my fault

Board imp

* Kohlrausch's Law:

- according to this law, limiting molar conductivity of an electrolyte, at infinite dilution, can be expressed as sum of individual contribution of anion and cation of electrolytes.

- if limiting molar conductivity of cation is denoted by λ°_+ and that of anion by λ°_- then limiting molar conductivity of electrolyte:

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

ν_+ and ν_- are number of cation and anion per formulae of electrolyte.

→ Application:

1.) calculation of molar conductivities of weak electrolyte at infinite dilution.

2.) determine degree of dissociation:
- ratio of molar conductivity at specific concn 'c' to molar conductivity at infinite dilution.
- denotion → α.

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

3.) Determine dissociation constant (K) of weak electrolyte
- $K = \frac{c\alpha^2}{1-\alpha}$
- $K = \frac{c\Lambda_m^2}{\Lambda^{\circ 2}_m\left[1 - \frac{\Lambda_m}{\Lambda^\circ_m}\right]} = \frac{c\Lambda_m^2}{\Lambda^\circ_m(\Lambda^\circ_m - \Lambda_m)}$

K = dissociation constant
C = concentration of electrolyte
α = degree of ionization.

4.) Determine solubility of sparingly soluble salt:

$$\Lambda^\circ_m = \frac{K \times 1000}{\text{molarity}} = \frac{K \times 1000}{\text{solubility}}$$

$$\therefore \text{Solubility} = \frac{K \times 1000}{\Lambda^\circ_m}$$

Q: 25. at 18°C, equivalent conductance of H^+ and CH_3COO^- at infinite dilution are 315 and 35 mho cm² eq⁻¹ resp. Equivalent conductivity of CH_3COOH at ∞ dilution is

→ $\Lambda^\circ_m = 315 + 35 \longrightarrow \underline{350}$. mho cm² eq⁻¹

$(\Lambda eq)_{H^+}$ $(\Lambda eq)_{CH_3COO^-}$

Q: 26. molar conductance at infinite dilution of $AgNO_3$, AgCl and NaCl are 116.5, 121.6 and 110.3 resp. molar conductance of $NaNO_3$ is:

→ $AgNO_3 = 116.5$ $AgCl = 121.6$ $NaCl = 110.3$

$$AgNO_3 + NaCl \longrightarrow AgCl \downarrow + NaNO_3$$

$$(\Lambda^\circ_m)_{NaNO_3} = [((\Lambda m)_{AgNO_3}) + ((\Lambda m)_{NaCl})] - [(\Lambda m)_{AgCl}]$$
$$= [116.5 + 110.3] - [121.6]$$
$$= \underline{105.2}$$

Q: 27. at infinite dilution, eq. conductance of CH_3COONa, HCl and CH_3COOH are 91, 426, 391 mho cm² at 25°C. Eq. conductance of NaCl at ∞ dilution be:

→ $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$.

$$(\Lambda^\circ_m)_{NaCl} = [(\Lambda m)_{CH_3COONa} + (\Lambda m)_{HCl}] - [(\Lambda m)_{CH_3COOH}]$$

$$(\Lambda^{\circ}_m)_{NaCl} = (91+426) - (391)$$
$$= \underline{126} \text{ mho cm}^2$$

Q:28 Value of λ^{∞}_m for NH_4Cl, $NaOH$ and $NaCl$ are 129.8, 248.1 and 126.4 $ohm^{-1}\ cm^2\ mol^{-1}$ resp. Calculate λ^{∞}_m for NH_4OH solution (in $ohm^{-1}\ cm^2\ mol^{-1}$)

→ $NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$.

$$(\Lambda^{\circ}_m)_{NH_4OH} = [(129.8) + (248.1)] - [126.4]$$
$$= [377.9] - [126.4] \longrightarrow 251.5$$

Q:29 Equivalent conductivity of 0.1 N CH_3COOH @ 25°c is 80 and at ∞ dilution is 400. α of CH_3COOH is:

→ $\alpha = \dfrac{\Lambda_m}{\Lambda^{\circ}_m} \longrightarrow \dfrac{\cancel{280}}{{}_{510}\cancel{400}} \longrightarrow \underline{0.2}$.

Q:30 Λ°_m for $CaCl_2$ and $MgSO_4$ from table.

→ $(\Lambda^{\circ}_m)_{CaCl_2} = (\Lambda^{\circ}_m)_{Ca^{2+}} + 2(\Lambda^{\circ}_m)_{Cl^-}$
$= (119) + 2\ (76.3)$
$= 119 + 152.6 \longrightarrow \underline{\underline{271.6}}\ S cm^2 mol^{-1}$

$(\Lambda^{\circ}_m)_{MgSO_4} = (\Lambda^{\circ}_m)_{Mg^{+2}} + (\Lambda^{\circ}_m)_{SO_4^{2-}}$
$= (106) + (160) \longrightarrow \underline{266}\ S cm^2 mol^{-1}$

Q:31 conductivity = 0.001028 of acetic acid is 4.95×10^{-5} S cm^{-1}. if Λ_m is 390.5 S $cm^2\ mol^{-1}$

→ $\Lambda_m = \dfrac{K}{C} \longrightarrow \dfrac{4.95 \times 10^{-5}}{1028 \times 10^{-7}} \times 1000\ \dfrac{cm^3}{Ltr}$

$\longrightarrow \dfrac{4950 \times 10^{-5}}{1028 \times 10^{-7}} \longrightarrow 4.815 \times 10^{+2}$

$\rightarrow \underline{\underline{48.15}}$.

$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{48.15}{390.5} \rightarrow 0.1233$

$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{(1028 \times 10^{-7}) \times (1520289 \times 10^{-8})}{1 - 0.1233}$

$\rightarrow \frac{1562857092 \times 10^{-15}}{8767 \times 10^{-4}} = 178265.893 \times 10^{-11}$

$\rightarrow \underline{\underline{1.78 \times 10^{-5}}}$

Q: 32 $K_a = 25 \times 10^{-6}$ $c = 0.01M$ $\Lambda = 19.6$ $\Lambda^\circ_{eq} = ?$

$\rightarrow$ $K_a = c\alpha^2$

$\alpha = \sqrt{\frac{K_a}{c}} \rightarrow \sqrt{\frac{25 \times 10^{-6}}{1 \times 10^{-2}}} \rightarrow \alpha = 5 \times 10^{-2}$

$\alpha = \frac{\Lambda_{eq}}{\Lambda^\circ_{eq}} \rightarrow \Lambda^\circ_{eq} = \frac{\Lambda_{eq}}{\alpha} = \frac{19.6}{5 \times 10^{-2}} = \underline{\underline{392}}$.

* Commercial cells:

- any battery consists of two or more than two Galvanic cells connected in series where chemical energy through redox reaction.
- there are mainly two types of batteries:

1.) Primary cells (batteries):

- these cells are not chargeable because electrode reaction occurs only once and after use over a period of time cells become dead and cannot be used.

eg: Dry cell (Leclanche cell) ; Mercury cell.

A.) **Dry cell:** (torch વાળા pencil cell)

Anode → Zn

Cathode → MnO_2 + C (graphite)

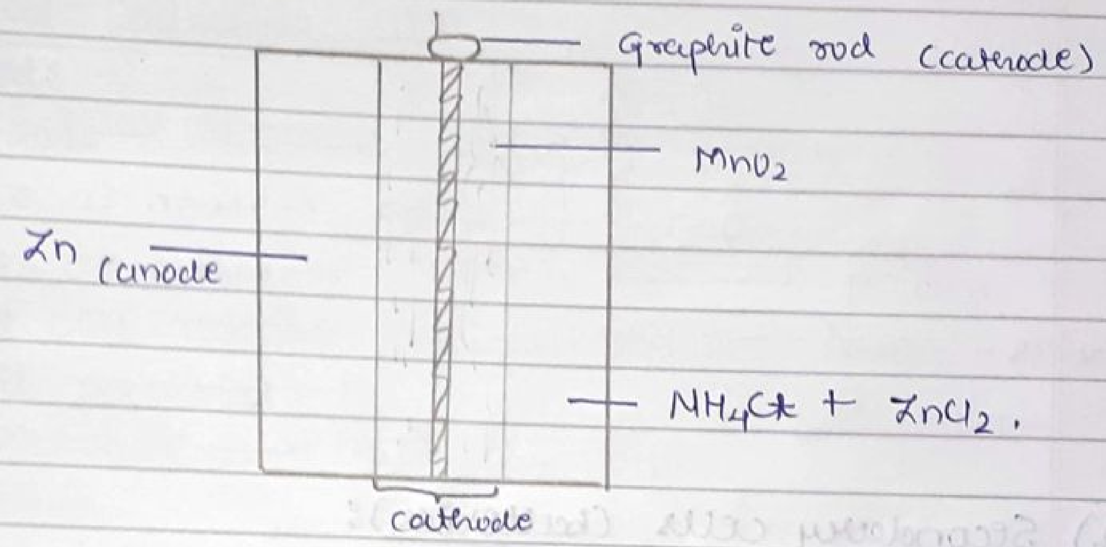
Electrolyte → NH_4Cl + $\underbrace{ZnCl_2}$ converts NH_4Cl_2 into complex salt for ↑ battery life

Reaction at anode → $Zn_{(s)} \longrightarrow Zn^{+2} + 2e^-$

Reaction at cathode → $MnO_{2(s)} + NH_4^+{}_{(aq)} \longrightarrow NH_3^+(\uparrow) + MnO_{(OH)}$

Met cell reaction → $Zn + MnO_2 + NH_4^+ \longrightarrow Zn^{+2} + (MnO_{(OH)} + NH_3$

cell potential → 1.5 volt.



Q833 write role of $ZnCl_2$ in dry cell (Leclanche cell).

→ • Role of $ZnCl_2$ in dry cell is to combines with NH_3 produced to form complex salt otherwise pressure developed due to NH_3 would crack seal of cell.

$$2NH_{3(g)} + ZnCl_{2(aq)} \longrightarrow [Zn(NH_3)_4]Cl_2$$

tetra ammine zinc(+2) chloride

- in this reaction, zinc ion, primarily from $ZnCl_2$, is acting as a Lewis acid; complex formed solubilizes gas

B.) Mercury cell: (Button cell of wristwatch)

Anode → Zn-Hg or Zn(Hg) Amalgam

Cathode → HgO + C (graphite)

Electrolyte → KOH + ZnO

Reaction at anode → $Zn(Hg) + 2OH^- \longrightarrow ZnO_{(s)} + H_2O + 2e^-$

Reaction at cathode → $HgO_{(s)} + H_2O + 2e^- \longrightarrow Hg_{(l)} + 2OH^-$

Net cell reaction → $Zn(Hg) + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

cell potential ⟶ 1.35 volt.

diag from NCERT

2.) Secondary cells (batteries):

- rechargeable and can be used again and again.
- it is recharged by passing current through it from an external source.

eg: lead storage cell; Nickel-cadmium cell.

A.) Lead Storage Cell:

Anode → Pb

Cathode → PbO_2

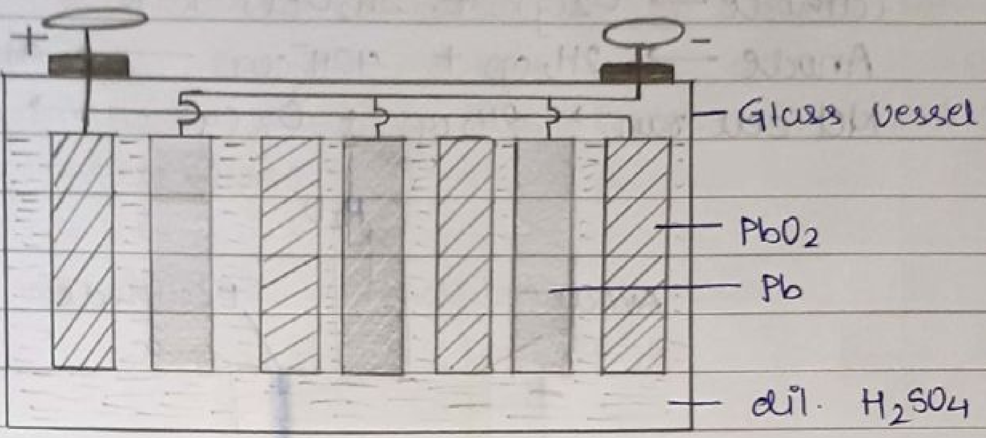
Electrolyte → 38% H_2SO_4

Reaction at anode → $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

Reaction at cathode → $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Net cell reaction ⟶

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$



B.) Nickel - Cadmium cell:

Anode → Cd

cathode → Ni

Rxn at anode → $Cd_{(s)} \longrightarrow \overset{+2}{Cd}O$.

Rxn at cathode → $\overset{+3}{Ni}(OH)_3 \longrightarrow \overset{+2}{Ni}(OH)_2$

Net cell reaction → $Cd_{(s)} + 2Ni(OH)_{3(s)} \longrightarrow CdO_{(s)} + 2Ni(OH)_2 + H_2O_{(l)}$

cell potential →

Electrolyte → NaOH or KOH

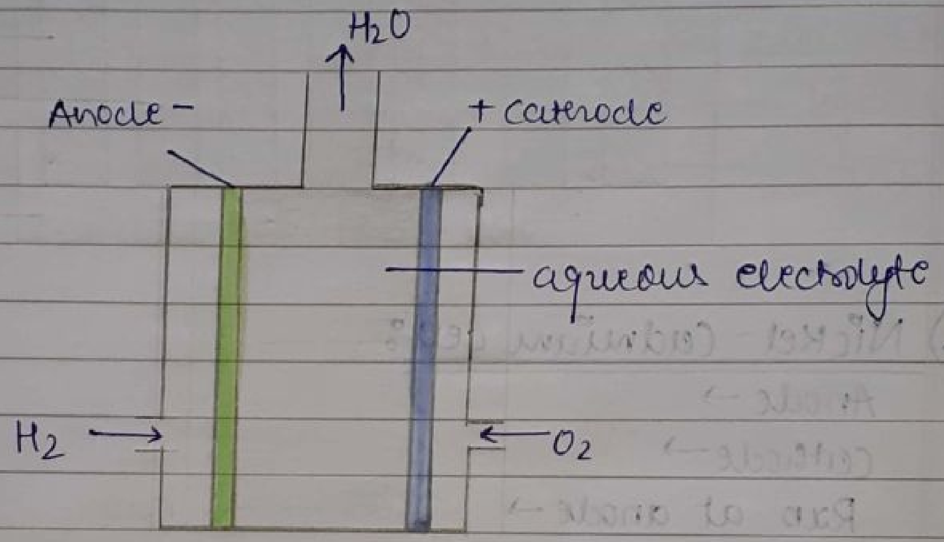
pic print (NCERT)

* Fuel cells:

- produce electrical energy directly from combustion of fuels such as hydrogen, carbon monoxide or methane.
- most successful fuel cell, H_2-O_2 cell utilizes reaction b/w H_2 and O_2 to produce water.
- H_2 and O_2 are bubbled through porous carbon electrode in cell into concentrated aqueous NaOH.
- catalysts are incorporated into electrode.
-

Electrode reactions are:

Cathode → $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
Anode → $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$
Net cell rxn → $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$



* Advantages of fuel cells:

- pollution free device
- efficiency is about 75% which is higher than conventional cells.
- continous source of energy if supply of gases is maintained.
- light in weight as compared to electrical generators to produce corresponding quantity of power.

* Corroision:

- Gradual loss of metal from its surface in presence of air and moisture is CORROISION.
- chemically rust is hydrated ferric oxide. '$Fe_2O_3 \cdot xH_2O$'
- corroision may be considered as an electrochemical phenomenon.

- In these miniature corroision cells, pure iron act as anode, surface area acts as cathode and moisture having dissolved CO_2 and O_2 acts as electrolyte.

- Reaction at Anode: Oxidation of iron.

$$2Fe(s) \xrightarrow{oxid^n} 2Fe^{+2} + 2e^- \qquad \left(E^\circ_{Fe^{+2}/Fe}\right) = -0.44V$$

- electrons are picked up by H^+ ion which are produced from H_2CO_3, while H_2CO_3 is formed due to dissolution of CO_2 in moisture of water.

$$[H_2CO_3 \longrightarrow 2H^+ + CO_3^{2-}]$$

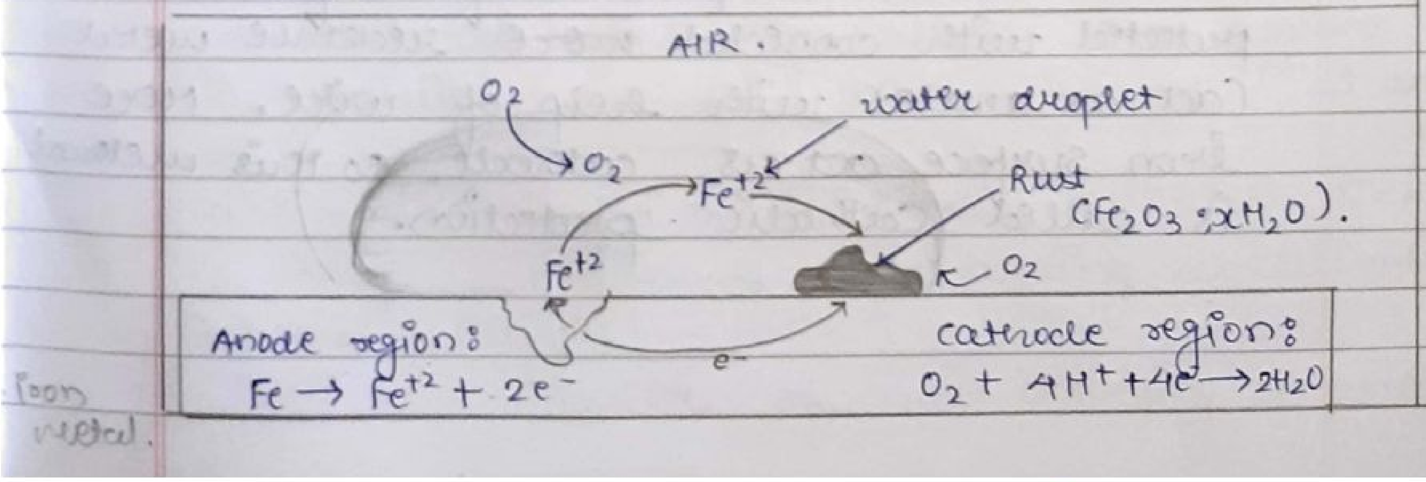
red^n

- R/At cathode: $O_2(g) + 4H^+(aq) + 4e^- \xrightarrow{red^n} 2H_2O(l)$ $E^\circ_{H^+/O_2/H_2O} = 1.23V$
- Net Reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^+(aq) + 2H_2O(l)$

$E^\circ_{cell} = 1.67V.$

- The ferrous ions so formed move through water and come at surface where these are further oxidised by atmospheric oxygen to ferric ions and forms rust which is hydrated ferric oxide, $(Fe_2O_3 \cdot xH_2O)$.

$$2Fe^{+2} + 1/2\ O_2 + H_2O \longrightarrow Fe_2O_3 + 4H^+$$
$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O.$$



→ Prevention of Corrosion:

(I.) Barrier protection:

- thin film is introduced between iron and atmospheric gases and moisture like-
  - (a) by covering surface with paint or thin film of grease.
  - (b) by electroplating iron with some non-corrosive metals.
    - i.e. Cu, Ni, Cr, etc.

(II.) Sacrificial protection:

- in this method iron surface is covered with more electropositive metal than iron which gets oxidised in preference to iron.
- more electropositive metal loses electrons instead of irons and thus this metal is sacrificed at cost of iron.
- iron is coated with zinc and the process is known Galvanization.

(III.) Electrical protection (cathodic prot.):

- used for protection of underground water pipes or iron tanks.
- in this method, exposed surface of iron is protected with connected more reactive metal (act as anode) with help of wire. here iron surface act as cathode, so this method is called cathodic protection.

Q:34 Write about electrochemical series and its significance

→ • Table is which reduction potential of various electrodes have been arranged in increasing order is called Electrochemical series or electromotive series or activity series.

	Electrode	Electrode reaction	E°(volts)	
SRP↑	Li^+/Li	$Li^+ + e^- \rightarrow Li$	−3.045	(least)
or	Zn^{2+}/Zn	$Zn^{+2} + 2e^- \rightarrow Zn$	−0.763	
oxidising stren↑	H^+/H (Pt)	$2H^+ + 2e^- \rightarrow H_2$	0.0	(std)
	Cu^{+2}/Cu	$Cu^{+2} + 2e^- \rightarrow Cu$	+0.334	
↓ Reduc. stren↓	F_2/F (Pt)	$F_2 + 2e^- \rightarrow 2F^-$	+2.887	(high)

• Significance:

I.) Relative strength of oxidising and reducing agen

II.) Calculating E.M.F of cell.

III.) Predicting feasibility of redox reaction

→ predict whether a metal can liberate hydrogen from acids or not. Metals which have negative reduction potential can only liberate hydrogen from acids.

→ metals which have low S.R.P value have greater rate of corroision.

→ cations having higher SRP value will discharge first at cathode and anions having low S.R.P value discharge 1st at anode

(a) $K^+ < Ca^+ < Na^+ < Mg^+ < Al^{+3} < Zn^{+2} < Fe^{2+} < H^+ < Cu^{+2} < Hg^{2+} < Ag^+ < Au^+$
(order of discharging at cathode)

(b) $SO_4^{2-} < OH^- < Cl^- < Br^- < I^-$
(order of discharging at anode)

* Conductivity cell:

- consists two platinum electrode coated with platinum black.
- they've area of cross-section 'A' and are separated by distance 'l'.
- resistance of such a column of solution is given by following equation:

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

conductivity = conductance × cell constant.

$$\boxed{\kappa = G \times \frac{l}{A}}$$

19/04/24