EXAMS ROAD

"Bringing Excellence to Students"

Handwritten Notes

On

Electrochemistry

26/12/17

Electrochemistry

Electrochemistry is the branch of chemistry that deals with interconversion of chemical & electrical energy.

Chemical energy ⇌ (Galvanic cell / Electrolytic cell) Electrical Energy

Electrolyte:- Substances which conduct electricity in aq. & molten state through ions c/a electrolyte.

eg. Acid, Base, salt.

- Strong Electrolyte
  complete ionisable
  $\alpha = 1$
- Weak Electrolyte
  Incomplete ionisable
  $\alpha < 1$

Conductor:- which allow electric current to pass through them.

- Metallic
  - Charge carrier are free e^-
  - Matter does not takes place
  - No chemical change takes place
  - Conductance is very high.
  - T ↑ R ↑ conductance ↓
  - Faraday law is not followed
- Electrolytic
  Charge carrier are ions.
  - Matter transfer takes place.
  - Chemical change takes place.
  - Very low

T ↑ R ↓ cond ↑

- Faraday law followed.

Some imp. terms related to Conductance

Resistance : Ohm's law

$V \propto I$

$V = IR$

$$R = \frac{V}{I}$$

Unit : Ω or ohm

Conductance (G)

$$G = \frac{1}{R}$$ Unit Ω^{-} or mho seimen

Specific Resistance / Resitivity (ρ)

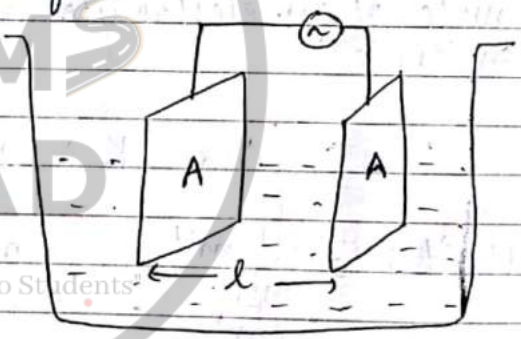
$R \propto l$ (length b/w electrodes)

$R \propto \frac{1}{A}$ (A → Area of electrode plate)

$R \propto \frac{l}{A}$

$R = \rho \frac{l}{A}$

$$\rho = R \frac{A}{l}$$



Unit : Ω cm or Ω m

$A = 1\,cm^2$, $l = 1\,cm$] $V = 1\,cm^3$ $\rho = R$

Therefore resistivity is the resistance of $1\,cm^3$ electrolyte.

Sp. Conductance / conductivity (K) Kappa

$$K = \frac{1}{\rho}$$

$$K = \frac{1}{R}\left(\frac{l}{A}\right)$$

$G \rightarrow$ Conductance

$$G^* = \frac{l}{A} \rightarrow \text{cell const}$$

Unit = cm^{-1} or m^{-1}

$$K = G \cdot G^* \rightarrow$$ $\Omega^{-1} cm^{-1}$ or $\Omega^{-1} m^{-1}$

$l = 1\,cm \quad A = 1\,cm^2$

$G^* = \frac{l}{A} = 1\,cm^{-1}$

$\boxed{K = G^*}$

Conductivity → Conductance of unit volume ($1cm^3/1m^3$) of an electrolyte is c/a sp. conductance or conductivity.

Molar conductance : Conductance of 1 mole of an electrolyte. (Λ_m) or λ_m

Conductance of $1\,cm^3$ of an electrolyte = K

" " $V\,cm^3$ " " " " = K × V

Let

conc^n of an electrolytes is M

M mole of an electrolyte are +nt in = 1 L = $1000\,cm^3$

1 ~~molt~~mole " " " " = $\frac{1000}{M}\,cm^3$

$$\boxed{\Lambda_m = K \times \frac{1000}{M}}$$

Unit : $\frac{\Omega^{-1} cm^{-1}}{\frac{mol}{cm^3}} = ohm^{-1} cm^{-1} cm^3 mol^{-1} = ohm^{-1} cm^2 mol^{-1}$

If unit of K is given in $ohm^{-1} m^{-1}$ then

$$\boxed{\Lambda_m = \left(K \times \frac{1000}{M}\right) \times 10^{-6}} \; ohm^{-1} m^2 mol^{-1}$$

Equivalent Conductance :- Conductance of 1 equivalent of an electrolyte.

$$\boxed{\Lambda_{eq} = K \times \frac{1000}{N}}$$

$ohm^{-1} cm^2 eq^{-1}$

$$\Lambda_m = K \times \frac{1000}{M} \times \frac{V.F.}{V.F.}$$

$$\Lambda_m = K \times \frac{1000}{N} \times V.F.$$

$$\boxed{\Lambda_m = \Lambda_{eq} \times V.F.} \qquad V.F. \geq 1$$

$$\boxed{\Lambda_m \geq \Lambda_{eq}}$$

Ques A certain conducting cell is filled with 0.05 M K_2SO_4 sol^n, if it had a resistance of 300 Ω then Calculate. (specific conductance = $0.0025\ \Omega^{-1}\ cm^{-1}$)

① cell const.

$$G_1^* = \frac{l}{A} \qquad G_1^* = \frac{K}{G_1} = \frac{0.0025}{0.003} \times \frac{1}{2} = \frac{5}{6} = 0.8$$

② Conductance $G_1 = \frac{1}{R} = \frac{1}{300} = 0.003$

③ eq. conductance Λ_{eq}

$$\Lambda_{eq} = K \times \frac{1000}{N} = 0.0025 \times \frac{1000}{2 \times 0.05}$$

$$= \frac{25}{2 \times 0.05} \times \frac{100}{1000} = 10$$

④ molar conductance $\Lambda_m = \Lambda_{eq} \times V.F.$

$$= 10 \times 2 = 20$$

Ques The sp. conductance of a 0.1N KCl sol^n at 23°C is $0.012\ \Omega^{-1}cm^{-1}$. The resistance of containing sol^n at same Temp. is 55 Ω. Then cell constant will be

① $0.142\ cm^{-1}$ ② $0.66\ cm^{-1}$ ③ $0.918\ cm^{-1}$ ④ $1.12\ cm^{-1}$

$$K = G_1 G^*$$

$$KR = \frac{K}{G_1} = G^* = 0.012 \times 55$$

$$= 0.660$$

Ques The electrical resistance of a 0.05 mol L^{-1} NaOH sol^n of diameter 1 cm & length 50 cm is 5.55×10^3 ohm. Calculate its resistivity & molar conductivity.

$$\rho = R\frac{A}{l} = \frac{5.55 \times 10^3 \times 0.50 \times 0.50 \times \frac{11}{7}}{100 \times 50 \times 100} \quad (10, 2, 2)$$

$$= \frac{111 \times 11}{7 \times 2} = \frac{1221}{14} = 87.21$$

$$\Lambda_m = K \times \frac{1000}{M}$$

$$= \frac{1}{1221} \times 14 \times \frac{1000}{0.05} \times 100 \quad (20)$$

$$= \frac{28 \times 10^4}{1221} = \frac{280000}{1221} = 229.32$$

Q.4 The eq. conductance of 0.1N sol^n of $MgCl_2$ is 100 ohm cm^2 eq^{-1} at 25°C. A cell with electrode having surface area 1 cm^2 & 0.5 cm apart is filled with 0.1 N $MgCl_2$ sol^n. How much current will flow when potential diff. b/w electrode is 5 V

$V = IR$

N = 0.1 N
Λ_{eq} = 100
A = 1 cm^2
l = 0.5 cm
V = 5 V

$$\Lambda_{eq} = \frac{1}{\rho} \times \frac{1000}{N}$$

$$\Lambda_{eq} = \frac{l}{RA} \frac{1000}{N}$$

$$100 = \frac{0.5 \times 1000}{R \times 1 \times 0.1} \quad (5)$$

$$R = 50\ \Omega$$

$$V = IR$$

$$I = \frac{V}{R} = \frac{5}{50} = \frac{1}{10} = 0.1\ A$$

Ques The conductance of 0.1N NaOH sol^n is 0.022 S cm^{-1}. When equal vol. of 0.1N HCl sol^n is added. The conductivity of resultant sol^n is decreased to 0.0055 S cm^{-1} then calc. eq. conductance of resultant

$$\underset{0.1N}{NaOH} + \underset{0.1N}{HCl} \longrightarrow \underset{0.1N}{NaCl}$$

$G_1 = 0.22$

Λm

$N = \frac{0.1}{2} = 0.05$

$$\Lambda_{eq} = \frac{K \times 1000}{N} \qquad \frac{1}{R} = G = 0.0055$$

$$= \frac{0.0055 \times 1000}{0.05} \qquad \Lambda_m \times \frac{1}{1000}$$

$$\Lambda_{eq} = 110$$

Factors affecting Electrolytic conductance :-

1. Ionic interaction :- Conductance ↓
2. Nature of Solvent : Dielectric const ↑ ionisation ↑ cond. ↑
3. Viscosity of medium Viscosity ↑ cond. ↓
4. Solvation / Hydration of ions :

Hydration ↑ cond ↓

LiCl NaCl KCl RbCl CsCl

size ↑ hydration ↓ cond. ↑

5. Effect of Dilution : As dilution ↑ses, cond. ↑

For strong electrolyte ($K = 1$) as dilution ↑ ion interaction ↓ cond ↑

For weak electrolyte ($\alpha < 1$) as dilution ↑ α ↑ cond ↑

Dilution:

Molar conductance (Λm)

$$\Lambda m = K \times \frac{1000}{M}$$

dilution ↑ V ↑ M ↓ Λm ↑

Eq. conductance (Λeq)

$$\Lambda eq = K \times \frac{1000}{N}$$

dilution ↑ V ↑ N ↓ Λeq ↑

Sp. conductance

Conductance for 1 cm^3 volⁿ

dilution ↑ no. of ions per unit Vol. ↓ cond ↓

Molar conductance at infinite dilution & zero concⁿ :-

Debye Huckle Onsgar eqⁿ :-

$$\Lambda m = \Lambda_m^\circ - b\sqrt{c}$$

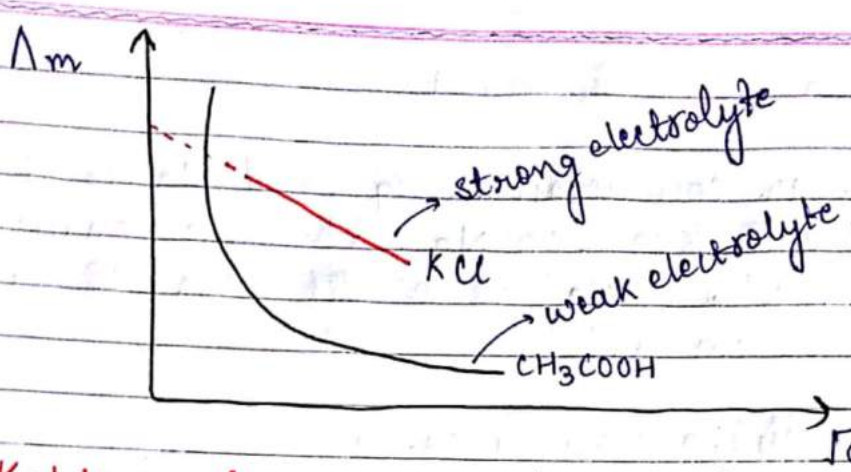
Λm → Molar conductance at any conc.

Λ_m° or Λ_m^∞ → Molar conductance at infinite dilution or zero concⁿ.

b → Debye const.

↳ at const temp, it is same for same type of electrolyte.

NaCl	1 : 1 electrolyte
KCl	1 : 1
$MgCl_2$	2 : 1
Na_2SO_4	1 : 2
$MgSO_4$	2 : 2



Kohlrausch law of Independent migration

It states that molar conductivity of an electrolyte at infinite dilution is sum of individual molar conductance of cation & anion.

$$\Lambda^\circ_m \text{ or } \Lambda^\infty_m = \lambda^\circ_+ + \lambda^\circ_-$$

$$\Lambda^\circ_{m\,NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

↑ molar cond. of Na^+ at ∞ dil.

generally, If ν_+ cations & ν_- anions are +nt in electrolyte.

$$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$$

eg $\Lambda^\circ_{m\,MgCl_2} = \lambda^\circ_{Mg^{2+}} + 2\lambda^\circ_{Cl^-}$

$$\Lambda^\circ_{eq} = \lambda^\circ_{+eq} + \lambda^\circ_{-eq}$$

$$\Lambda^\circ_{eq} = \frac{\Lambda^\circ_m}{V.F.}$$

Ques The ionic conductance of Mg^{2+} & Cl^- at ∞ dilution are 110 & 76 $S\,cm^2\,mol^{-1}$. Cal. molar & eq. cond. of $MgCl_2$ at ∞ dilution?

Λ°_m = ~~Λm~~ do 110 + 2×76

= 110 + 152 = 262

$$\Lambda^{\circ}_{eq} = \frac{262}{2} = 131$$

Ques Calc. molar conductance & eq. conductance at ∞ dil^{n} of salt KOOC.COONa. The ionic conductance of $C_2O_4^{2-}$, K^+ & Na^+ at ∞ dil^{n} are 148.2, 50.2, 73.74 $\Omega^{-1} cm^2 mol^{-1}$

$$\Lambda_m = 148.2 + 50.2 + 73.74$$
$$= 272.14$$

$$\Lambda_{eq} = \frac{272.14}{2} = 136.07$$

Application of Kohlrausch law:

To determine molar conductance for weak electrolyte:

$$\Lambda^{\circ}_{CH_3COOH} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+}$$

$$\Lambda^{\circ}_{CH_3COONa} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+} \quad — (1)$$

$$\Lambda^{\circ}_{HCl} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-} \quad — (2)$$

$$\Lambda^{\circ}_{NaCl} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-} \quad — (3)$$

(1) + (2) − (3) $\quad \Lambda^{\circ}_{CH_3COONa} + \Lambda^{\circ}_{HCl} - \Lambda^{\circ}_{NaCl} = \lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{H^+}$

To calculate D.O.D. (α)

$$\alpha = \frac{\text{molar cond. at conc}^{n}\ C}{\text{molar cond. at } \infty \text{ dilution or zero conc}^{n}}$$

$$\alpha = \frac{\Lambda^{c}_{m}}{\Lambda^{\infty}_{m}}$$

or $$\alpha = \frac{\Lambda^{c}_{eq}}{\Lambda^{\infty}_{eq}}$$

To determine calculate ionisation const :-

eq : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

	C	0	0
	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$K_a \approx C\alpha^2$$

Ques Limiting molar conductivity of NH_4OH i.e. $\Lambda^\circ_m (NH_4OH)$ is equal to

(1) $\Lambda^\circ_m (NH_4Cl) + \Lambda^\circ_m (NaCl) - \Lambda^\circ_m (NaOH)$
(2) $\Lambda^\circ_m (NaOH) + \Lambda^\circ_m (NaCl) - \Lambda^\circ_m (NH_4Cl)$
(3) $\Lambda^\circ_m (NH_4OH) + \Lambda^\circ_m (NH_4Cl) - \Lambda^\circ_m (HCl)$
(4) $\Lambda^\circ_m (NH_4Cl) + \Lambda^\circ_m (NaOH) - \Lambda^\circ_m (NaCl)$

Ques Equivalent conductance of NaCl, HCl & C_2H_5COONa at ∞ dil^ are 126.45, 426.16 & 91 Ω^{-1} cm^2 resp. Calc. eq: cond. of C_2H_5COOH

(1) 201.28 Ω cm^2 (2) 390.71 $\Omega^{-1}cm^2$ (3) 698.28 Ω cm^2 (4) 340.48 $\Omega^{-1}cm^2$

$$\Lambda^\circ_{eq\ C_2H_5COOH} = -\Lambda_{eq\ NaCl} + \Lambda_{eq\ HCl} + \Lambda_{eq\ C_2H_5COONa}$$
$$= -126.45 + 426.16 + 91$$
$$= -126.45 + 517.16$$
$$= 390.71$$

517.16
126.45
390.71

Ques The molar conductance of an ∞ dilution sol^n of NH_4Cl is 150 $\Omega^{-1}cm^2 mol^{-1}$ & ionic conductance of $[OH^-]$ & $[Cl^-]$ ions 198 & 76 $\Omega^{-1}cm^2 mol^{-1}$, what will be the molar cond. of NH_4OH at ∞ dil if conductivity of 0.01 M sol^ of NH_4OH is 9.52×10^{-5} Ω^{-1} cm^2 also cal. D.O.D.

$\Lambda^\infty_m\ NH_4Cl = 150$ $\quad$ $K = 9.52 \times 10^{-5}$

$\Lambda_{OH^-} = 198$ $\quad$ $\Lambda_{Cl^-} = 76$ $\quad$ $M = 0.01$

$\Lambda^{\infty}_{NH_4OH} = \Lambda_{NH_4Cl} + \Lambda_{OH^-} - \Lambda_{Cl^-}$

$= 150 + 198 - 76$

$= 348 - 76 = 272$

$\Lambda^{c}_{NH_4OH} = K \times \frac{1000}{M}$

$= 9.52 \times 10^{-5} \times \frac{1000}{0.01} \times 100$

$= 9.52$

$\alpha = \frac{9.52}{272} \times \frac{100}{100}$

$= 3.5\%$

Ques The eq. conductance of M/32 soln of weak monobasic acid is 8 mho cm^2 & at ∞ dil^n is 400 mho cm^2. The dissociation const. of this acid is -

① 1.25×10^{-5} ② 1.25×10^{-6} ③ 6.25×10^{-4} ④ 1.25×10^{-4}

$\alpha = \frac{8}{400} = 0.02$

$K = C\alpha^2$

$= \frac{1}{32} \times \frac{2}{16} \times \frac{2}{8} \times 10^{-4} = 0.1 \times 10^{-4} = 1.25 \times 10^{-5}$

To determine solubility of sparingly soluble salt.

eg AgCl, $BaSO_4$

Saturated soln of a sparingly soln can be considered as ∞ dil.^{n}

Saturated sol^n = ∞ diluted sol^n

$$\Lambda_m^\infty = K \times \frac{1000}{S}$$

M = Solubility
M = S at ∞ dilution

Ques Conductivity of a saturated sol^n of AgCl is $2.2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ & conductivity of water is $0.8 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. If at ∞ dil^n molar conductance of $AgNO_3$, HCl & HNO_3 are 135, 426 & 421 $\Omega^{-1} cm^2\ mol^{-1}$ resp. Calculated solubility & solubility product.

$K_{AgCl} = 2.2 \times 10^{-6}$ $K_{H_2O} = 0.8 \times 10^{-6}$

$$\Lambda_m\ AgCl = \Lambda_{AgNO_3} + \Lambda_{HCl} - \Lambda_{HNO_3}$$
$$= 135 + 426 - 421$$
$$= 561 - 421 = 140$$

$$K_{AgCl} = K_{AgCl\ sol^n} - K_{H_2O}$$
$$= 2.2 \times 10^{-6} - 0.8 \times 10^{-6}$$
$$= 10^{-6}(2.2 - 0.8)$$
$$= 10^{-6}(1.4)$$
$$= 1.4 \times 10^{-6}$$

$$\Lambda_m = K \times \frac{1000}{S}$$

$$140 = 1.4 \times 10^{-6} \times \frac{10^3}{S}$$

$$S = \frac{1.4 \times 10^{-3}}{140} \times 10 = 10^{-5}$$

$$K_{sp} = S^2$$
$$= 10^{-10}$$

Electrochemical Cell :-

Galvanic cell
Chemical reac^n takes place
Δ E.E. is produced.

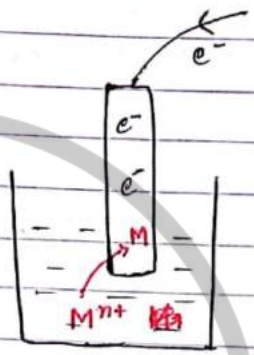
Electrolytic cell
In this cell chemical reac^n takes place when electricity is passed.

Galvanic Cell :-

1. Reduction

$M^{n+} + ne^- \rightarrow M$

$E_{M^{n+}/M} \rightarrow$ R.P.



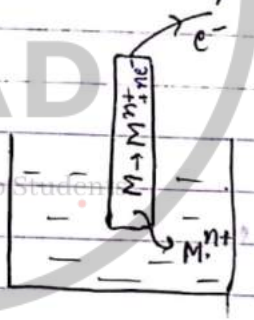
If Std. cond^n :-
P = 1 atm
C = 1M
T = any (generally → 25°C)

$E^\circ_{M^{n+}/M} \rightarrow$ SRP

Oxidation

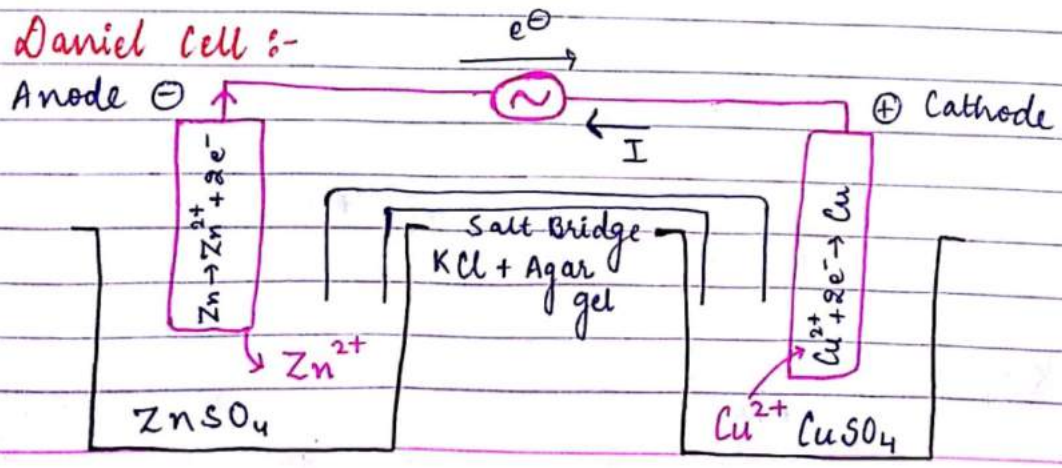
$M \rightarrow M^{n+} + ne^-$

$E_{M/M^{n+}} \rightarrow$ O.P.



If Std. cond^n
$E^\circ_{M/M^{n+}} \rightarrow$ SOP

Daniel Cell :-



Left → anode
charge = −ve

$\begin{bmatrix} e^{\ominus} & L \to R \\ I & R \to L \end{bmatrix}$

Right = cathode
charge = +ve

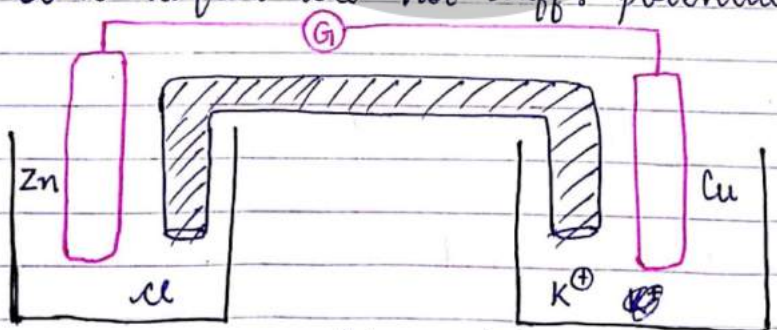
Oxidation
Wt. of zinc Rod ↓
$[Zn^{2+}]$ ↑ in sol^{n}
$[SO_4^{2-}]$ same

Reduction
Wt. of Cu Rod ↑
$[Cu^{2+}]$ ↓
$[SO_4^{2-}]$ same

Salt Bridge :- In salt bridge, Agar or gelatin is dissolved in hot & conc^{n} inert solvent like KCl, NH_4NO_3 etc. After that we make a paste & fill it in a U-shaped glass tube. This U-shaped glass tube is placed inverted b/w 2 vessels.

→ In salt brigde, cationic & anionic mobility must be similiar

Functions of Salt Bridge :-
- It complete the electric circuit.
- Avoids mechanical mixing.
- Maintain electrical neutrality in both vessels.
- It avoids liquid - liquid Junction Potential (∵ both liquid are not diff. potential)



Cell Represented
$Zn/Zn^{2+}||Cu^{2+}/Cu$
↓
Salt Bridge

anode : $Zn \rightarrow Zn^{2+} + 2e^-$
cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
Cell Reac^{n} : $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

E.M.F.

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

$E_{Zn^{2+}/Zn} = -0.76\ V$
$E_{Cu^{2+}/Cu} = +0.34\ V$

जिसका red. Potential बड़ा ✓ उसका red. होगा (cathode बनेगा)

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$
$$= 0.34 - (-0.76)$$
$$= 1.1\ V$$

Acc^n to IUPAC, std. reduction Potential is considered std. electrode Potential

Oxid. Potential = - red. Potential

ex $E^\circ_{cell} = ?$ $E^\circ_{Fe^{2+}/Fe} = -0.44\ V$ (oxid) $E^\circ_{Ag^+/Ag} = +0.80\ V$ (red)
red. Potential ज्यादा

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

Anode ⇒ $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode ⇒ $2Ag^+ + 2e^- \longrightarrow 2Ag$

$Fe + 2Ag^+ \longrightarrow Fe^{2+} + 2Ag$

$Fe(s) \mid Fe^{2+}(aq.) \parallel Ag^+(aq) \mid Ag(s)$

$E^\circ_{cell} = 0.80 - (-0.44) = 1.24\ V$

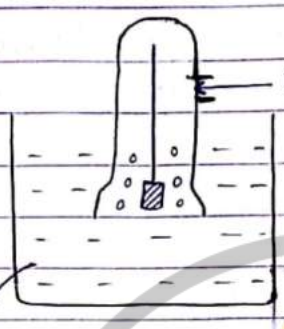
Electrode Potential depend on :-

1. Temp.
2. Nature of Electrode
3. Conc^n of ions.

Imp Ag^+, F_2, Br_2, Ag^+, Fe^{3+}, Cu^+, Cu^{2+}, Pb^{2+}, Ni, H_2

Reference Electrode (Hydrogen Electrode) (SHE)

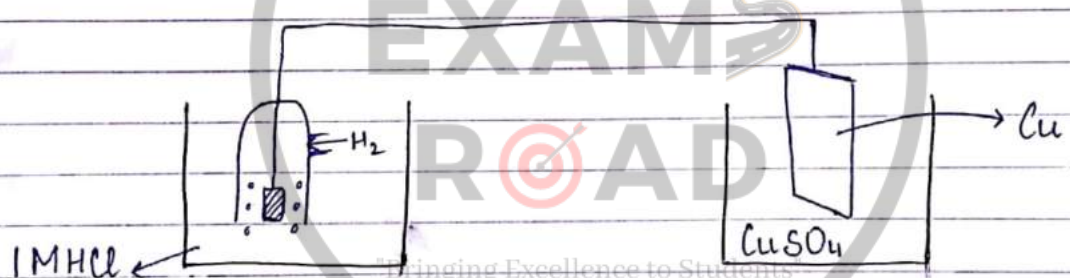
Acc^n to IUPAC :- Std. ~~Potential~~ Electrode Potential of Hydrogen electrode is assumed to be zero.



$Pt / H_2(g) / H^+(1M)$

As Anode :- $H_2 \rightarrow 2H^+ + 2e^-$ (oxid.)

As cathode :- $2H^+ + 2e^- \rightarrow H_2$ (red.)



$E^\circ_{cell} = E^\circ_R - E^\circ_L$

$E^\circ_{cell} = E^\circ_R - 0$

$E^\circ_{cell} = E^\circ_R$

for Cu = 0.34 V
Zn = − 0.76 V
] SRP for diff. electrode

$Pt / H_2(g) / H^+(1M) // M^{n+}(1M) / M$

*** Element below H_2 work as reducing agent & above element work as oxidising agent in electrochemical Series.

* जितना ज्यादा negative electrode Potential or Reduction Potential उतना ही Strong reducing agent.

* जितना ज्यादा +ve electrode Potential or oxidation Potential उतना ही strong oxidising agent.
  Strong oxidising Agent = F
  Strong Reducing Agent = Li
* Electrochemical Series मे ऊपर जाने पर Reduction Potential की Value ↑es होती है i.e. metal की Reducing Power ↓es होती है (e⁻ देने की tendency ↓se होती है)

E.C.S.

imp ✓ $F_2 + 2e^- \rightarrow 2F^{\ominus}$ ⊕ve value

✓ Au
  ⟶ Cl
  ⟶ O_2
✓ Pt
✓ Ag
  ⟶ Br_2
  Hg
  ⟶ I_2
✓ Cu
✓ H_2
✓ Pb
✓ Sn
✓ Ni
  =
✓ Fe
✓ Cr
✓ Zn
  -
✓ Al
✓ Mg
✓ Na
  Ca
  Ba
✓ Li
— ⊖ve value

Oxidising Power ↓
Reducing Power ↑
Reactivity of metal ↑

Ques Which of following weakest Reducing agent ?
① $F^{\ominus}$ ② $Br^{\ominus}$ ③ $Cl^{\ominus}$ ④ $I^{\ominus}$

Acc^n to Electrochemical Series anode is made up of lower elemen of (E.C.S.) and cathode is made up of upper element of E.C.

★ Oxide of metal which are placed above Cu are unstable and easly reduced to metal when heated.

Oxidising Power Halogens : $F_2 > Cl_2 > Br_2 > I_2$
Reducing Character of Halides = $HF < HCl < HBr < HI$

Halide Replacement :-

$Br_2 + 2KI \longrightarrow 2KBr + I_2$
$Cl_2 + 2KI \longrightarrow 2KCl + I_2$
$F_2 + 2KI \longrightarrow 2KF + I_2$
$F^{\ominus} \longrightarrow F_2$ ×
$Cl^{\ominus} \longrightarrow Cl_2$ F_2 ✓
$Br^{\ominus} \longrightarrow Br_2$ F_2, Cl_2 ✓
$I^{\ominus} \longrightarrow I_2$ F_2, Cl_2, Br_2 ✓

Ques which of following reac^n is spontaneous ?
1. $\overset{0}{Br_2} + KF \longrightarrow \overset{-1}{KBr} + F_2$
2. $Cl_2 + KI \longrightarrow KCl + I_2$
3. $KCl + Br_2 \longrightarrow KBr + \overset{0}{Cl_2}$
4. $KF + Cl_2 \longrightarrow KCl + F_2$

Ques Identify which process is spontaneous or not.
1. $Zn + CuSO_4 \rightarrow \overset{+2}{Zn}SO_4$.
2. $Fe + CuSO_4 \rightarrow \overset{+2}{Fe}SO_4 + Cu$
3. $2Ag + CuSO_4 \rightarrow \overset{+1}{Ag}_2SO_4 + Cu$
4. $Pb + SnCl_2 \rightarrow \overset{+2}{PbCl_2} + \overset{0}{Sn}$
5. $Al + ZnSO_4 \rightarrow Al_2(SO_4)_3 + Zn$

Ques Arrange following metal in ↑ order of reducing Power.

	X	Y	Z	W
$E_{M^{n+}/M}$	+0.3	−0.134	−2.05	+2.05

W < X < Y < Z

Ques Identify strongest Oxidising Agent.
① Fe^{2+} ② Cu^{2+} ③ Zn^{2+} ④ Ag^{+}

Ques Identify strongest oxidising Agent.
① Li^{+} ② Zn^{2+} ③ Cu ④ Ag
(Cu, Ag — do not Reactively)

Ques Arrange in Torder of S.O.P.
① $2A^{\ominus} + B_2^{\circ} \rightarrow 2B^{-} + A_2^{\circ}$
② $2C^{\ominus} + B_2 \rightarrow$ ~~3C~~
③ $2D^{\ominus} + A_2^{\circ} \rightarrow 2A^{-} + D_2^{\circ}$

B < C < A < D

Displacement of Hydrogen :-

Metal which is placed below Hydrogen can easily displace H_2 gas from aq. sol^n of acid.

eg: $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
$Li + HCl \rightarrow LiCl_3 + H_2$

Displacement of Hydrogen from water :-

* Metal which are placed below Mg can easily displace H_2 gas from water. Metal from Mg to Cr can displace H_2 from ~~hot~~ hot water.
* Fe can displare H_2 from water steam.

Ques Arrange following in ↑ order of SRP.

① $A + H_2SO_4 \rightarrow ASO_4 + H_2$

② $C + ACl_2 \rightarrow CCl_2 + A$

③ $C + ECl_2 \rightarrow X$

④ $D + 2BCl_2 \rightarrow DCl_2 + 2B$

⑤ $D + H_2SO_4 \rightarrow X$

$E^\circ < C < A < H_2SO_4 < D < B$

Nerst Equation:- It is use to calculate electrode potential or emf of cell.

We calculate std. Electrode Potential (E°) at std. condⁿ ⇒ 25°C / 1 bar / 1M

If std. condⁿ are not given :-

$M^{n+}(aq) + ne^\ominus \rightarrow M(s)$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$[M] = 1$ solid

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

R = Universal gas const. = 8.314 J/K/mol

T = Temp. (K)

n = no. of $e^\ominus$

F = Faraday const. = 96487 C mol^{-1}

≈ 96500 C mol^{-1}

For Daniel Cell :-

$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq.)$

anode = $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^\ominus$

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303RT}{2F} \log \frac{1}{[Zn^{2+}]}$$

cathode :- $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{2.303RT}{2F} \log \frac{1}{[Cu^{2+}]}$$

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

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

$$E_{cell} = E^{\circ}_{Cu^{2+}/Cu} - \frac{2.303RT}{2F}\log\frac{1}{[Cu^{2+}]}$$

$$= E_{Zn^{2+}/Zn} + \frac{2.303RT}{2F}\log\frac{1}{[Zn^{2+}]}$$

$$E_{cell} = (E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Zn^{2+}/Zn})$$

$$= -\frac{2.303RT}{2F}\log\frac{1}{[Cu^{2+}]} + \frac{2.303RT}{2F}\log\frac{1}{[Zn^{2+}]}$$

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Que $Ni \mid Ni^{2+} \,||\, Ag^{+} \mid Ag$

$$Ni + 2Ag^{+} \rightarrow 2Ag + Ni^{2+}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{2F}\log\frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

For a reacⁿ :- $aA + bB \rightarrow cC + dD$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303}{nF}RT\log a$$

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

at 298 K R, F

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}}$$

For Daniel Cell :-

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

$$\boxed{E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Application of Nerst Equation :-

1. To calculate electrode Potential.

$$M^{n+} + ne^- \longrightarrow M(s)$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

Ques Calculate electrode potential of Cu if Cu electrode is dipped to 0.1 M $CuSO_4$ at 25°C. The std. electrode Potential of Cu^{2+}/Cu is 0.34 V

Ques A piece of Zn metal is dipped in 0.1 M sol^n of $ZnSO_4$. The salt is dissociated to the extent of 20%. Calculate that electrode Potential of Zn if $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

Ques Calculate change in electrode Potential of Zn/Zn^{2+} if sol^n is diluted upto 10 times?

Let initial conc^n of $[Zn^{2+}] = 1$

then $(E_{Zn^{2+}/Zn})_1 = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{1}$

$(E_{Zn^{2+}/Zn})_1 = E^\circ(Zn^{2+}/Zn) \Rightarrow E_{Zn/Zn^{2+}} = -E^\circ_{Zn^{2+}/Zn}$

diluted upto 10 times

$[Zn^{2+}] = \frac{1}{10} M$

$E(Zn^{2+}/Zn)_2 = -E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2} \log \frac{1}{1/10}$

$= E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2}$

$(E_{Zn/Zn^{2+}})_2 = -E^\circ_{Zn^{2+}/Zn} + \frac{0.0591}{2}$

$(E_{Zn/Zn^{2+}}) = (E_{Zn/Zn^{2+}})_1 = \frac{0.0591}{2}$

2. To calculate Electrode Potential of Hydrogen electrode :-

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

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

$$E_{cell} = -\frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

at atm. press. = 1 atm

$$E_{H^+/H_2} = -\frac{0.0591}{2} \log_{10} \frac{1}{[H^+]^2}$$

$$E_{H^+/H_2} = 0.0591 \log_{10} [H^+]$$

$$E_{H_2/H^+} = -0.0591 \log [H^+]$$

Ques Calc. electrode Potential of Hydrogen electrode when pH of acidic sol^n is 3 HCl/H_2 (10atm)/Pt

$$pH = 3 \qquad [H^+] = 10^{-3}$$

$$E_{H^+/H_2} = -\frac{0.0591}{2} \log \frac{10}{[10^{-3}]^2}$$

$$= -\frac{0.0591}{2} \times \log 10^7$$

$$= -\frac{0.0591}{2} \times 7 = -\frac{0.4137}{2} = -0.2068 = -0.0591 \times 4 = -0.2364$$

Ques A Hydrogen gas electrode is made by dipping Platinum wire in a sol^n of HCl of pH 10 & passing H_2 gas around the Pt wire at 1 atm Pr. The oxi. Potential of electrode would be -

(a) 0.059 V (b) 0.59 V (c) 0.118 V (d) −0.591 V

$$pH = 10 \qquad [H^+] = 10^{-10}$$

$$E_{H_2/H^+} = -0.0591 \log_{10} 10^{-10}$$

$$= +0.0591 \times 10$$

$$= 0.59$$

3. To calculate E_{cell}

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

Ques The red. Potential for the following half cell reaction are

$Zn \longrightarrow Zn^{2+} + 2e^-$ $\quad E^\circ_{Zn^{2+}/Zn} = -0.76\,V$

$Fe \longrightarrow Fe^{2+} + 2e^-$ $\quad E_{Fe^{2+}/Fe} = -0.44\,V$

find the emf for cell reaction

$Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$

$E^\circ_{Zn/Zn^{2+}} = 0.76\,V$

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

$= 0.76 - (-0.44) = 0.76 + 0.44 = 1.20$

Ques The std. oxi. potential of Zn & Cu are 0.76 V & -0.34 V resp. Calc. emf of following cell

1.39V

$Zn / ZnSO_4 \,(0.01M) \,||\, CuSO_4 \,(0.1M) / Cu$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[anode]}{[cathode]}$$

$$= 1.10 - \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-1}}$$

$$= 1.10 + \frac{0.0591}{2} \log 10$$

$$= 1.10 + 0.029$$

0.76 + 0.34

1.10

Que Calc. emf of cell

$Cu / Cu^{2+}(0.001M) \,||\, Cu^{2+}(0.1M) / Cu$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-1}}$ $\quad 10^{-2}$

$= + \frac{0.0591 \times 2}{2} \log 10$

$= 0.0591$

Que Calc. emf of cell $Ni / Ni^{2+}(0.1M) \,||\, Ag^+(0.1M) / Ag$

given $E_{Ag^+/Ag} = 0.80V$ $\quad E_{Ni^{2+}/Ni} = -0.25V$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{10^{-1}}{(10^{-1})^2}$ $\quad -0.25 - 0.80 = +1.05$

$= 1.05 - \frac{0.0591}{2} \log 10$

$= 1.05 + 0.0295$

$= 1.087$

$Ni \rightarrow Ni^{2+} + 2e^-$

$2Ag^+ + 2e^- \rightarrow 2Ag$

Que Calculate emf $Al / Al^{3+}(10^{-2}M) \,||\, Co^{2+}(10^{-1}M) / Co$

$E^\circ_{Al^{3+}/Al} = -1.66\,V$ $\quad E^\circ_{Co^{2+}/Co} = -0.20\,V$

$2Al \rightarrow 2Al^{+3} + 6e^-$

$3Co^{2+} + 3 \times 2e^- \rightarrow 3Co$

Que $Pt(s) / Br_2(l) \,||\, Br^-(0.01M) \,||\, H^+(0.01M) / H_2(g)\,1bar / Pt$

$E_{Pt/Br_2/Br^-} = 1.09\,V$ $\quad E_{cell} = ?$

$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Br_2/Br^-}$
$= 0 - 1.09 = -1.09\ V$

$2Br^- \rightarrow Br_2 + 2e^-$
$2H^+ + 2e^- \rightarrow H_2$

$$E^\circ_{cell} = -\frac{0.0591}{2} \log \frac{[Br_2][P_{H_2}]}{[Br^-]^2[H^+]^2}$$

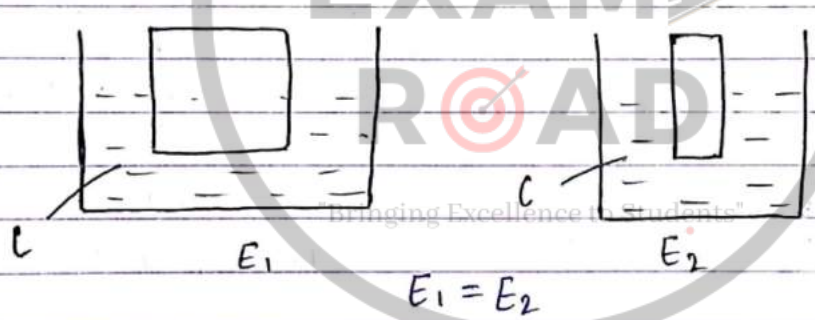
Note:

1. For a given electrode, Electrode Potential does not change when reacⁿ is multiplied or divided by coefficient.

$X_2 + 2e^- \rightarrow 2X^-$ $\quad E_{X_2/X^-} = a\ V$

$\frac{1}{2}X_2 + e^- \rightarrow X^-$ $\quad E_{X_2/X^-} = a\ V$

2. Value of Electrode Potential does not depend upon size of electrode and amt. of solⁿ but depends upon concⁿ of solⁿ.
3. Electrode Potential is an intensive property.



$E_1 = E_2$

Eqᵐ constant for Nernest Eqⁿ :-

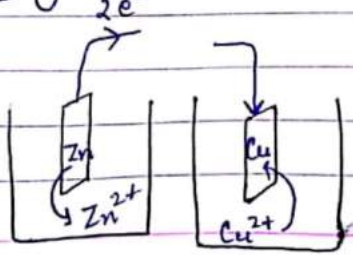
eg In Daniell Cell :- $[Zn^{2+}]$ ↑ & $[Cu^{2+}]$ ↓ continuou

After some $[Zn^{2+}]$ = const. $[Cu^{2+}]$ = const] state of eqⁿ.

↳ no flow of $e^\ominus$ emf of cell = 0

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$0 = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$



Reduction Potential ↑ → Cathode

$E^\circ_{cell} = \frac{0.0591}{2} \log_{10} K_c$

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$

$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

In Generally $E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K_c$

Ques Calc. the eqm const. for the reacⁿ

$Fe(s) + 2Ag^+(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$

$E^\circ_{Ag^+/Ag} = 0.80V$ & $E^\circ_{Fe/Fe^{2+}} = 0.44V$

$E^\circ_{cell} = 0.80 - (-0.44) = 1.24$

$E^\circ_{cell} = \frac{0.0591}{2} \log K_c$

$\frac{1.24 \times 2}{0.06} = \log K_c$

$\frac{2.48}{0.06} \times 100 = \frac{248}{6} = \log K_c = 41$

$K_c = 10^{41}$

Ques $Ag + I^- \rightarrow AgI + e^-$ $E^\circ = 0.152\ V$

$Ag \rightarrow Ag^+ + e^-$ $E^\circ = -0.80\ V$

Find Ksp of AgI

$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.80\ V$

$E^\circ_{cell} = 0.80 - 0.152 = \frac{0.0591}{1} \log \frac{[Ag^+][I^-]}{[AgI]^1}$

$\frac{0.648}{0.06} = \log [Ag^+][I^-]$

$108 \frac{648 \times 10^{-2}}{6 \times 10^{-3}} = 10.8 = \log K_c$

$K_c = 10^{10.8}$

Electrochemical Cell & Gibbs free Energy :-

useful work (electrical work done) — non useful work (mechanical)

$W_{electrical}$ = Charge ⊕ ⊖ × Potential

$= q \times E_{cell}$

$W_{electrical} = nFE_{cell}$

$\Delta G = -W_{electrical}$

$\Delta G = -nFE_{cell}$

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

$1e^- = 1.6 \times 10^{-19}\ C$

$1\ mole^- = 6.022 \times 10^{23} \times 1.6 \times 10^{-19}\ C$

$= 96487\ C$

$1F \simeq 96500\ C$

n mol e^- = nF

charge of 'n' mol e^- = $q = nF$

$\Delta G = \Delta G^\circ + 2.303\ RT \log_{10} Q$

$-nFE_{cell} = -nFE^\circ_{cell} + 2.303\ RT \log_{10} Q$

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log_{10} Q}$$

$\Delta G = -nFE_{cell}$

spont. $\Delta G < 0$ $\Delta E_{cell} > 0$

non spont. $\Delta G > 0$ $\Delta E_{cell} < 0$

at ⇌ $\boxed{\Delta G = 0}$ $\boxed{E_{cell} = 0}$

$$0 = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log_{10} K_c$$

$$\boxed{E^\circ_{cell} = \frac{2.303\ RT}{nF} \log_{10} K_c}$$

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

$$\boxed{\Delta G^\circ = -2.303\ RT \log_{10} K_c}$$

$\Delta G^\circ < 0$	$\log K_c > 0$	$K_c > 1$
$\Delta G^\circ > 0$	$\log K_c < 0$	$K_c < 1$
$\Delta G^\circ = 1$	$\log K_c = 0$	$K_c = 1$

AIPMT-11

Date _____ Page ____

Ques The electrode Potential for

$Cu^{2+}(aq) + e^- \rightarrow Cu^+$ $\Delta G_1 = -1 \times F \times 0.15$

$Cu^+(aq) + e^- \rightarrow Cu(s)$ $\Delta G_2 = -1 \times F \times 0.5$ are +0.15 V & 0.50 V resp.

Then value of $E^\circ_{Cu^{2+}/Cu}$ will be

(1) 0.325 V (2) 0.650 V (3) 0.150 V (4) 0.500 V

$E_{Cu^{2+}/Cu^+} = 0.15$

$E_{Cu^+/Cu} = 0.50$

$E_{Cu^{2+}/Cu} = 0.15 + 0.50 = 0.65$

$\Delta G_1 + \Delta G_2 = \Delta G_3$

$-1 \times F \times 0.15 - 1 \times F \times 0.5 = -2 \times F \times E_{Cu^{2+}/Cu}$

$0.65 = 2 E_{Cu^{2+}/Cu}$

AIPMT-14

Ques For the reduction of silver ions with copper metal, the std. cell potential was found to be +0.46 V at 25°C. find the value of ΔG°? $F = 96500\ C\ mol^{-1}$

(1) -0.89 KJ (2) -89.0 J (3) -44.5 KJ (4) -98.0 KJ

$E_{cell} = 0.46$

$2Ag^+ + 2e^- \rightarrow 2Ag$

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

$\Delta G^\circ = -nFE_{cell}$

$= -2 \times 96500 \times 0.46$

$= -$

96500 × 3 = 579000

Ques $\frac{4}{3}Al + O_2 \rightarrow \frac{2}{3}Al_2O_3$ $\Delta G = -827$ KJ mol^{-1}

Find the min^m emf req^d to carry the electrolysis of Al_2O_3? ($F = 96500\ C\ mol^{-1}$)

$\Delta G = -nFE_{cell}$

$-827000 = -4 \times 96500 \times E_{cell}$

$Al \rightarrow Al^{3+} + 3e^-$

$n = \frac{4}{3} \times 3 = 4$

AIPMT - 97, 04

Ques $Zn / Zn^{2+} \| Cu^{2+}(aq) | Cu$ $E^\circ_{cell} = 1.10\ V$ at 25°C
The eqm const. for the reach
$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$ it is of the order.

① 10^{37} ② 10^{28} ③ 10^{18} ④ 10^{17}

$$E^\circ_{cell} = \frac{2.303\,RT}{nF} \log_{10} K_c$$

$$1.10 = \frac{2.303 \times 0.08 \times 300}{2 \times 96500} \log_{10} K_c$$

$$\frac{1.10 \times 2 \times 96500}{2.303 \times 0.08 \times 3000} = \log_{10} K_c$$

$$\frac{1 \times 1 \times 100 \times 965}{2 \quad 4 \quad 3}$$

Ques $Cu^+(aq)$ is unstable in sol^n undergoes simultaneous oxidation & reduction ace^n to the reac^n
$2Cu^+(aq) \rightleftharpoons Cu^{+2}(aq) + Cu(s)$
Find E°_{cell}
If $E_{Cu^{2+}/Cu} = 0.34\ V$ & $E^\circ_{Cu^{2+}/Cu^+} = 0.15\ V$

$Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad E^\circ_{Cu^{2+}/Cu} = 0.34\ V$
$Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad E^\circ_{Cu^{2+}/Cu^+} = 0.15\ V$
$Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad \Delta G_1 = -2 \times F \times 0.34$
$Cu^+ \longrightarrow Cu^{2+} + e^-$ $\quad \Delta G_2 = -2 \times F \times (-0.15)$
$Cu^+ + e^- \longrightarrow Cu$ $\quad \Delta G_3 = \Delta G_1 + \Delta G_2$

$$-1 \times F \times E_{Cu^+/Cu} = -2 \times F \times 0.34 + 2 \times F \times 0.15$$

$$E_{Cu^+/Cu} = 0.34\ V$$

$Cu^+(aq) \longrightarrow Cu(s)$ $\quad \Delta G_3 = -1 \times F \times 0.34\,V$

$Cu^+(aq) \longrightarrow Cu^{2+}(aq)$ $\quad \Delta G_4 = -1 \times F \times (-0.15\,V)$

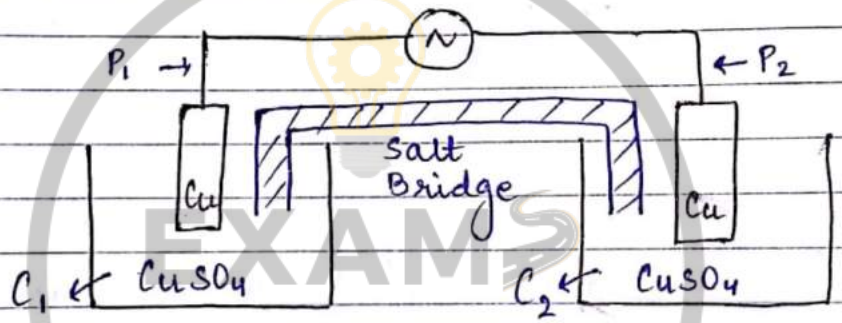
$2Cu^+ \rightarrow Cu + Cu^{2+}$ $\quad \Delta G_1 = \Delta G_3 + \Delta G_4$

$-1 \times F \times E^\circ = -1 \times F \times 0.34 + 1 \times F \times 0.15$

$+E^\circ = +0.19\,V$

Concentration Cell :-

When 2 similiar electrode with different conc^n of electrolytic sol^n are connected then cell is called conc^n cell.



anode : $Cu(s) \longrightarrow Cu^{2+}(aq)$ $\quad E^\circ_{Cu/Cu^{2+}} = +x$

cathode : $Cu^{2+}(aq) \rightarrow Cu(s)$ $\quad E^\circ_{Cu^{+2}/Cu} = -x$

$E^\circ_{cell} = c - a$

$= -x - (-x) = 0$

E°_{cell} for conc^n cell is always zero.

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{(anode)}{(cathode)}$$

$$E_{cell} = -\frac{0.0591}{2} \log \frac{C_1}{C_2}$$

$$\boxed{E_{cell} = +\frac{0.0591}{2} \log \frac{C_2}{C_1}}$$

$E_{cell} > 0 \quad \log \frac{C_2}{C_1} > 0 \quad \frac{C_2}{C_1} > 1$

$C_2 > C_1$

at $t = t$ $\quad E_{cell} = \frac{0.0591}{2} \log \frac{C_2 - x}{C_1 + x}$

if $E_{cell} = 0$ $\quad \frac{C_2 - x}{C_1 + x} = 1$

$C_2 - x = C_1 + x$

$x = \frac{C_2 - C_1}{2}$

Appln of Conc^n cell :-

$Pt \,/\, H_2 \,/\, H^+(aq) \;//\; H^+(aq) \,/\, H_2$

$P_1 \quad C_1 \qquad\qquad C_2 \quad P_2$

anode : $H_2(P_1) \rightarrow \underset{C_1}{2H^+} + 2e^- \quad E^\circ_{H_2/H^+} = 0$

$2H^+ + 2e^- \rightarrow H_2 \; P_2 \quad E^\circ_{H^+/H_2} = 0$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{(C_1)^2 P_2}{P_1 (C_2)^2}$

$$\boxed{E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2} \left(\frac{C_2}{C_1}\right)^2}$$

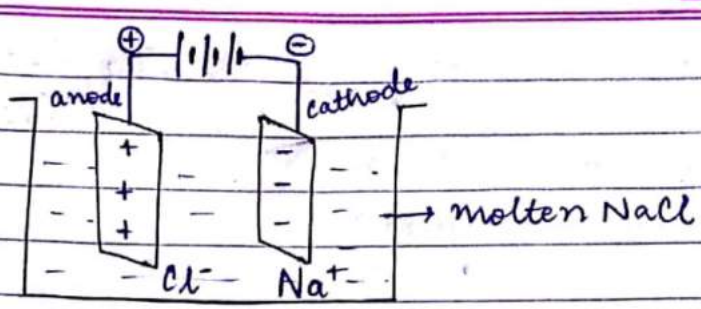
If $P_1 = P_2$ $\quad E_{cell} = 0.0591 \log \frac{C_2}{C_1}$

If $C_1 = C_2$ $\quad E_{cell} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$

Electrolysis :- The process of chemical decomposition of electrolytes by passage of electricity.

→ Device in which electrolysis takes place is k/n as Electrolytic cell or voltmeter.

Electrolytic cell : Electrical energy is converted into chemical energy.



Anode : $Cl^{\ominus} \rightarrow 1/2\ Cl_2(g) + e^{\ominus}$

Cathode : $Na^{+} + e^{\ominus} \rightarrow Na(s)$

$Na + Cl^{\ominus} \rightarrow Na(s) + 1/2\ Cl_2(g)$

Prod. of Electrolysis of Molten NaCl :-

Anode : Cl_2 gas is liberate
Cathode : $Na(s)$ is obtained

Electrolysis of aq. NaCl

anode	Cathode
Cl^-	Na^+
OH^-	H^+
H_2O	H_2O

Cathode :- जिसका red. Potential ज्यादा उसका cathode पर red. होगा।

$Na^+ + e^- \rightarrow Na(s)$ $E_{red} = -2.71V$ ✗

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E_{red} = -0.83V$ ✓

$H^+ + e^- \rightarrow 1/2\ H_2$ $E_{red} = 0V$

→ very less in amount (10^{-7} M)

Anode : जिसका ox. Potential ज्यादा होगा उसका Oxidation होगा।

$Cl^{\ominus} \longrightarrow 1/2\ Cl_2 + e^{\ominus}$ $E_{ox} = -1.36\ V$

$2H_2O \longrightarrow O_2 + 4H^+ + e^{\ominus}$ $E_{ox} = -1.23\ V$

Nearly same but देखो Cl की Conc. बहुत ज्यादा होगा इसलिए ox. Cl का होगा।

$2OH^{\ominus} \longrightarrow 1/2\ O_2 + H_2O + 2e^{\ominus}$

Very less in amount (10^{-7} M)

Anode :- $Cl^{\ominus} \longrightarrow 1/2\ Cl_2 + e^{\ominus}$

Cathode : $2H_2O + 2e^{\ominus} \rightarrow H_2(g) + 2OH^{\ominus}$

{ aq. NaCl → anode ⇒ Cl_2 gas, cathode ⇒ H_2 gas }

At cathode : Tendency to reduce

① Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+} $< H_2O$ → Cathode H_2 gas ★

② Fe^{2+}, Ni^{2+}, Sn^{2+}, Pb^{2+}, Cu^{2+} $> H_2O$ → Metal ★

③ Highly acid Medium :

S.A. → H_2SO_4, HNO_3

$H^+ + e^{\ominus} \longrightarrow 1/2\ H_2$ ✓

At Anode : Tendency to get oxidise

① $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$ $> H_2O$ → X_2

② SO_4^{2-}, $NO_3^{\ominus}$ $< H_2O$ → O_2 gas

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3. Highly Basic Medium :-

$$2\,OH^- \longrightarrow 1/2\,O_2 + H_2O + 2e^{\ominus}$$

Summary :-

aq. NaCl	aq. $CuSO_4$
Cathode : $2H_2O + 2e^- \rightarrow 2H_2\uparrow + 2OH^{\ominus}$	Cathode $\Rightarrow Cu^+ + e^{\ominus} \rightarrow Cu(s)$
Anode : $Cl^- \rightarrow 1/2\,Cl_2\uparrow + e^{\ominus}$	Anode $\Rightarrow 2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^{\ominus}$

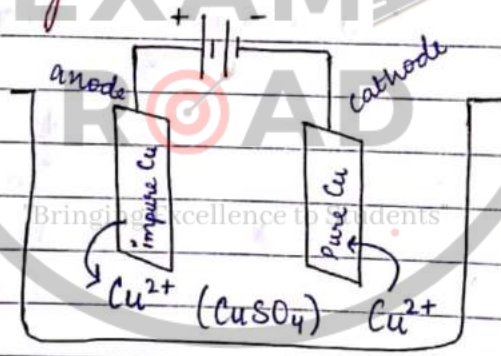
aq. LiCl

Cathode : $2H_2O + 2e^- \longrightarrow 2H_2\uparrow + 2OH^{\ominus}$

anode : $Cl^{\ominus} \longrightarrow 1/2\,Cl_2\uparrow + e^{\ominus}$

Thermodynamic efficiency of cell $= \frac{\Delta G}{\Delta H} = -\frac{nFE_{cell}}{\Delta H}$

Electroplating :-



Anode : $Cu\,(impure) \longrightarrow Cu^{2+} + 2e^-$

$$\frac{Cu^{2+} + 2e^- \longrightarrow Cu\,(Pure)}{Cu\,(impure) + Cu^{2+} \rightarrow Cu^{2+} + Cu\,(Pure)}$$

Electroplating :
Anode = Impure Metal
Cathode = Pure Metal

Quantitative Analysis :-

$1\ e^- = 1.6 \times 10^{-19}\ C$

$1\ mol\ e^- = 6.022 \times 10^{23} \times 1.6 \times 10^{-19}\ C$

$= 96487\ C$

$1\ mol\ e^{\ominus} = 1F \approx 96500\ C$

$Na^+ + e^- \rightarrow Na$

$1\ mol \longrightarrow 1\ mol\ Na$

$1F \longrightarrow 1\ mol$

$Mg^{2+} + 2e^{\ominus} \rightarrow Mg$

$2\ mol\ e^- \longrightarrow 1\ mol$

$2F \longrightarrow 1\ mol\ Mg$

$MnO_4^{\ominus} + 8H^{\oplus} + 5e^{\ominus} \rightarrow Mn^{2+} + nH_2O$

$5F \longrightarrow 1\ mol$

$Al^{3+} + 3e^{\ominus} \rightarrow Al$

$1\ mol \quad 3F \longrightarrow 1\ mol$

$3 \times 1\ g.eq. \quad 3F \longrightarrow 3 \times 1\ g.eq.\ of\ Al$

$n\ mole\ e^{\ominus} = nF \Rightarrow n\ g.eq.\ metal$

Law of Faraday :-

I st Law : The amount of substances deposite or liberated at an electrode is directly proportional to current pass through it.

$W \propto Q$

$W = ZQ$

weight ←

Z = Electrochemical equivalent

$Q = 1 \qquad W = 2$

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Electrochemical Equivalent is the amount of substance deposited or liberated when 1 C charge is passed through the Electrolytic soln.

$Q = it$

$\boxed{W = Zit}$

$Z = \frac{E}{96500}$

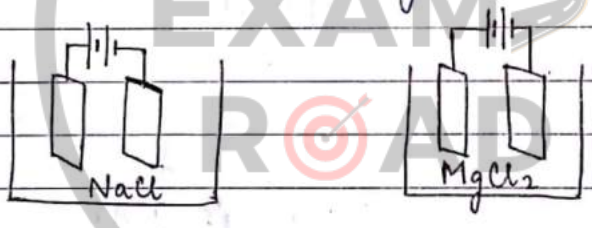
$Na^+ + 1e^- \longrightarrow Na$

$1F \longrightarrow 1\ g.eq.$

$E = \frac{\text{Molar Mass}}{n\text{-factor}}$

IInd Law :-

When same amount of charge is pass through 2 different Electrolytic soln (connected in series) then amount of substance deposited at Electrode will be directly proportional to their equivalent weight.



$W \propto E$

$\boxed{\frac{W}{E} = \text{const}}$ ★ $\boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2}}$

$W = ZQ$

$W \propto Z = \frac{E}{96500}$

$W \propto E$

More cells in series :-

$$\boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}}$$

Ques Calculate amount of Al deposited when 9.65×10^3 C charge is passed through molten $AlCl_3$

$W = ZQ$

$= \frac{9}{96500} \times \frac{9650 \times 10^{-3}}{1000} = \frac{9}{10}$

$= 0.9$

$Z = \frac{27}{3 \times 96500}$

Ques Calculate ~~amt.~~ wt. of Fe^{2+} & Fe^{3+} ions reduced by 1.5 F Given Mol. wt. of Fe = 56 g/mol

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

1 F 1 mol Fe^{2+}

AIPMT-05

Ques How much Electricity is required to prepare 5.12 kg of Al by Electrolysis

IIT-08

Ques Electrolysis of dil. aq. NaCl soln was carried out by passing 10 mA current. Find time req^d to liberate 0.01 mole of H_2 gas at cathode

(1F = 96500 mol^{-1})

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$I = 10 \times 10^{-3}$ A $Q = it$ $2H^+ + 2e^- \rightarrow H_2$

$2H^+ + 2e^- \rightarrow H_2$ $2F \rightarrow 1$ mole

1 mol H_2 is obtain by pass = 2F

0.01 mol ⟶ = 0.02 F

$Q = 0.02 \times 96500\ C = 10 \times 10^{-3} \times t$

$t = \frac{0.02 \times 96500}{10 \times 10^{-3}}$

Ques A 5A current is passed through a sol^n of Zinc sulphate for 40 min ? Find amount of Zinc deposited at cathode (At. mass of Zn = 63)

$Q = 5 \times 40 \times 60$

$= 12000C$

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

$2F \longrightarrow 1$ mol

≈ 63 g

$1 \longrightarrow \frac{63}{2} \times \frac{12000}{96500}$

Ques 4.5 g Al is deposited at Cathode from Al^{3+} sol^n by certain electric charge. The vol^m of H_2 produced at STP from $H^\oplus$ ions in sol^n by the same quantity of Electric Charge will be

① 44.8 L ② 22.4 L ③ 11.2 L ④ 5.6 L

$Al^{3+} + 3e^- \longrightarrow Al$

$3F \longrightarrow 1$ mol

27 g

27 g is obtain = 3F

1 g ⟶ = 3/27

4.5 g ⟶ $= \frac{3}{27} \times \frac{4.5}{10} = 0.5F$

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

$2F \longrightarrow 1\ mol\ H_2$

$0.5 \longrightarrow 1/2 \times 0.5\ mol\ H_2$

$= 0.25\ mol\ H_2$

$= 0.25 \times 22.4\ L$

$= 5.600\ L = 5.6\ L$

Ques How long a current of 3A should be passed through $AgNO_3$ soln to coat a metal surface $80\ cm^2$ of 0.005 mm thick layer density of this layer is $10.5\ g/cm^3$ ($Ag = 108\ g/mol$)

$d = \frac{M}{V} \Rightarrow M = d \times V = 10.5 \times 80 \times 0.005 \times 10^{-1}$

$= 10.5 \times 0.04 = 0.420\ gm$

$V = 80 \times 0.005 \times 10^{-1}\ cm^3$

$Ag^+ + e^- \longrightarrow Ag$

$1\ mole^- \longrightarrow 1\ mol\ Ag$

1F charge produced = 108 g Ag

108 g is ~~produced~~ obtained by from = 1F = 96500 C

1 g $\longrightarrow \frac{96500}{108}$

0.42 g $\longrightarrow \frac{96500}{108} \times 0.42\ C$

$\frac{96500}{108} \times 0.42 = it = 3 \times t$

$t = \frac{96500 \times 0.42}{54\ 108 \times 3 \times 100}$

$= \frac{965 \times 7}{54}$

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eq. of Cl_2 = eq. of Mg

Ques: ~~How long~~ Calculate vol. of chlorine gas at NTP produced during electrolysis of $MgCl_2$ which produce 8g Magnesium (At. wt. of Mg = 24 g/mol)

$Mg^{2+} + 2e^- \rightarrow Mg$

$2Cl^- \rightarrow Cl_2 + 2e^-$

$Mg^{2+} + 2Cl^- \rightarrow Mg + Cl_2$

$\frac{W_{Cl_2}}{W_{Mg}} = \frac{E_{Cl_2}}{E_{Mg}}$

$\frac{W_{Cl_2}}{8} = \frac{71/2}{24/2} = \frac{71}{3}$

$n_{Cl_2} = \frac{71/3}{71} = \frac{1}{3}$ mol

Vol. $= \frac{1}{3} \times 22.4$

$= \frac{22.4}{3}$ L

Ques 5 L of 1M $AgNO_3$ sol^n & 2 L of 1M NaCl sol^n are connected in series when electricity is passed, 54 g of Ag deposited on cathode in $AgNO_3$ sol^n. Then calculate vol. of H_2 gas at STP produced in NaCl sol^n (Mw. of Ag = 108 g/mol)

5 L 1M $AgNO_3$ sol^n — 2 L, 1M NaCl sol^n

Ag^+ (H+) H_2O ✓ → very less ← Na^+ (H+) H_2O ✓

$Ag^+ + e^- \rightarrow Ag$

1F → 108 g

108 g is obtained from 1F

1 g → $\frac{1}{108}$ F

54 g → $\frac{1}{108} \times 54$ F

$= 1/2$ F

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

2F → 2 g H_2

1F → $\frac{2}{2}$ = 1 g H_2

1/2 F → 1/2 g H_2

$= 1/4$ mol H_2

$= 22.4/4 = 5.6$ L

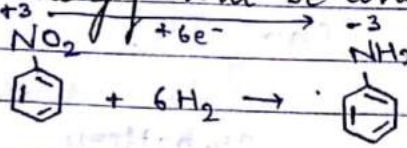
Series same

same current

i.e. same charge

Ques Calculate the electricity that would be required to reduce 12.3 g of nitrobenzene to aniline. If current efficiency is 50%

If the potential drop across the cell is 3.0 V How much energy will be consumed ?



$6F \rightarrow 123g$

123 g is obtained by Passing = 6F

1 g $\longrightarrow$ = $\frac{6}{123}$

12.3 g $\longrightarrow$ = $\frac{6}{123} \times 12.3$

$= 0.6F$

$= 0.6 \times 96500C$

current efficiency = 50% = $\frac{i_{used}}{i_{supplied}} \times 100$

$Q = it$

Charge efficiency = 50%

Total charge required = $0.6 \times 96500 \times \frac{100}{50}$

Q supplied = 115800 C

$E = Q \times V$

$= 115800 \times 3 = 347400 J$

$= 347.4 KJ$

Q supplied = Q used $\times \frac{100}{50}$

Ques A current of 3A was passed for 2h through a sol^n of $CuSO_4$. 3g of Cu^{2+} ions were discharged at cathode. Calculate current efficiency for this process.

$I = 3A \quad t = 2h \quad M = 3g \text{ of } Cu^{2+}$

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

$2F \longrightarrow 63.5g$

63.5g is obtained $\longrightarrow$ 2F

$3g \longrightarrow \frac{2}{63.5} \times 3F$

$Q_{used} = \frac{2}{63.5} \times 3 \times 96500 C$

$Q_{supplied} = it = 3 \times 2 \times 60 \times 60$

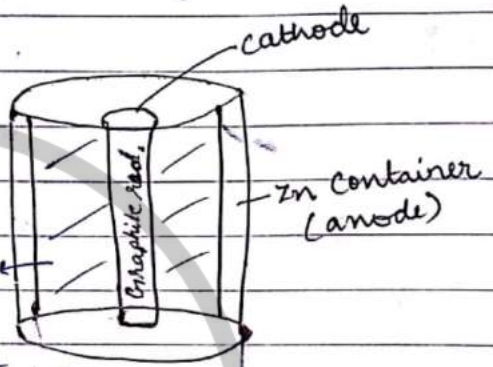
$\text{efficiency} = \frac{\frac{2}{63.5} \times 3 \times 96500}{3 \times 2 \times 60 \times 60} = \frac{3}{7} \times 100$

Battery :- redox reaⁿ C.E. → E.E.

Primary	Secondary
(non-chargable)	(Chargable)
dead after use	→ inverter battery
eg: remote cell, clock cell, radio cell	car battery

Primary Batteries :- Reacⁿ occur only once & after use over a period of time, battery is dead & can not be used

eg Leclanche cell / Dry cell



Anode : $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

$Mn^{4+} \longrightarrow Mn^{3+}$

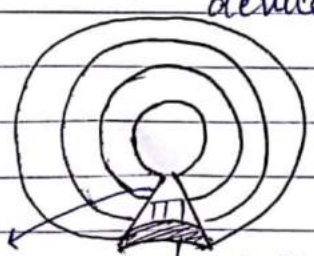
NH_3 produced in reacⁿ forms a complex with Zn^{2+}

→ $[Zn(NH_3)_2]^{2+}$

Ecell = 1.5 V

Use → in transistor & clocks.

Mercury Cell :- Suitable for low current devices like hearing devices, watches etc.



anode Zn(Hg) → cathode Ca paste of HgO & C

Electrolyte apart of KOH + ZnO

Anode : $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

Cathode : $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

$Zn(Hg) + HgO \rightarrow ZnO(s) + Hg(l)$

$E_{cell} = 1.35\ V$

remains const. during its life as overall reac^n does not involve any ion in sol^n whose conc^n can change during its conc^n.

Secondary Batteries :- A secondary cell after use can be recharged by passing current through it in the opposite directions so that it can be used again.

eg : Lead storage battery : used in automobiles, invertors.

$Pb / PbSO_4 / H_2SO_4$ (38%) $/ PbO_2 / PbSO_4$

Anode : $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{\ominus}$

Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^{\ominus} \rightarrow PbSO_4(s) + 2H_2O(l)$

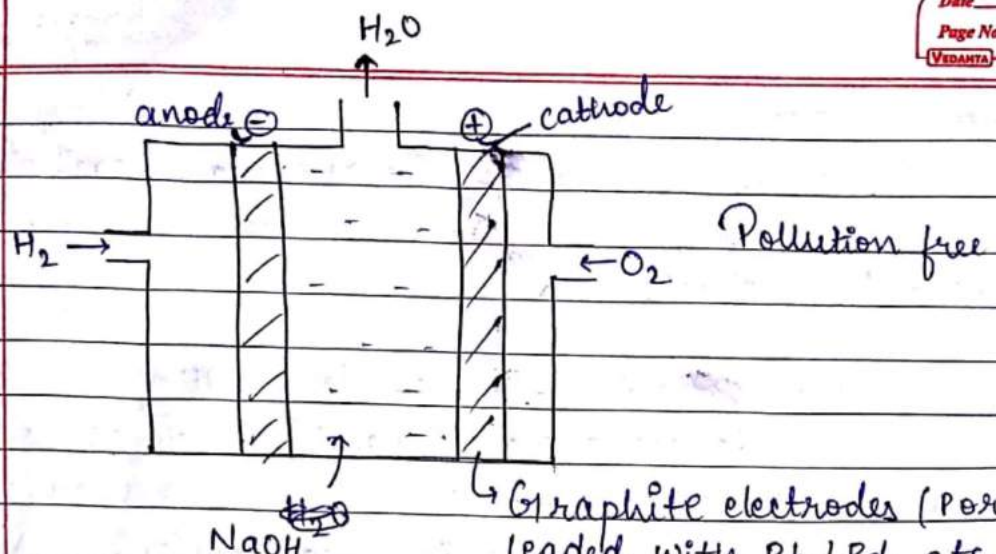
Cell reac^n : $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

On charging the battery, the reac^n is reversed & $PbSO_4(s)$ on anode & cathode is converted into Pb & PbO_2 respectively.

Nickel - Cadmium Cell : Longer life than Lead storage Battery but it is expensive.

Cell reac^n : $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

Fuel Cell :- Galvanic cell that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc directly into electrical energy are c/a fuel cells.



Anode: $H_2(g) + 4OH^- \rightarrow 4H_2O(l) + 4e^-$

Cathode $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Efficiency of fuel cell is 70% while that of thermal plant is about 40%.

Cell efficiency $= \frac{\Delta G}{\Delta H} = \frac{-nF E_{cell}}{\Delta H}$

Corrosion :- Rusting of Iron, green coating on copper & bronze in corrosion a metal is oxidised by loss of $e^\ominus$ to oxygen & form its oxide

Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$

$E^\circ_{Fe^{2+}/Fe} = -0.44\,V$

→ $e^\ominus$ released at anodic spot move through the metal to another spot & react with oxygen in +nce of H^+ (from acids which are formed in atmosphere due to reac^n of acidic oxides & atmospheric water eg H_2CO_3)

This spot behave as cathode

Cathode: $O_2(g) + 4H^+(aq) + e^\ominus \rightarrow 2H_2O(l)$ $E^\circ_{H^+/O_2/H_2O} = 1.23\,V$

Overall Reac^n: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

$E^\circ_{cell} = 1.57\,V$

⇒ Ferrous ions are further oxidised by atmospheric oxygen to ferric ions which comes out as rust in the form of hydrated ferric oxide. ($Fe_2O_3 . x H_2O$) & Further $H^{\oplus}$ ions are produced.

Prevention of Corrosion :-

1. By covering surface of metal with paint a some chemical like Bisphenol.

2. By covering metal with inert metal like Sn, Zn.

3. By Electroplating of Mg, Zn etc.