Electrochemistry

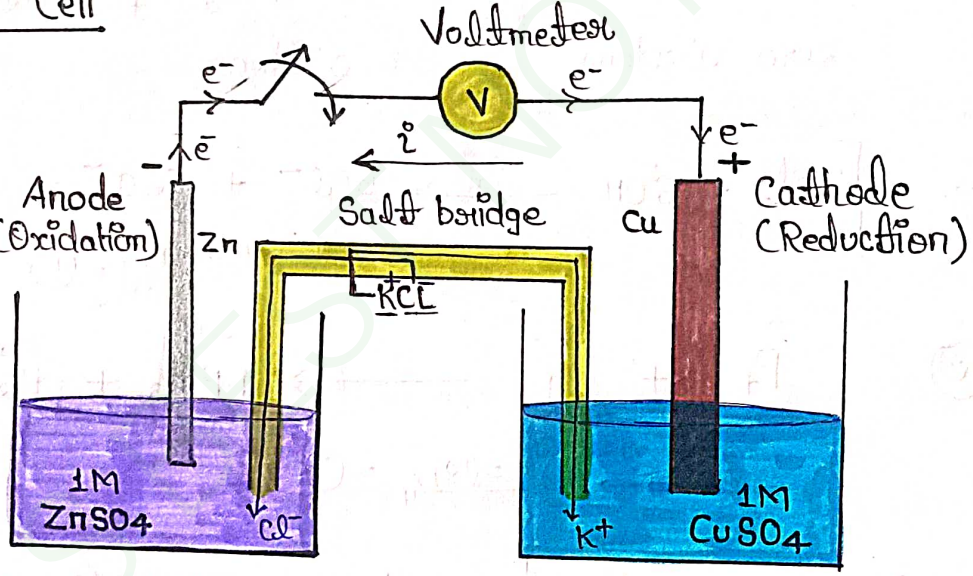
covered all the topics widely

Electrochemistry

① Electrochemical cell or voltaic cell or Galvanic cells.

⇒ The device which is used to convert chemical energy into electrical Energy.

Daniel Cell



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

$[Zn^{+2}] > [SO_4^{2-}]$

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

$[Cu^{+2}] < [SO_4^{2-}]$

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

Cell representation

L ↓ R L ↓ R

$Zn_{(s)} \mid Zn^{+2}_{(aq)}\ 1M \;\|\; Cu^{+2}_{(aq)}\ 1M \mid Cu_{(s)}$

↓ Salt Bridge

E° ↓ standard state. (1 atm, 25°C, 1 M)

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Cell Potential difference.

$E^\circ_{cell} = 1.1\ V$

E°_{cell} = Higher Potential − Lower Potential.

$$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$$

Standard Electrode Potential is taken to be standard Reduction Potential.

Salt Bridge

→ Inert electrolytes + Paste of Polysaccharides (Agar-Agar).

Inert Electrolytes :→ The electrolytes whose ions do not take part in main cell rxn. eg., KCl, KNO_3, NH_4NO_3, etc. (~~Inert~~ Ionic mobility of cation ≈ Ionic mobility of anion) to maintain electrical neutrality.

KCl is not use in Ag, Tl, Pb, Hg electrodes (as it forms ppt).

Main functions of Salt Bridge :→

→ To maintain electrical neutrality.

→ To complete inner circuit without mixing of the two solutions.

→ To reduce liq-liq junction potential.

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Salt Bridge ke left side Oxidn hoga or wo anode past R.

Q. For Galvanic Cell :-

$$\overset{L}{Zn_{(s)}} \mid \overset{R}{Zn^{+2}_{(aq)}\ (1M)} \parallel \overset{L}{Cu^{+2}_{(aq)}\ (1M)} \mid \overset{R}{Cu_{(s)}}$$

Write cell rxn and find E°_{cell}.

Given :→ $E^\circ_{Zn/Zn^{+2}} = +0.76\ V$ (Oxidn) } $E^\circ_{Zn^{+2}/Zn} = -0.76\ V$ (Redn)

$E^\circ_{Cu^{+2}/Cu} = +0.34\ V$ (Redn)

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

$$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$$

$$E^\circ_{cell} = 0.34 - (-0.76)$$

$$E^\circ_{cell} = 1.1\ V.$$

Q. For Electrochemical cell – $Fe_{(s)} \mid Fe^{+2}_{(aq)\ (1M)} \parallel Cu^{2+}_{(aq)\ (1M)} \mid Cu_{(s)}$

Write cell rxn and find E°_{cell}.

Given :- $E^\circ_{Fe/Fe^{+2}} = +0.44\ V$ } $E^\circ_{Fe^{+2}/Fe} = -0.44\ V$ (Anode)

$E^\circ_{Cu/Cu^{+2}} = -0.34\ V.$ } $E^\circ_{Cu^{+2}/Cu} = 0.34\ V$ (Cathode)

$$Fe_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Fe^{+2}_{(aq)} + Cu.$$

$$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$$

$$E^\circ_{cell} = 0.34 - (-0.44)$$

$$E^\circ_{cell} = 0.78\ V$$

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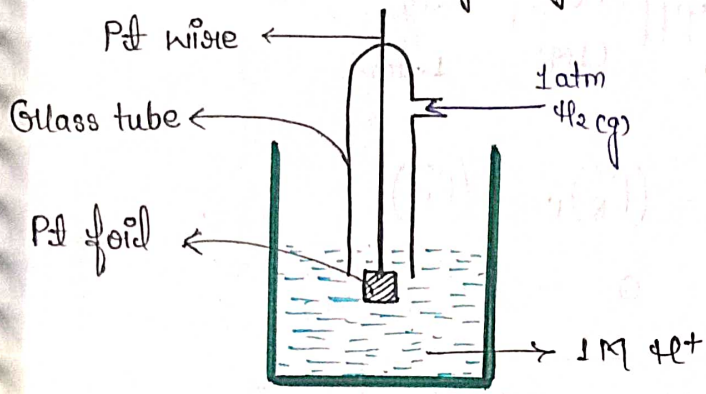
S.H.E (Standard Hydrogen Electrode)



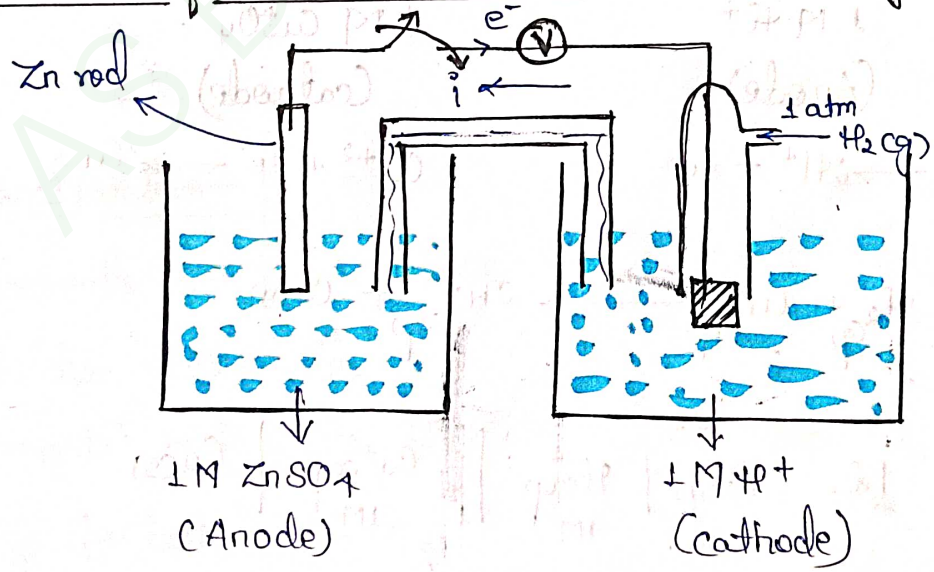
Case (1). If SHE acts as anode.

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^- \quad E^\circ_R = 0 \quad \text{(oxidation)}$$

Case (2). If SHE acts as cathode.

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad E^\circ_R = 0 \quad \text{(Reduction).}$$

Calculation of standard Electrode Potential of Zn



$Zn \longrightarrow Zn^{+2} + 2e^-$ $\qquad$ $2H^+ + 2e^- \longrightarrow H_2$

Net Cell Rxn $\qquad Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + H_{2(g)}$.

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Applications :— (T → B Electropositive nature ↓es ; Electro-ve nature ↑es)

① Top to bottom, Reducing power decreases or oxidising power increases.

② **Metal displacement Rxn →** The metal which lie above in ECS can displace the metal from its salt which lie below in ECS.

eg.,

$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu.$ — Zn ⋮ Cu

$Cu + FeSO_4 \longrightarrow$ No rxn. — Fe ⋮ Cu.

③ **Non-Metal displacement Rxn. →** The non-metal which lie below in ECS can displace the non-metal from its salt which lie above in ECS.

eg.,

F_2 → KCl → $KF + Cl_2$
F_2 → KBr → $KF + Br_2$
F_2 → KI → $KF + I_2$

Cl_2 → KF → No rxn
Cl_2 → KBr → $KCl + Br_2$
Cl_2 → KI → $KCl + I_2$.

Br_2 → KF → No rxn
Br_2 → KCl → No rxn
Br_2 → KI → $KBr + I_2$

I_2 → KF → No rxn
I_2 → KCl → No rxn
I_2 → KBr → No rxn.
I_2 → KI → $K^+ I_3^-$

Lewis Acid-Base Rxn

$(I_3^\ominus \rightarrow I^\ominus \rightarrow I\text{-}I)$

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Electrochemical series.

Li		Cu
K		I
Ba		Ag
Sr		Hg
Ca		Br
Na	H	Pt
Mg		O
Al		Cl
Mn		Au
Zn		F
Cr		
Fe		
Cd		
Co		
Ni		
Sn		
Pb		

Characteristics—

1. Elements which lie above H have -ve E°_R.
2. H has zero E°_R.
3. Elements which lie below H have +ve E°_R.
4. Top to bottom E°_R ↑es.

Li → Minimum E°_R

F → Maximum E°_R.

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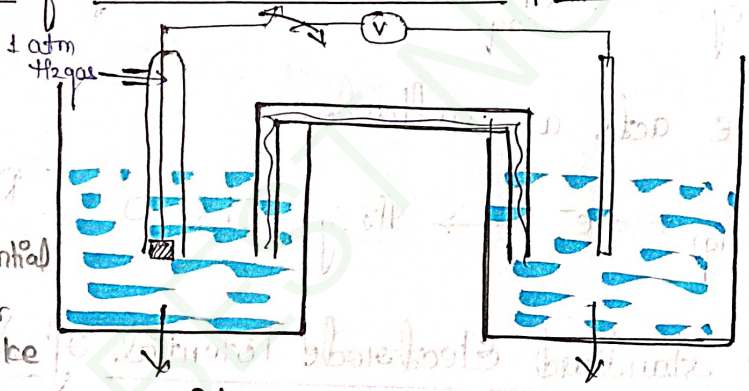
Cell rep. :→ $Zn_{(s)} \mid Zn^{+2}_{(aq)} \,(1M) \,\|\, H^{+}_{(aq)} \,(1M) \mid H_{2(g)}$, Pt (1 atm.)

Cell Potential diff. :→ $E^{\circ}_{cell} = (E^{\circ}_R)_C - (E^{\circ}_R)_A$

experimentally → $0.76 = 0 - (E^{\circ}_{Zn^{+2}/Zn})$

$$\boxed{E^{\circ}_{Zn^{+2}/Zn} = -0.76\ V}$$

Calculation of standard electrode potential of Cu.



(SHE jb Anode ke side lga hoga to Potential +ve aega, or agar cathode ke side lga hoga to potential -ve aega)

(Anode) $H_2 \longrightarrow 2H^+ + 2e^-$

(Cathode) $Cu^{+2} + 2e^- \longrightarrow Cu.$

Cell Rxn. $H_{2(g)} + Cu^{+2}_{(aq)} \longrightarrow 2H^+_{(aq)} + Cu_{(s)}$

Cell Rep. $Pt, H_{2(g)} \,(1\ atm.) \mid H^+_{(aq)} \,(1M) \,\|\, Cu^{+2}_{(aq)} \,(1M) \mid Cu_{(s)}$

Cell Potential Diff. $E^{\circ}_{cell} = (E^{\circ}_R)_C - (E^{\circ}_R)_A$

$0.34 = E^{\circ}_{Cu^{+2}/Cu} - 0$

experimentally $\boxed{E^{\circ}_{Cu^{+2}/Cu} = +0.34\ V}$

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$$E_{cell} = E^{\circ}_{cell} - \frac{0.06}{n} \log_{10} Q$$

Q. Find EMF of cell ?

$$Mg_{(s)} \mid Mg^{+2}_{(aq)}\ (0.2M) \;\|\; Ag^{+}_{(aq)}\ (0.001M) \mid Ag_{(s)}$$

Given :→ $E^{\circ}_{cell} = 3.17\ V$

Sol :→

$$\overset{0}{Mg}_{(s)} + 2\overset{+1}{Ag}^{+}_{(aq)} \longrightarrow \overset{+2}{Mg}^{+2}_{(aq)} + 2\overset{0}{Ag}_{(s)} \quad (nf = 2)$$

(2 × 1 = 2 ; 1 × 2 = 2)

$$E_{cell} = 3.17 - \frac{0.06}{2} \log_{10} \frac{0.2}{(10^{-3})^2}$$

$$E_{cell} = 3.17 - 0.03 \log_{10} (2 \times 10^{-5})$$

$$= 3.17 - 0.03 \left(\log_{10} 2 + \log_{10} 10^{-5}\right)$$

$$= 3.17 - 0.03\ (0.3 - 5)$$

$$= 3.17 - (-0.141)$$

$$[E_{cell} \approx 3.01\ V]$$

Q. Find EMF of cell ?

$$Zn_{(s)} \mid Zn^{+2}_{(aq)}\ (1M) \;\|\; Ag^{+}_{(aq)}\ (0.1M) \mid Ag_{(s)}$$

Given :→ $E^{\circ}_{Zn|Zn^{+2}} = +0.76\ V$ } $E^{\circ}_{Zn^{+2}|Zn} = -0.76\ V$

$E^{\circ}_{Ag^{+}|Ag} = +0.80\ V$

$$E^{\circ}_{cell} = (E^{\circ}_{R})_{C} - (E^{\circ}_{R})_{A}$$

$$= 0.80 - (-0.76)$$

$$= 1.56\ V$$

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Q④. Compare reactivity (Ba, Zn, K, Cu)

⇒ K
Ba
Zn
Cu
↓ decreases.

Nernst Equation

Nernst introduced an eqn by which we can calculate EMF of the cells (E_{cell}) for given conc and pressure.

$$\left[E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF}\log_{10} Q\right]$$

E_{cell} = EMF of cell at given conc & pressure.

E°_{cell} = standard emf of cell

R = gas constant

T = Temperature (K)

n = no. of e⁻s involve in Reaction

F = Faraday's constant = 96500 C

Q = Reaction quotient.

$$\alpha A_{(s)} + \beta B_{(aq)} \longrightarrow \gamma C_{(aq)} + \delta D_{(aq)}$$

$$Q = \frac{[C]^\gamma [D]^\delta}{[B]^\beta}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log_{10} Q$$

Electrochemistry

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④ Reactivity. Top to bottom Reactivity decreases.

⑤ Thermal stability of oxides. Top to bottom, Thermal stability ↓es.

Ques ① Compare reducing Power.

Metal	E°_R
X	−1.2 V
Y	+0.5 V
Z	−3 V

(Top to bottom, Reducing power decreases).

(E°_R Km, RP jyda)

$\Rightarrow$ Z > X > Y

Q ② $E^\circ_{F_2/F^-} = +2.05\,V$ (Khud ko reduce krega (OA)), $E^\circ_{Cl_2/Cl^-} = +1.36\,V$

$E^\circ_{Br_2/Br^-} = +1.06\,V$, $E^\circ_{I_2/I^-} = +0.53\,V$

(Khud ko oxidise krega = RA)

$\Rightarrow$ strongest reducing Agent :→ $I^\ominus$ (E°_R sbse Km)

$\Rightarrow$ strongest oxidising agent :→ F_2 (E°_R sbse jyda)

Q ③

Metal	E°_R ($E^\circ_{M^{n+}/M}$)
Li	−3.05 V
Ba	−2.90 V
Na	−2.71 V
Mg	−2.37 V (Mg^{+2}/M)

strongest OA → Mg^{+2}.

(E°_R sbse jyda)

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ΔG° is an additive quantity but EMF of the cell is not additive quantity.

Q. Given. ① $Cu^{+2} + e^- \xrightarrow{n_1=1} Cu^+$ $\quad E_1^\circ = +0.15\ V$

② $Cu^+ + e^- \xrightarrow{n_2=1} Cu$ $\quad E_2^\circ = +0.5\ V$

find $E^\circ_{Cu^{+2}|Cu} = ?$

Sol:- ③ $Cu^{+2} + 2e^- \xrightarrow{n_3=2} Cu$

③ = ① + ②

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

$-n_3 F E_3^\circ = -n_1 F E_1^\circ - n_2 F E_2^\circ$

$n_3 E_3^\circ = n_1 E_1^\circ + n_2 E_2^\circ$

$2 \times E_3^\circ = 1 \times 0.15 + 1 \times 0.5$

$2 E_3^\circ = 0.65$

$[E_3^\circ = 0.325\ V]$ Ans

Q. Given $\quad E^\circ_{Fe^{+2}|Fe} = -0.441\ V$

$E^\circ_{Fe^{+3}|Fe^{+2}} = 0.771\ V$

Find E° for $Fe + 2Fe^{+3} \longrightarrow 3Fe^{+2}$

cathode

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

Anode

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at eqm, $E_{cell} = 0$

$$0 = E^\circ_{cell} - \frac{RT}{nF} \ln K_{eq}$$

$$[nF E^\circ_{cell} = RT \ln K_{eq}] \quad \text{——— (2)}$$

from (1) and (2),

$$\boxed{\Delta G^\circ = -nF E^\circ_{cell}}$$

Calculation of ΔG°, maximum work, and Eqm constant 'Keq' for Daniel Cell :—

ΔG°

$$\Delta G^\circ = -nF E^\circ_{cell}$$
$$= -2 \times 96500 \times 1.1$$
$$= -212300 \text{ J/mol}$$
$$[\Delta G^\circ = -212.3 \text{ KJ/mol}]$$

Max. Work

W_{max} = Decrease in free Energy

$$W_{max} = -\Delta G^\circ$$
$$[W_{max} = 212.3 \text{ KJ/mol.}]$$

Keq

$$\Delta G^\circ = -RT \ln K_{eq}$$
$$-212300 = -25/3 \times 298 \times 2.3 \log_{10} K_{eq}$$
$$\frac{212300 \times 3}{25 \times 298 \times 2.3} = \log_{10} K_{eq}$$
$$\log_{10} K_{eq} = 37$$
$$[K_{eq} = 10^{37}]$$

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$2 \times 1 = 2$

$Zn_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + 2Ag_{(s)}$ $(nf = 2)$

$$E_{cell} = 1.56 - \frac{0.06}{2} \log_{10} \frac{10^2}{(10^{-1})^2}$$

$$E_{cell} = 1.56 - 0.03 \log 10^3$$

$$= 1.56 - 0.03 \times 3$$

$$= 1.56 - 0.09$$

$$[E_{cell} = 1.47\ V.]$$

Relation b/w ΔG° (Standard free Energy change) & E°_{cell}

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$$

ΔG = free energy change at T K

ΔG° = standard free energy change

R = gas constant, T = temp (K), Q = Rxn Quotient.

At eqm, $\Delta G = 0$, $Q = K_{eq}$,

$$0 = \Delta G^\circ + RT \ln K_{eq}$$

$$[\Delta G^\circ = -RT \ln K_{eq}] \quad \text{——— (1)}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.3RT}{nF} \log_{10} Q$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

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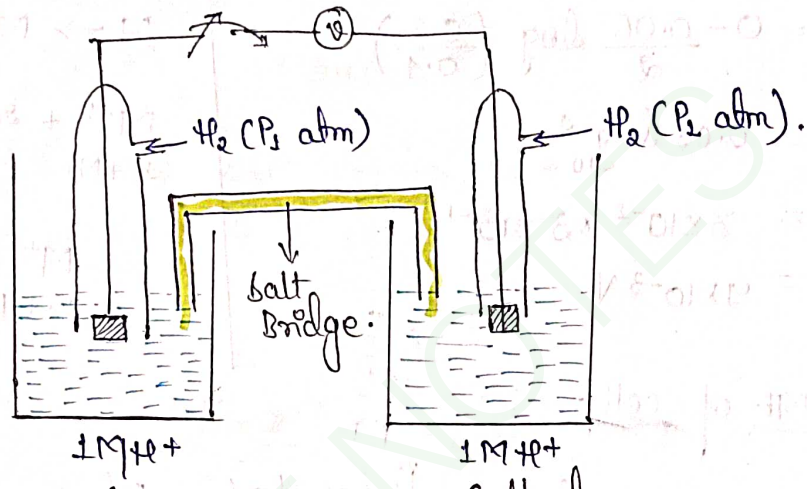
Condition for spontaneity:-

$\Delta G = -nFE_{cell}$; $\Delta G < 0$; $E_{cell} > 0$; $C_2 > C_1$

\# Pressure.



Anode

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

P_1 atm ; 1M

Cathode

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

1M ; P_2 atm

Net Cell Rxn.

$H_{2(g)}$ (P_1) $\longrightarrow$ $H_{2(g)}$ (P_2)

Cell Representation.

$Pt, H_{2(g)}, H^+_{(aq)} \,|\, H^+_{(aq)}, H_{2(g)}, Pt$

(P_1 ; 1M ‖ 1M ; P_2)

Cell Potential Diff. $E^\circ_{cell} = 0$

$$E_{cell} = 0.03 \log_{10}\left(P_1/P_2\right)$$

Condⁿ for spont.

$\Delta G = -nFE_{cell}$; $\Delta G < 0$, $E_{cell} > 0$

$(P_1 > P_2)$

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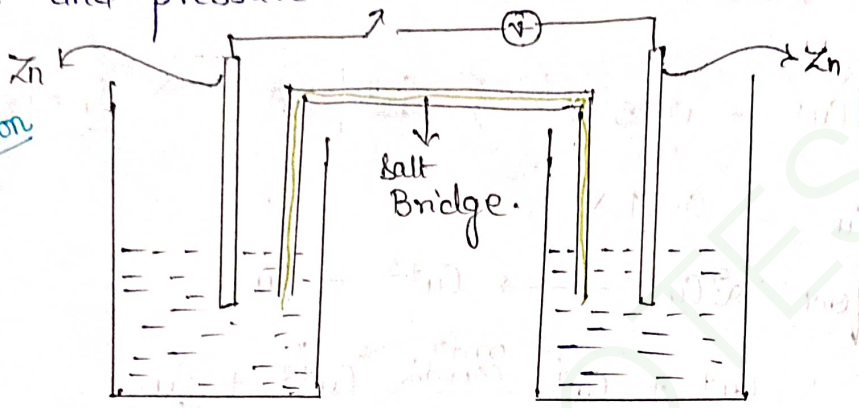
Concentration Cells.

Two solutions of same material are present with different concen. and pressure.

Concentration



ANODE

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

$C_1\ M$

CATHODE

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

$C_2\ M$

Net Cell Rxn:

$Zn^{+2}_{(aq)}\ (C_2\ M) \longrightarrow Zn^{+2}_{(aq)}\ (C_1\ M)$

Cell Representation

$Zn_{(s)} \mid Zn^{+2}_{(aq)}\ (C_1\ M) \parallel Zn^{+2}_{(aq)}\ (C_2\ M) \mid Zn_{(s)}$

Cell Potential Diff / Emf of the cell:— # $E^\circ_{cell} = 0$ (same materia

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{n} \log_{10}\left(\frac{C_1}{C_2}\right)$$

$$E_{cell} = 0 - \frac{0.06}{2} \log_{10}\left(\frac{C_1}{C_2}\right)$$

$$\boxed{E_{cell} = 0.03 \log_{10}\left(\frac{C_2}{C_1}\right)}$$

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$E^\circ_{Cell} = (E^\circ_R)_C - (E^\circ_R)_A$

$= 0.771 - (-0.441)$

$= 1.212\ V$

Q. $E^\circ_{Cu^{+2}|Cu^+} = 0.15\ V$ → Anode

$E^\circ_{Cu^{+2}|Cu} = 0.34\ V$

Find E° for $2Cu^+ \longrightarrow Cu^{+2} + Cu$.

$Cu^+ + Cu^+ \xrightarrow{\text{Oxdn (Anode)}} Cu^{+2} + Cu$

Redn (cathode)

$E^\circ_{Cell} = (E^\circ_R)_C - (E^\circ_R)_A$

$= 0.53 - 0.15$

$[E^\circ_{Cell} = 0.30\ V]$

① $Cu^{+2} + e^- \xrightarrow{n_1=1} Cu^+$ $E^\circ_1 = 0.15\ V$

② $Cu^{+2} + 2e^- \xrightarrow{n_2=2} Cu$ $E^\circ_2 = 0.34\ V$

③ $Cu^+ + e^- \xrightarrow{n_3=1} Cu$ $E^\circ_3 = ?$

$-\Delta G^\circ_1 + \Delta G^\circ_2 = \Delta G^\circ_3$

$n_1 F E^\circ_1 - n_2 F E^\circ_2 = -n_3 F E^\circ_3$

$1 \times 0.15 - 2 \times 0.34 = -1 \times E^\circ_3$

$0.68 - 0.15 = E^\circ_3$

$E^\circ_3 = 0.53\ V$

$(Cu^+|Cu)$

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Q. Find EMF of cell

$$M_{(s)} \mid M^{2+}_{(aq)} \; (0.2\,M) \;\Big\|\; M^{2+}_{(aq)} \; (0.4\,M) \mid M_{(s)}$$

(L ↓ R)

$$E_{cell} = 0 - \frac{0.06}{2} \log \left(\frac{0.2}{0.4}\right)^{RHS}_{LHS}$$

$$E_{Cell} = 0.03 \log_{10} 2$$

$$= 3 \times 10^{-2} \times 3 \times 10^{-1}$$

$$= 9 \times 10^{-3}\,V$$

$$M \xrightarrow{(0.2M)} M^{+2} + 2e^-$$

$$M^{+2} + 2e^- \xrightarrow{(0.4M)} M$$

$$M^{+2} \;(0.4\,M) \longrightarrow M^{+2} \;(0.2\,M)$$

Q. Find EMF of cell –

$$Pt_{(s)} \; Cl_2 \mid Cl^- \;\Big\|\; Cl^- \mid Cl_2 \; Pt$$

(Red^n | Oxid^n)

P_1 atm, 1M | 1M, P_2 atm.

Left side always Oxidation, so correct rxn will be –

(i) $2Cl^- \longrightarrow Cl_2 + 2e^-$; Cl^- (1M), Cl_2 P_1 atm.

(ii) $Cl_2 + 2e^- \longrightarrow 2Cl^-$; Cl_2 P_2 atm, Cl^- (1M)

(i) + (ii) $\Rightarrow$ Cl_2 (P_2 atm) $\longrightarrow$ Cl_2 (P_1 atm)

$$E_{cell} = 0 - \frac{0.06}{2} \log \left(\frac{P_1}{P_2}\right)$$

$$E_{cell} = 0.03 \log \left(\frac{P_2}{P_1}\right)$$

Condn for spont :– $\Delta G < 0$, $\Delta E_{cell} > 0$ $\Rightarrow$ $P_2 > P_1$

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Q. Find E_{cell} –

$Pt, H_{2(g)} \,|\, H^+_{(aq)} \,||\, H^+_{(aq)} \,|\, H_{2(g)}, Pt$

(1 atm) 10^{-6} M 10^{-4} M (1 atm)

(i) $H_2 \longrightarrow 2H^+ + 2e^-$ (10^{-6} M)

(ii) $2H^+ + 2e^- \longrightarrow H_2$ (10^{-4} M)

(i) + (ii) $\Rightarrow$ $2H^+ \longrightarrow 2H^+$

(10^{-4}) (10^{-6})

$$E_{cell} = 0 - \frac{0.06}{2} \log \frac{(10^{-6})^2}{(10^{-4})^2}$$

$$E_{cell} = 0.03 \log 10^4$$

$$= 0.03 \times 4$$

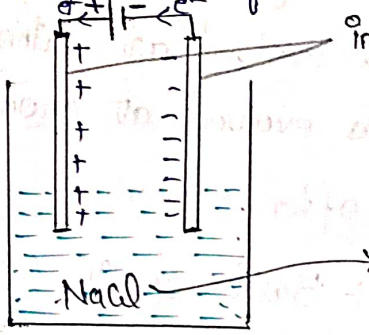
$$= 0.12 \text{ V}$$

Electrolytic Cell

The device which is used to convert Electrical Energy into chemical Energy.

(or)

The device in which process of Electrolysis occurs.



At Anode :→ (Oxidn)

$Cl^\ominus \longrightarrow \frac{1}{2} Cl_{2(g)} + e^\ominus$

At cathode :→ (Redn)

$Na^+ + e^- \longrightarrow Na_{(s)}$

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Product of electrolysis:

(1) Na metal deposited at Cathode

(2) Cl_2 gas evolved at anode.

Preferential Discharge theory (when inert electrode +nt)

Case (1) For cations: When two diff. ions +nt in the soln then that ion will migrate first which has higher RP. (neeche wala migrate krega).

Case (2) for anions: Ease of deposition or tendency to migrate.

$$SO_4^{2-} < NO_3^- < OH^- < Cl^- < Br^- < I^-$$

Q. Find the product of Electrolysis aq NaCl.

$$NaCl \longrightarrow Na^+ + Cl^-$$
$$H_2O \longrightarrow H^+ + OH^-$$

At cathode $H^+ + e^- \longrightarrow \frac{1}{2} H_2(g)$

At Anode $Cl^- \longrightarrow \frac{1}{2} Cl_2(g) + e^-$

Products of Electrolysis

(1) H_2 gas evolved at cathode

(2) Cl_2 gas evolved at anode

Nature of soln after Electrolysis

↳ Basic soln (NaOH)

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$W \propto Q$

$[W = ZQ]$.

W = wt of ion discharged

Q = charge in coulomb

Z = Electrochemical Equivalence.

Electrochemical Equivalence. ## The wt of ion discharged by passing 1 Ampere current through 1 second.

$W = ZQ$

$W = \frac{Ewt}{F} Q.$

$\frac{W}{Ewt} = \frac{Q}{F}$

$$n \times nf = \frac{it}{F}$$

F ≈ Faraday's constant

n = moles

nf = no. of e^- involve in rxn

i = current

t = time (sec).

1 F = charge of 1 mol of e^-

$1F = N_A \times 1.6 \times 10^{-19}$

$$1F = 96500C$$

Q. How long should a current of 0.25 A be passed through a molten metal salt to deposit that much weight of metal, which is equal to its Electrochemical Equivalence?

Sol:→.

$W = Z$ (Given)

$W = ZQ$

$Q = 1$

$it = 1$

$t = 1/i$

$t = \frac{1}{0.25}$

$\Rightarrow t = 4$ sec.

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(d)* Conc. H_2SO_4 with Pt electrode. (agar dil H_2SO_4 h, do acd. to PDT)
(Product → H_2, O_2)

H^+ HSO_4^{2-}

At Cathode

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

At Anode

$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$

(dianion of Marshal acid)

Electrolyte	Product at Cathode	Product at anode
(1) Aq. NaOH with Pt electrode	H_2 gas	O_2 gas
(2) Aq. $AgNO_3$ with Pt electrode	Ag metal	O_2 gas
(3) Aq. $AgNO_3$ with Ag electrode	~~$Ag \rightarrow Ag^+ + e^-$~~ $Ag^+ + e^- \rightarrow Ag$	$Ag \rightarrow Ag^+ + e^-$
(4) dil H_2SO_4 with Pt electrode	H_2 gas	O_2 gas
(5) Aq. $PbCl_2$ with Pt electrode.	H_2 gas	Cl_2 gas

Faraday's law

1st law # The weight of ion discharged is directly proportional to the quantity of charge passed through it.

Electrochemistry

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Q. Find the product of Electrolysis -

(a) aq. $CuSO_4$ with Pt electrode.

$CuSO_4 \longrightarrow Cu^{+2} + SO_4^{2-}$

$H_2O \longrightarrow H^+ + \bar{O}H$

At Cathode. $2Cu^{+2} + 4e^- \longrightarrow 2Cu(s)$

At Anode $4\bar{O}H \longrightarrow 2H_2O + O_{2(g)} + 4e^-$

Products

① Cu is deposited at Cathode

② O_2 is evolved at anode.

Nature of Sol^n ⇒ Acidic (H_2SO_4).

(b) aq $CuSO_4$ with Cu electrode. (PDT → Preferential Disch. Theory not apply here as electrode is reactive)

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

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

(as electrolyte & electrode are of same material that's why they're reactive)

(c)* aq. NaCl with Hg electrode. → iske wjh se Na^+ migrate krega

$NaCl \rightarrow Na^+ + Cl^-$

$H_2O \rightarrow H^+ + \bar{O}H$

At Cathode $Na^+ + e^- \longrightarrow Na(s) \xrightarrow{Hg} Na(Hg)$

At Anode $Cl^- \longrightarrow \frac{1}{2}Cl_{2(g)} + e^-$

Electrochemistry

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Q On passing a current of 6 A for 965 sec. through acidulated water. 0.56L of H_2 gas was collected at Cathode at STP. Find current Efficiency.

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

$nf = 2$

Sol

$$n \times nf = \frac{it}{F}$$

$$\frac{0.56}{22.4} \times 2 = \frac{i \times 965}{96500}$$

$$i = \frac{100}{20} = 5 \text{ Amp.}$$

$$\% \text{ CE} = \frac{\text{Calculated}}{\text{Given}} \times 100$$

$$= \frac{5}{6} \times 100$$

$$= 83.3\%$$

Q: A 5 Amp. current is passed through a soln of $ZnSO_4$ for 10 min. The amount of Zn deposited at Cathode is-

Sol:→ $Zn^{+2} + 2e^- \longrightarrow Zn$ $\quad nf = 2$

$$n \times nf = \frac{it}{F}$$

$$n \times 2 = \frac{5 \times 10 \times 60}{96500}$$

$$W = \frac{6000}{96500} \times 63.4$$

$$W = 4 \text{ gm.}$$

2nd Law → When same amount of electricity is passed through two or more different soln then weight of ion deposited at electrode is directly proportional to Electrochemical Equivalence.

$n.nf = \text{constant}$

$n \propto \frac{1}{nf}$

$W \propto Z$

$W \propto \frac{EW}{F}$

$W \propto EW$

$$\frac{W_1}{EW_1} = \frac{W_2}{EW_2}$$

$$n_1 \times nf_1 = n_2 \times nf_2$$

Electrochemistry

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(iii) 1 mol MnO_4^- to Mn^{+2} ? $\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{+2}$

$5F \rightarrow 1$ mol Mn^{+2}

$\rightarrow$ (1F)

Q. How much electricity is req. in terms of faradays to produce 20 gm Ca from electrolysis of molten $CaCl_2$.

Sol:-

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

$2F \rightarrow 1$ mol Ca

$2F \rightarrow 40$ gm Ca

$1F \rightarrow 20$ gm Ca.

Ans

Weight of Ca = moles x Mw

$= 1 \times 40$

$= 40$ gm.

Q. How many coulombs of charge is req. to convert 12.3 gm of nitrobenzene to aniline?

Sol:-

$Ph-NO_2 + 6H^+ + 6e^- \longrightarrow Ph-NH_2 + 2H_2O$

$6F \rightarrow 1$ mol $PhNO_2$

$\frac{6F}{10} \rightarrow \frac{123}{10}$ gm $PhNO_2$

$0.6F \left(\frac{6F}{10}\right) \rightarrow 12.3$ gm $PhNO_2$

$0.6 \times 96500 = 57900$ C

Electrochemistry

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$n_i^\circ = 1 \times 1 = 1$

Q: 1 L of 1 M $CuSO_4$ soln is electrolysed by passing 1.5 F charge. Final molarity of the soln will be ?

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

Sol:-

$n \times n_f = \frac{it}{F}$

$n \times n_f = \frac{Q}{F}$

$n \times 2 = \frac{1.5\cancel{F}}{\cancel{F}}$

$n = \frac{1.5}{2} = 0.75$ (moles deposited)

$n_{left} = 1 - 0.75$

$= 0.25$

final $M = \frac{0.25}{1}$

$= 0.25$ M.

Trick to solve questions of Faraday law

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

$[nF \longrightarrow 1 \text{ mol } M]$

eg., 1. $Na^+ + e^- \longrightarrow Na$.

$1F \longrightarrow 1$ mol Na.

2. $Mg^{+2} + 2e^- \longrightarrow Mg$

$2F \longrightarrow 1$ mol Mg

Q: How much charge is req. for the following rxns—

(i) 1 mol Al^{+3} to Al ? $Al^{+3} + 3e^- \longrightarrow Al$

$\boxed{3F} \longrightarrow 1$ mol Al.

(ii) 1 mol Cu^{+2} to Cu ? $Cu^{+2} + 2e^- \longrightarrow Cu$

$\boxed{2F} \longrightarrow 1$ mol Cu

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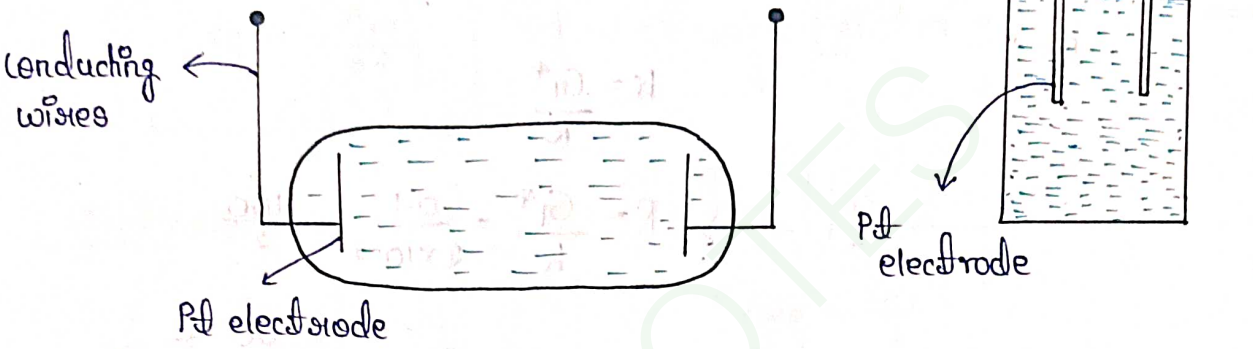
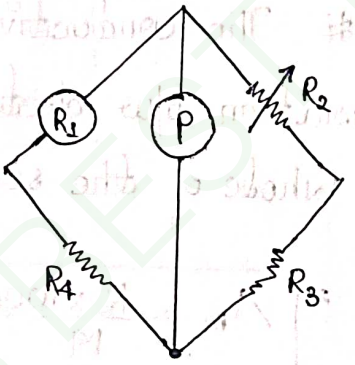
⑤ Cell Constant # (σ or G^*)

$$\sigma = \frac{l}{A}$$





Variable Resistance.

$$\frac{R_1}{R_4} = \frac{R_2}{R_3}$$

$$K = \frac{l}{R_1 A}$$

$$R_1 = \frac{R_2 R_4}{R_3}$$

$$K = \frac{G^*}{R_1}$$

Q: If K of 0.1 N KCl is 1.2×10^{-2} S cm^{-1} and R is 60 Ω then find G^*?

Sol:→ $K = 1.2 \times 10^{-2}$ S cm^{-1}

$R = 60\ \Omega$

$K = \frac{G^*}{R}$

$G^* = 1.2 \times 10^{-2} \times 60$

$G^* = 72 \times 10^{-2}\ cm^{-1}$

Ans

Electrochemistry

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Resistance | Resistivity | Conductance | conductivity | Cell constant

① **Resistance** # The hindrance offered by the solution is called Resistance.

$R \propto l$; $R \propto \frac{1}{A}$

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

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

R = Resistance

ρ = specific resistance (Restivity).

Resistance when separation b/w electrodes is 1 cm and area of the cross section is 1 cm^2.

l = separation b/w electrodes

A = Area of cross-section.

Unit of R # ohm (Ω).

② **Resistivity (or) specific resistance (ρ)** # $R = \frac{\rho l}{A}$

Unit # ohm cm.

$\rho = \frac{RA}{l}$

③ **Conductance (G).** # Reciprocal of resistance is called conductance.

$G = \frac{1}{R}$

Unit # $(ohm)^{-1}$ (or) mho (or) Ω^{-1} (or) υ (or) siemens (S)

④ **Conductivity (K)** # Reciprocal of resistivity is called conductivity.

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

Unit # $(ohm\ cm)^{-1}$ / mho cm^{-1} / $\upsilon\ cm^{-1}$ / $S\ cm^{-1}$ / $(\Omega)^{-1}\ cm^{-1}$

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Q. Find the molar ratio of Na, Ca, and Fe produced at cathode of three electrolytic cell connected in series and containing molten $NaCl$, $CaCl_2$, and $FeCl_3$, when 3F (same current) charge is passed?

Sol:-

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

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

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

$$n_1 : n_2 : n_3 = \frac{1}{nf_1} : \frac{1}{nf_2} : \frac{1}{nf_3}$$

$$n_1 : n_2 : n_3 = \frac{1}{1} : \frac{1}{2} : \frac{1}{3}$$

$$n_1 : n_2 : n_3 = 6 : 3 : 2$$

Ans

Q. If same amount of electricity is passed through $CuCl$ and $CuSO_4$, the ratio of wt of Cu deposited from $CuSO_4$ and $CuCl$ is — ?

Sol:->

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

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

$$n_1 \times nf_1 = n_2 \times nf_2$$

$$n_1 \times 2 = n_2 \times 1$$

$$\frac{n_1}{n_2} = 1/2$$

$$\boxed{\frac{W}{W_2} = 1/2.}$$ as Aw same (Cu).

Q. The same current is passed through soln of $AgNO_3$ and $CuSO_4$ connected in series. if the wt of Ag deposited is 1.08 gm. Cal. wt of Cu deposited.?

Sol.

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

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

$$n_1 \times nf_1 = n_2 \times nf_2$$

$$\frac{1.08}{108} \times 1 = \frac{W_2}{63.5} \times 2$$

$$W_2 = \frac{63.5}{200}$$

$W_2 = 0.3175$ gm.

Electrochemistry

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Effect of Dilution

1) V ↑ conc ↓ conductivity (K) ↓

2) V ↑ conc ↓ molar conductivity (Λ_m) ↑

3) V ↑ conc ↓ Equivalent conductivity (Λ_{eq}) ↑

Variation of Λ_m and $\sqrt{C}$

$$\left[\Lambda_m = \Lambda_m^\circ - A\sqrt{C}\right]$$

Λ_m = molar conductivity at conc C.

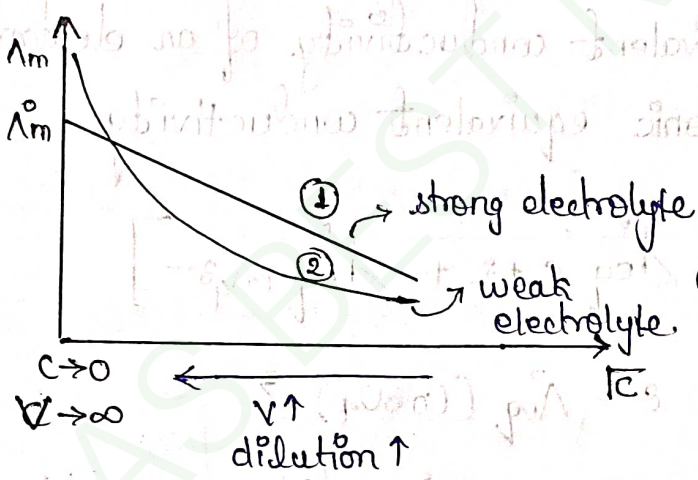
$C \to 0$

Λ_m° or Λ_m^∞ = limiting molar conductivity

$V \to \infty$

A = constant depends on nature of solvent

C = conc.



① For strong electrolyte, we can calculate Λ_m°.

② For weak electrolyte, we can not calculate Λ_m°.

*KOHLRAUSCH Law ##

The limiting molar conductivity of an electrolyte is the sum of ionic molar conductivity of ions multiply with the respective stoichiometric coefficient.

Electrochemistry

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Relation b/w Λ_{eq} & Λ_m

$N = n_f \times M$

$\Lambda_{eq} = \dfrac{K \times 1000}{M \times n_f}$

$\Lambda_{eq} = \dfrac{\Lambda_m}{n_f}$ $\quad n_f$ = charge (either +ve or -ve).

Q. Electrolyte $\quad n_f$ $\quad$ Relation b/w Λ_m and Λ_{eq}

1.	$\overset{+}{N}aCl$	1	$\Lambda_{eq} = \dfrac{\Lambda_m}{1}$
2.	$\overset{+2}{B}aCl_2$	2	$\Lambda_{eq} = \dfrac{\Lambda_m}{2}$
3.	$\overset{+3}{A}lCl_3$	3	$\Lambda_{eq} = \dfrac{\Lambda_m}{3}$
4.	$\overset{+3}{Fe}_2(SO_4)_3$	6	$\Lambda_{eq} = \dfrac{\Lambda_m}{6}$

Q. Calculate molar conductivity & Equivalent conductivity of 10^{-2} M $\overset{+2}{A}B_2$. Given: $k = 4 \times 10^{-2}$ S cm^{-1}

Sol:-

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{4 \times 10^{-2} \times 10^3}{10^{-2}} = 4 \times 10^3 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{eq} = \frac{\Lambda_m}{n_f} = \frac{\Lambda_m}{2} = \frac{4 \times 10^3}{2}$$

$$= 2 \times 10^3 \text{ S cm}^2 \text{ gmeq}^{-1}$$

Ans

Electrochemistry

covered all the topics widely

Q. A conductance cell was filled with a 0.02 M KCl soln which has conductivity 2×10^{-3} S cm^{-1}. Find the Resistance when σ is 0.1 cm^{-1}?

Sol:→ $K = 2 \times 10^{-3}$ S cm^{-1} $\quad \sigma$ or $G^* = 0.1$ cm^{-1}

$R = ?$

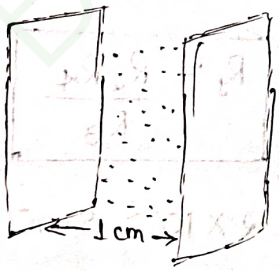
$$K = \frac{G^*}{R}$$

$$\Rightarrow R = \frac{G^*}{K} = \frac{0.1}{2 \times 10^{-3}} = \frac{100}{2}$$

$$= 50\ \Omega$$

Ans

Molar conductivity (Λ_m) ## The conductivity of 1 mol of an electrolyte when separation b/w electrodes is 1 cm and area is so large that whole of the soln is contained b/w them.



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

Λ_m = molar conductivity ($S cm^2 mol^{-1}$)

K = conductivity

M = Molarity (mol/ℓ).

Equivalent conductivity (Λ_{eq}) ## The conductivity of 1 gm-eq of an electrolyte when separation b/w electrodes is 1 cm and area is so large that whole of the soln is contained b/w them.

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

Λ_{eq} = equi. conductivity ($S\ cm^2\ gmeq^{-1}$)

K = conductivity

N = Normality ($gmeq/\ell$).

Electrochemistry

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$$A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$$

$$K_{sp} = (xs)^x (ys)^y$$

$$K_{sp} = x^x y^y s^{x+y}$$

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

Q: The conductivity of 0.01 M CH_3COOH is 3.9×10^{-5} S cm^{-1}. Find K_a & α if Λ_m^c of CH_3COOH is 390 cm^2/mol.

Sol:

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{3.9 \times 10^{-5} \times 10^3}{10^{-2}} = 3.9$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^c} = \frac{3.9}{390} = \frac{39}{3900} = 0.01$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{10^{-2} \times (10^{-2})^2}{1 - 10^{-2}} = 10^{-6}$$

Q: The conductivity of saturated solution of $Ba_3(PO_4)_2$ is 1.2×10^{-5} S/cm and Λ_m^c of $Ba_3(PO_4)_2$ is 1200 cm^2/mol. If K_{sp} of salt is $A \times 10^{-25}$. Find $\frac{A}{R}$?

Sol:

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

$$1200 = \frac{1.2 \times 10^{-5} \times 10^3}{10 \times S}$$

$$S = 10^{-5}$$

∴ Find Λ°_{eq} $BaCl_2$ and Λ°_m $BaCl_2$?

Given:- $\lambda^\circ_{eq} Ba^{+2} = 63.5 \ S\,cm^2\,eq^{-1}$

$\lambda^\circ_{eq}\ Cl^- = 76 \ S\,cm^2\,eq^{-1}$

$$\Lambda^\circ_{eq}(BaCl_2) = \lambda^\circ_{eq}(Ba^{+2}) + \lambda^\circ_{eq}(Cl^-)$$

$$= 63.5 + 76$$

$$\Lambda^\circ_{eq} = 139.5 \ S\,cm^2/eq.$$ Ans

$$\Lambda^\circ_{eq} = \frac{\Lambda^\circ_m}{nf} = \frac{\Lambda^\circ_m}{2}$$

$$\Lambda^\circ_m = 139.5 \times 2$$

$$\Lambda^\circ_m = 279 \ S\,cm^2/mol.$$ Ans

Applications of Kohlrausch law –

(1). To determine degree of dissociation of weak electrolyte.

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m}$$

(2) To find dissociation constant of weak electrolyte.

$$AB \rightleftharpoons A^+ + B^-$$

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

(3) To find solubility and solubility product of sparingly soluble salt.

Electrochemistry

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$$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$$

$$\Lambda_m^\circ (A_xB_y) = x \times \Lambda_{m\,A^{y+}}^\circ + y \times \Lambda_{m\,B^{x-}}^\circ$$

$$\Lambda_m^\circ NaCl = \Lambda_{m\,Na^+}^\circ + \Lambda_{m\,Cl^-}^\circ$$

$$\Lambda_m^\circ MgCl_2 = \Lambda_{m\,Mg^{+2}}^\circ + 2\Lambda_{m\,Cl^-}^\circ$$

$$\Lambda_m^\circ CH_3COOH = \Lambda_{m\,CH_3COO^-}^\circ + \Lambda_{m\,H^+}^\circ$$

$$\left[\Lambda_m^\circ Ca_3(PO_4)_2 = 3\Lambda_{m\,Ca^{+2}}^\circ + 2 \times \Lambda_{m\,PO_4^{3-}}^\circ\right]$$

The limiting equivalent conductivity of an electrolyte is the sum of ionic equivalent conductivity.

$$\left[\Lambda_{eq}^\circ Ca_3(PO_4)_2 = \Lambda_{eq\,Ca^{+2}}^\circ + \Lambda_{eq\,PO_4^{3-}}^\circ\right]$$

Q. Find $\Lambda_m^\circ (CaSO_4)$ & $\Lambda_{eq}^\circ (CaSO_4)$?

Given: $\Lambda_{m\,Ca^{+2}}^\circ = 119 \ S\,cm^2\,mol^{-1}$

$\Lambda_{m\,SO_4^{2-}}^\circ = 160 \ S\,cm^2\,mol^{-1}$

$$\Lambda_m^\circ (CaSO_4) = \Lambda_m^\circ (Ca^{2+}) + \Lambda_m^\circ (SO_4^{2-})$$

$$= 119 + 160$$

$$= 279 \ S\,cm^2\,mol^{-1}$$

$$\Lambda_{eq}^\circ = \frac{\Lambda_m^\circ}{n_f} = \frac{279}{2} = 139.5 \ S\,cm^2\,gmeq^{-1}$$

Electrochemistry

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$Ba_3(PO_4)_2$

$\Rightarrow K_{sp} = 3^3 \times 2^2 \times s^{3+2}$

$= 27 \times 4 \times s^5$

$= 27 \times 4 \times 10^{-25}$

$A = 27 \times 4$

$\frac{A}{12} = \frac{\cancel{27} \times \cancel{4}}{\cancel{12}\ \cancel{3}} = 9$

$\frac{A}{12} = 9$ Ans

(4) To find Λ_m° of an electrolyte when Λ_m° of other electrolytes are given.

eg. $\Lambda_m^\circ (CH_3COOH) = ?$

$\Rightarrow \Lambda_m^\circ (CH_3COOH) = \Lambda_m^\circ (CH_3COONa) + \Lambda_m^\circ (HCl) - \Lambda_m^\circ (NaCl)$

$= \lambda_{m CH_3COO^-}^\circ + \lambda_{m Na^+}^\circ + \lambda_{m H^+}^\circ + \lambda_{m Cl^-}^\circ - \lambda_{m Na^+}^\circ - \lambda_{m Cl^-}^\circ$

Given :- $\Lambda_m^\circ (CH_3COONa)$

$\Lambda_m^\circ (HCl)$

$\Lambda_m^\circ (NaCl)$

Q. Cal. $\Lambda_m^\circ (CH_3COOH)$

Given :-

Electrolyte	Λ_m° ($Scm^2 mol^{-1}$)
CH_3COONa	91
HCl	426
NaCl	126

$\Lambda_m^\circ (CH_3COOH) = \Lambda_m^\circ (CH_3COOH) + \Lambda_m^\circ (HCl) - \Lambda_m^\circ (NaCl)$

$= 91 + 426 - 126$

$= 391\ Scm^2/mol.$

Electrochemistry

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Q. Find Λ_m° $Ba(OH)_2$

Given:

Electrolyte	Λ_m° ($Scm^2 mol^{-1}$)
NaOH	248
NaCl	126
$BaCl_2$	280

$$\Lambda_m^\circ (Ba(OH)_2) = \Lambda_m^\circ (BaCl_2) - 2\Lambda_m^\circ (NaCl) + 2\Lambda_m^\circ (NaOH)$$

$$= 280 - 2 \times 126 + 2 \times 248$$

$$= 280 - 252 + 496$$

$$= 524 \ Scm^2/mol.$$