. $Mg(s) \mid \underset{anode}{Mg^{+2}} (0.1M) \parallel \underset{cathode}{Ag^{+}} (0.001M) \mid Ag(s)$

G: $E^\circ cell = 3.17$ volt. find cell potential @ 298K.

→ $Mg \longrightarrow Mg^{+2} + 2e^{-}$ }×1 $Ag^{+} + 1e^{-} \longrightarrow Ag$ }×2

$\longrightarrow Mg + 2Ag^{+} \longrightarrow Mg^{+2} + 2Ag$.

n-fact = 2.

$$\therefore, Ecell = E^\circ cell - \frac{0.0591}{n} \log \frac{[Prod]}{[Reac]} \quad \frac{anode}{cathode}$$

$$= 3.17 - \frac{\overset{0.03}{\cancel{0.06}}}{\cancel{2}} \log \frac{[10^{-1}]}{[10^{-3}]^2}$$

$$= 3.17 - 0.03 \log(10^{5}).$$

$$= 3.17 - (0.03 \times 5)$$

$$Ecell = 3.17 - 0.15 \longrightarrow \underline{\underline{3.02}}.$$

Q:3 What is electrode potential (in V) of following @ 25°C:

-0.28 $Ni^{2+} (0.1 M) \mid Ni(s)$ (SRP is −0.25V); $\frac{2.303RT}{nF} = 0.06$.

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

(SRP) 0.76 (SOP)

Q:4 find emf of $E^\circ_{Pb^{2+}/Pb} = -0.12V$ $E^\circ_{Zn^{2+}/Zn} = -0.76V$.

>0.637 $Zn \mid Zn^{+2}(0.1)M \parallel Pb^{+2}(1M) \mid Pb$

Q:5 $Zn(s) + Cu^{2+}(0.1M) \longrightarrow Zn^{+2}(1M) + Cu(s)$.

>1.07V $E^\circ cell = 1.10v$ $Ecell$? $\frac{2.303RT}{F} = 0.0591$.

⟹ (4.) $Zn + Pb^{+2} \longrightarrow Zn^{+2} + Pb$. $\underline{n=2}$.

$$E^\circ cell = E_{cathode} - E_{anode}$$
$$= -0.12 + 0.76$$
$$= \underline{0.64}.$$

$$Ecell = 0.64 - \frac{\overset{0.03}{\cancel{0.06}}}{\cancel{2}} \log \frac{[10^{-1}]}{[1]}$$
$$= 0.64 - (0.03)(-1).$$
$$= 0.64 + 0.3 \longrightarrow \underline{0.67}.$$

⟹ (5.) $E^\circ cell = 1.10V$. n fact = 2.

$$Ecell = 1.10 - \frac{\overset{0.03}{\cancel{0.06}}}{\cancel{2}} \log \frac{(10^{-1})}{(1)}$$
$$= 1.10 - 0.03$$
$$= \underline{1.07}.$$

⟹ (4.) n fact :- 2 (×2) → $\underline{4}$.

~~$\Delta G = -nFE^\circ cell$.~~
~~$-475 = 4 \times 96500 \times E^\circ$~~
~~$E^\circ cell =$~~

$$\Delta G = -nFE^\circ cell.$$
$$\cancel{-}475 \times 10^3 = \cancel{-}4 \times 96500 \times E^\circ cell$$
$$\underline{\underline{E^\circ cell = 1.23}}$$

Q:6 $(A)_{(s)} + 2B^+_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + 2B_{(s)}$ KC has been found to be 10^{12}. E°cell is? n fact = 2.

$0 \longrightarrow -2$

Q:7 For fuel cell rxn $2H_2 + O_2 \longrightarrow ②H_2O$ $\Delta G^\circ = -475$ KJ. E°cell? n fac = 4 1.23

→

~~8)~~ $E^\circ_{cell} = \frac{0.06}{n} \log(KC)$.

$= \frac{\cancel{0.06}^{0.03}}{\cancel{2}} \log(10^{-12})$ 12×0.03 $= \underline{0.36}$ V

extra imp → (SRP) $E^\circ_A = -0.20V$ (SRP) $E^\circ_B = -1.0V$. which is cathode

SRP↑ works as cathode. SOP↑ → anode.

$\underline{-0.2} > \underline{-1}$. ∴ E°_A = cathode.

E°_B = anode.

Q:8 Given: $E^\circ_{cu^{+2}/cu^+} = 0.15V$ (n=1) $E^\circ_{cu^+/cu} = 0.5V$ (n=1) $E^\circ_{cu^{+2}/cu} = ?$

$E^\circ_{cu^{2+}/cu} = ?$ n=2. $E^\circ_1 = 0.15$ V $E^\circ_2 = 0.5V$. $\Delta G_3 = \Delta G_1 + \Delta G_2$.

→ $-n\cancel{F}E^\circ_{cell} = (-n\cancel{F}E^\circ_1) + (-n\cancel{F}E^\circ_2)$.

$-2 E^\circ_{cell} = (-1(0.15)) + (-1(0.5))$

$\cancel{-}2 E^\circ_{cell} = \cancel{-} \underline{0.65}$ $E^\circ_{cell} = \frac{0.65}{2} \longrightarrow \underline{0.325}$.

Q:9 SRP at 25°c of Li^+/Li; Ba^{+2}/Ba; Na^+/Na; Mg^{+2}/Mg are −3.05; −2.73; −2.71 and −2.37 volt. which one is strongest oxi. agent?

→ SRP↑ Oxi. Agent↑ Reduction↑. (at cathode).

reducing stren.↓ ∴ Answer is $\underline{Mg^{+2}}$.

Q:10 SRP of A, B and C is 0.5V; −3.0V; −1.2V . Reducing power?

→ −↑ reducing power↑ ∴ B > C > A reducing agen

* Nernst eqⁿ at equilibrium:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log Q_c.$$

- at equilibrium; $Q_c = K_c$ $E_{cell} = 0$.

$$\therefore\ 0 = E^{\circ}_{cell} - \frac{0.0591}{n} \log K_c.$$

$$\therefore\ \boxed{E^{\circ}_{cell} = \frac{0.0591}{n} \log K_c.} \qquad \therefore\ \boxed{\log K_c = \frac{n \cdot E^{\circ}_{cell}}{0.0591}}$$

* Concentration cell:

- cells in which electrodes and electrolytes are identical but their (electrolyte's) concentrations are different.

eg:

$$Zn(s) \mid Zn^{+}(C_1) \parallel Zn^{+2}(C_2) \mid Zn(s)$$

$$Ag(s) \mid Ag^{+}(C_1) \parallel Ag^{+2}(C_2) \mid Ag(s)$$

* Nernst eqn for concentration cell:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log Q_c.$$

- for concentration cell; $E^{\circ}_{cell} = 0$.

$$\therefore\ E_{cell} = 0 - \frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}$$

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$$\therefore \boxed{E_{cell} = -\frac{0.0591}{n} \log \frac{[C_1]}{[C_2]}} \quad \frac{\text{anode}}{\text{cathode}}$$

* CASE:01. if $C_2 > C_1$ conc^n cathode > conc^n anode

→ $E_{cell} = +ve$ $\Delta G = -ve$.

→ spontaneous process [feasible], cell at test, conc^n cell where conc^n of cathode electrolyte) is greater than conc^n of electrolyte at anode

* CASE:02. if $C_1 > C_2$ (conc^n anode > conc^n cathode

→ $E_{cell} = -ve$ $\Delta G = +ve$

→ non-spontaneous process. oxid^n @cathode

→ electrons flows from cathode to Anode.

* CASE:03. if $C_1 = C_2$ conc^n anode = conc^n cathode

→ $E_{cell} = 0$ $\Delta G = 0$.

→ it is an equilibrium condition hence there is no flow of electron current) through cell.

→ it isn't a concentration cell.

* Calculation of pH by Hydrogen electrode:

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

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{\overset{0.03}{\cancel{0.06}}}{\cancel{2}} \log. \frac{[H_2]}{[H^+]^2}$$

$$E_{H^+/H_2} = \cancel{E^\circ_{H^+/H_2}}^{0} - 0.03 \log \frac{\cancel{[H_2]}^{1}}{[H^+]^2}$$

$$\therefore E_{H^+/H_2} = -0.03 \log \frac{1}{[H^+]^2}$$

$$E_{H^+/H_2} = -\frac{0.0591}{\cancel{2}}\,\cancel{2}\left[-\log[H^+]^{2}\right]$$

$$\therefore \boxed{E_{H^+/H_2}\,(RP) = -0.0591\ pH.}$$

$$\boxed{E_{H_2/H^+}\,(OP) = +0.0591\ pH}$$

Q.11. write down the electrode potential of hydrogen electrode for 0.01 M HCl electrolyte solution. (OP નહીં કહે ત્યાં સુધી RP જ લેવાનું).

→ $E_{H^+/H_2}\,(RP) = -0.0591\ \log(10)^{-2}$

$= -0.0591 \cdot 2$

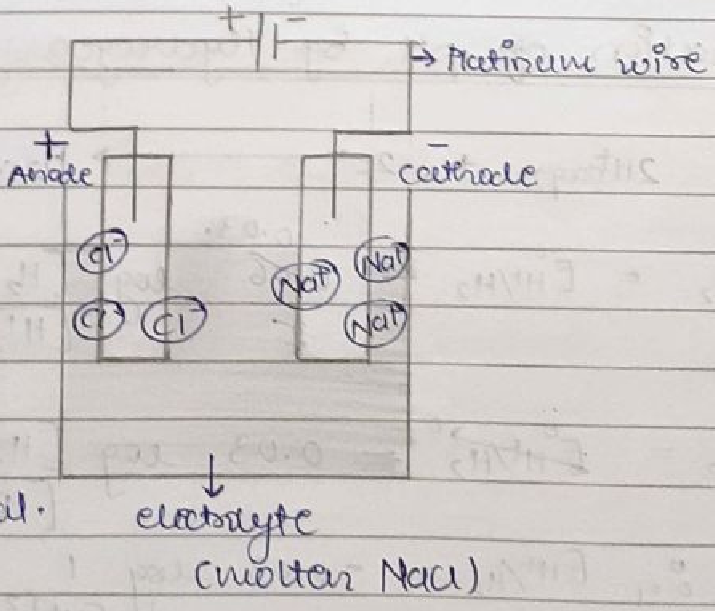
$= \underline{-0.1182}$

* **Electrolysis:**

- the decomposition of electrolyte solution by passing electric current, resulting into deposition of metals or liberation of gases at electrodes.

* **Electrolytic cell:**

- cell converting electrical energy to chemical energy



L: left
O: oxidation
A: anode
P: positive terminal.

- After electrolysis of electrolyte, the cation moves towards cathode and anion moves towards anode.
- Oxidation and Reduction are carried out at anode and cathode respectively.

- It's a 'Non-Spontaneous' process carried out in an electrolytic cell hence, $\Delta G = +ve$ and $E_{cell} = -ve$
- It is because the work done is in the presence of external force.

* Factors affecting 'Quantity of substance' deposited at electrodes in electrolytic cell:

depo.↑ depo.↓

1.) Nature of electrolyte (Strong / weak).
2.) Medium of electrolyte. (aq. / molten).
☆ 3.) Nature of electrode. (inert (Pt) / Activated (reac. Mt)

→ Nature of electrode:

- Two types of electrodes used:
  - A) INERT eg: Pt
  - B) ACTIVATED. eg: Zn, Ag, Cu, Hg, Au, etc.
- If an electrode is inert then the chemical reaction (Redox) depends upon the nature of electrolyte.
- If an electrode is activated then the chemical reaction depends upon nature of electrode only.

- Redox reaction of electrode of electrolytic cell:
  - Molten NaCl : $NaCl \longrightarrow Na^+ \; Cl^-$

    rxn @ Anode ⇒ $2Cl^- \longrightarrow Cl_2 + 2e^-$ (oxidation)

    rxn @ Cathode ⇒ $Na^+ + e^- \longrightarrow Na$ (reduction)

* Preferential discharge theory:

CASE:01. Tendency of migrated cation. (INERT electrode)

- in case of aqueous NaCl, Na^+ and H^+ ions are obtained after electrolysis.
- those cations having more reduction potential moves towards cathode.
- hence, H_2 gas liberates at cathode.

  * One being last or below (in lower position). will go 1st for deposition.

CASE:02. Tendency of migrated anion.

- $SO_4^- < NO_3^- < OH^- < F^- < Cl^- < Br^- < I^-$

eg: $NaCl + H_2O \longrightarrow \underset{(H^+)}{Na^+_{(aq)}} + \underset{(OH^-)}{Cl^-_{(aq)}}$

- those anions having more oxidation potential moves towards anode.
- hence, Cl^- ions liberates chlorine gas (from above eg) at anode after oxidation.

$$2Cl^-_{(aq)} \longrightarrow Cl_2 + 2e^-$$

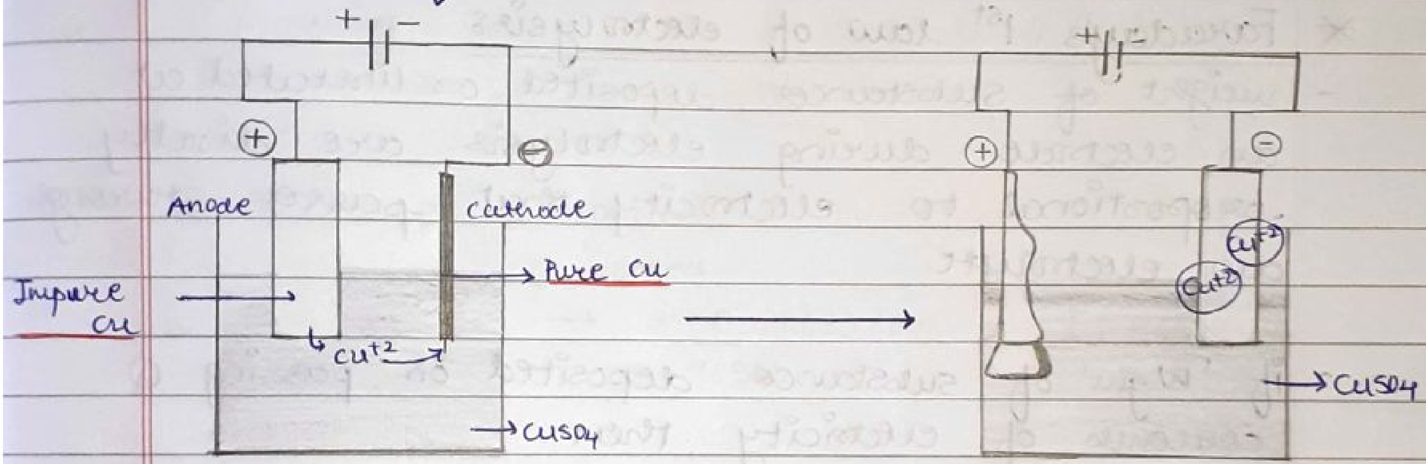
K Na Ca Mg Al Zn Fe Pb H Cu Hg Ag Au

*** NOTE:**

- in case of Oxidation of OH^- ion ; O_2 gas liberates at anode.

$$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$$

CASE:03. Deposition of substance. (ACTIVE electrode)



rxn at anode : $Cu\ (dis.) \longrightarrow Cu^{+2} + 2e^-$

rxn at cathode: $Cu^{+2} + 2e^- \longrightarrow Cu(s)$ (pure metal)

here,

- oxidation of impure metal electrode occurs and cation move towards cathode.
- after reduction at cathode, pure metal is deposited at anode.

Electrolyte	Electrode	Anode prod.	Cathode prod.	
NaCl (molten)	Pt	$Cl_2(g)$	$Na(s)$	
NaCl (aq.)	Pt	$Cl_2(g)$	$H_2(g)$	H^+ OH^-
Na_2SO_4 (aq.)	Pt	$O_2(g)$	$H_2(g)$	Na^+ SO_4^{2-}
$NaNO_3$ (aq.)	Pt	$O_2(g)$	$H_2(g)$	Na^+ NO_3^-
$AgNO_3$ (aq.)	Pt	$O_2(g)$	$Ag(s)$	Ag^+
$CuSO_4$ (aq)	Pt	$O_2(g)$	$Cu(s)$	$OH^- > NO_3^-$ (prior) (cause)