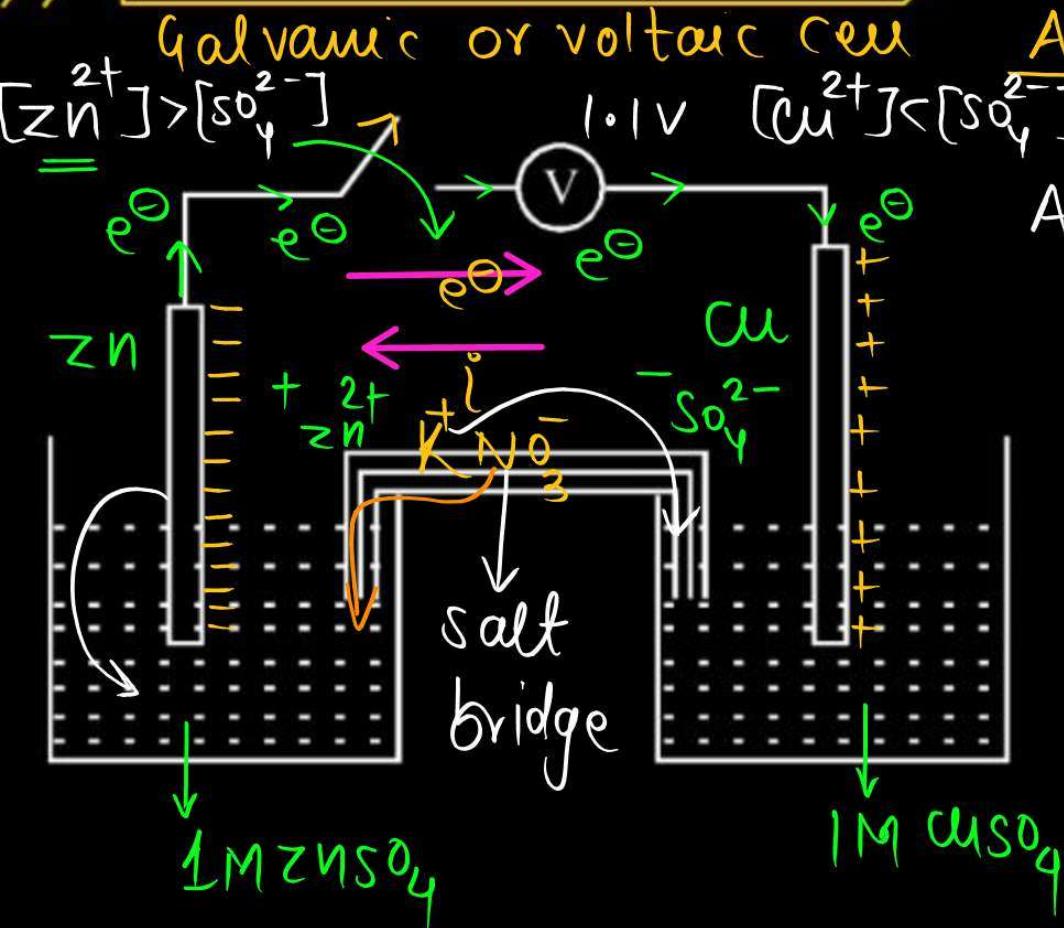
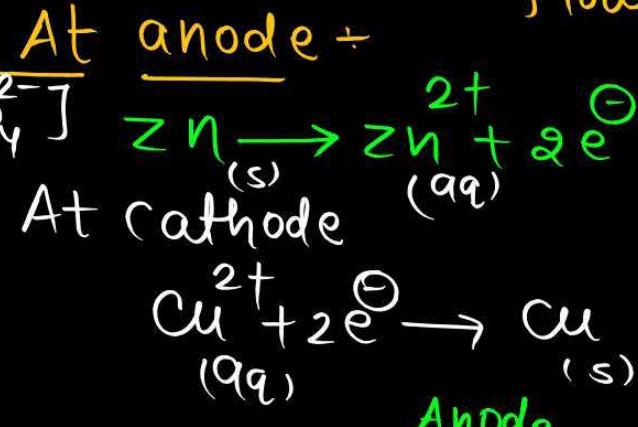


Electrochemistry Cell



Daniel Cell

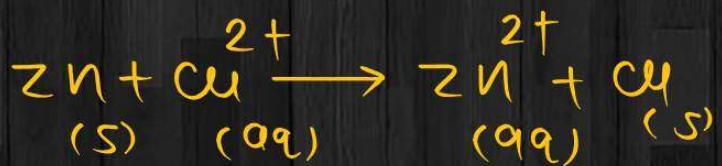


L O A N
Left oxidation Negative

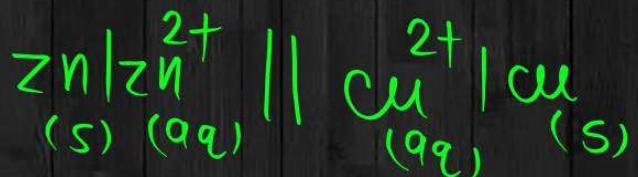
flow of e⁻ A → C
flow of i⁻ C → A

P W

Net cell Rxn:



Cell representation



Standard electrode potential is taken as standard reduction potential

Net cell potential

$$E_{\text{cell}}^{\circ} = 1.0 \text{ V}$$

$$E_{\text{cell}}^{\circ} = (E_C^{\circ})_R - (E_A^{\circ})_R$$

Salt Bridge and its funcⁿ

Salt bridge



Paste of polysaccharide (agar-agar)

+
Inert electrolyte

(whose ions do not take part in main
(cell Rxn))

KNO_3 , NH_4NO_3 etc

KCl is not used in

Ag, Tl, Pb, Hg

Aji Thailand Pyor Hoggia
main

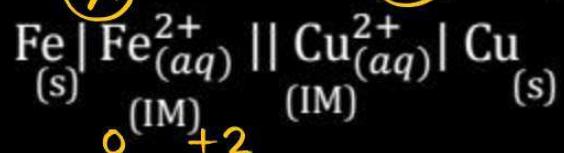
Ionic mobility of cation = ionic mobility of
Anion

main funcⁿ

- ① To maintain electrical neutrality
- ② To complete inner ckt without mixing of the two solⁿ
- ③ To minimise liq-liq Juncⁿ potential

$$E^\circ_{\text{cell}} = (E^\circ_R)_C - (E^\circ_R)_A = 0.34 - (-0.44)$$

Q. For Galvanic cell find E°_{cell} = 0.78 V



Given $E^\circ \text{Fe}|\text{Fe}^{2+} = +0.44 \text{ V}$ $\Rightarrow E^\circ_{\text{Fe}^{2+}|\text{Fe}} = -0.44 \text{ V}$
 $E^\circ \text{Cu}^{2+}|\text{Cu} = 0.34 \text{ V}$

» ΔG° and K_{eq} for Galvanic Cell

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

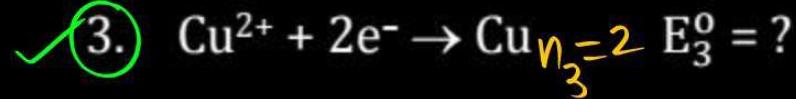
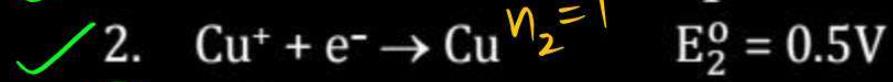
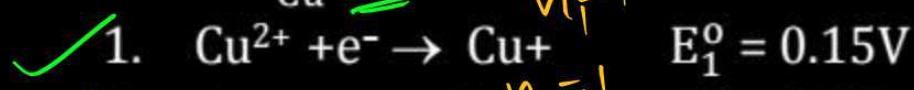
$$\Delta G^\circ = -RT \ln K$$

ΔG° is an extensive prop (Additive)

E°_{cell} is !! intensive prop (non additive)

Q. Given $E^\circ_{\text{Cu}^+ \mid \text{Cu}} = +0.15 \text{ V}$
 $E^\circ_{\text{Cu}^+ \mid \text{Cu}^-} = +0.5 \text{ V}$

Find $E^\circ_{\text{Cu}^{2+} \mid \text{Cu}}$?



$$\Delta E_3^\circ = \Delta E_1^\circ + \Delta E_2^\circ$$

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

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

$$2 E_3^\circ = E_1^\circ + E_2^\circ$$

$$E_3^\circ = \frac{0.15 + 0.50}{2}$$

$$= \frac{0.65}{2}$$

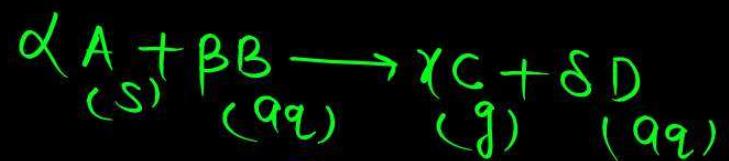
$$= 0.325 \text{ V}$$

Nernst Equation

$$F = 96500 \text{ C} , R = \frac{8.3}{3} , T = 298 \text{ K}$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.06RT}{nF} \log Q$$

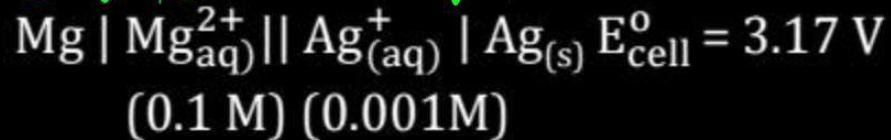
~~$$E_{cell} = E_{cell}^{\circ} - \frac{0.06}{n} \log Q$$~~



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



Q. Find EMF of cell

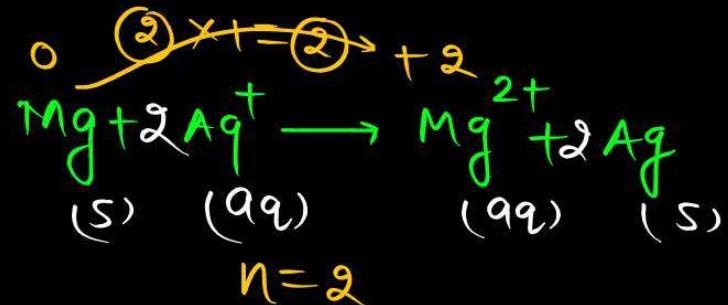


$$E_{\text{cell}} = 3.17 - \frac{0.06}{2} \log_{10} 10^5$$

$$= 3.17 - 0.03 \times 5$$

$$= 3.17 - 0.15$$

$$\begin{array}{r} 3.17 \\ - 0.15 \\ \hline 3.02 \end{array}$$



$$\vartheta = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} = \frac{10^{-1}}{(10^{-3})^2} = 10^5$$

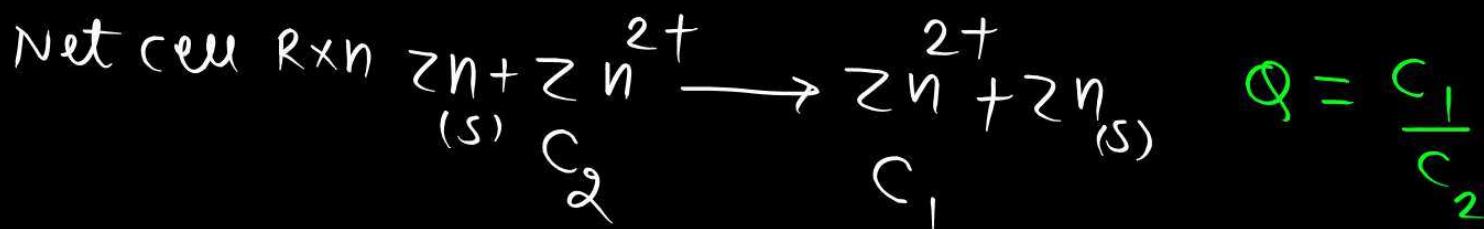
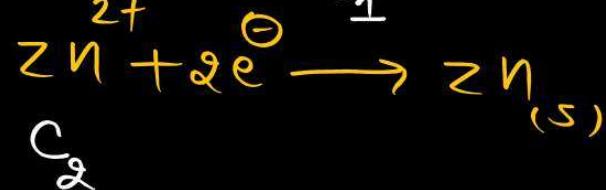
Conc. Cell

Same material is used with diff concⁿ

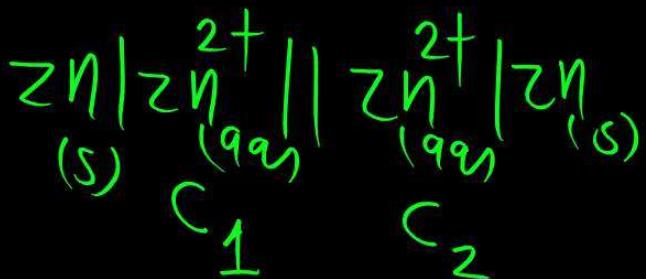
At Anode



At Cathode



Cell Repre.



Nernst eqn

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.06}{2} \log_{10} \left(\frac{c_1}{c_2} \right)$$

for concⁿ cell $E_{\text{cell}}^{\circ} = 0$

for spont. working
of cell

$$E_{\text{cell}} = - \frac{0.06}{2} \log_{10} \left(\frac{c_1}{c_2} \right)$$

$$\Delta q = -nF E_{\text{cell}}$$

$\Delta q < 0$ spont

$$E_{\text{cell}} = + \frac{0.06}{2} \log \left(\frac{c_2}{c_1} \right)$$

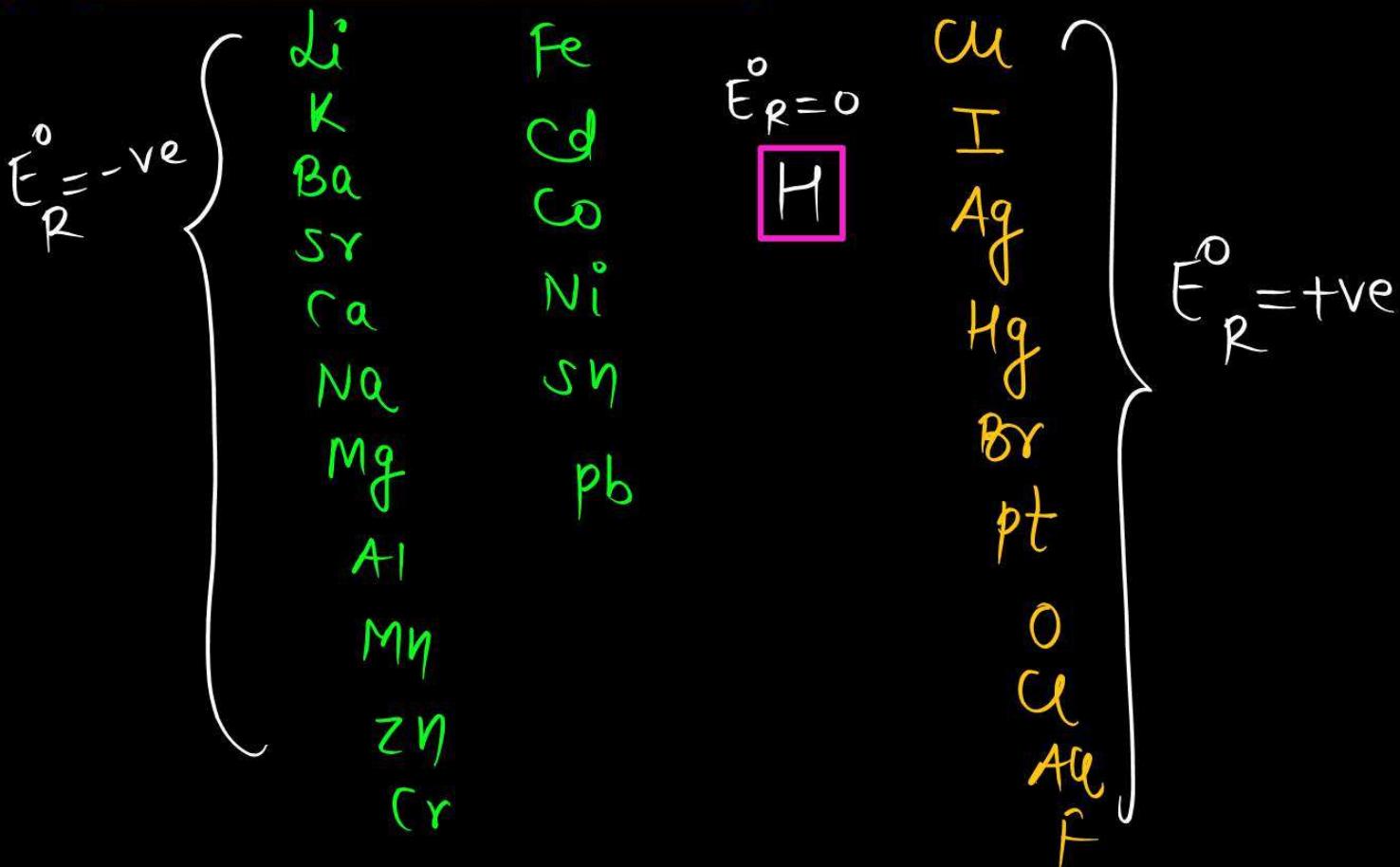
$$E_{\text{cell}} > 0$$

$$c_2 > c_1$$

S.H.E (standard hydrogen electrode)



Electrochemical series



Charac. Of ECS

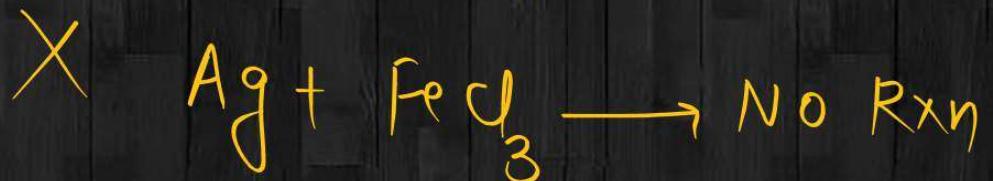
- ① $E_R^\circ H = 0$
- ② Elements lie above H have $E_R^\circ = -ve$
- ③ " " below H " " $E_R^\circ = +ve$
- ④ T to B $E_R^\circ \uparrow_{es}$
- ⑤ Li \rightarrow most -ve (sabse kam E_R°)
F \rightarrow most +ve (" jyada E_R°)

Application of ECS

- ① Reducing and oxidising power
T to B R.o.P decreases , O.o.P increases
($E_R^\circ \uparrow$)
- ② Reactivity
T to B decreases

③ Metal displacement :-

The metal which lie above in E.C.S can displace the metal from its salt which lie below in E.C.S



④ non metal displacement :-

The non metal which lie below in E.C.S can displace the non metal from its salt which lie above in E.C.S

I



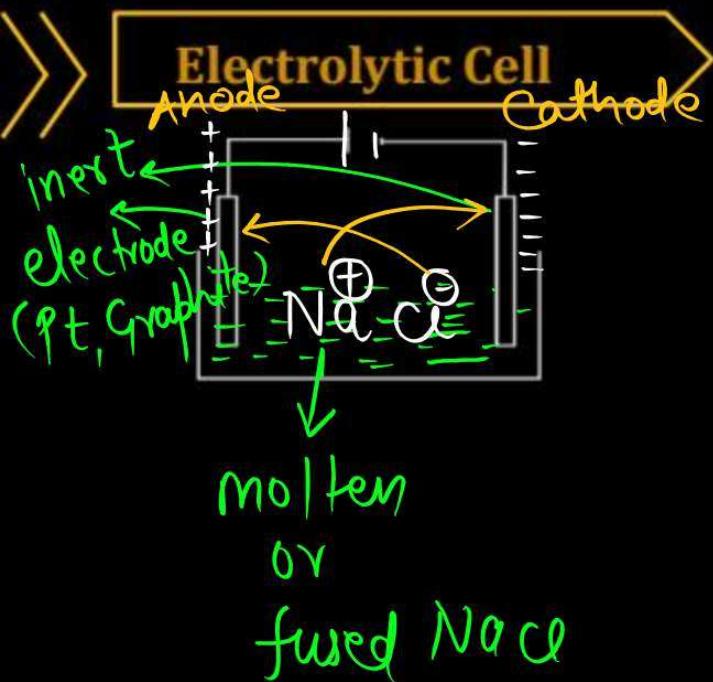
Br



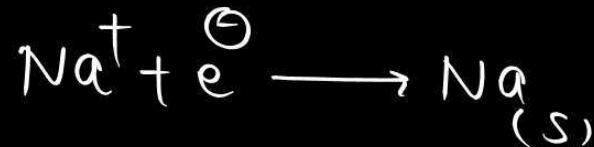
Cl

No Rxn

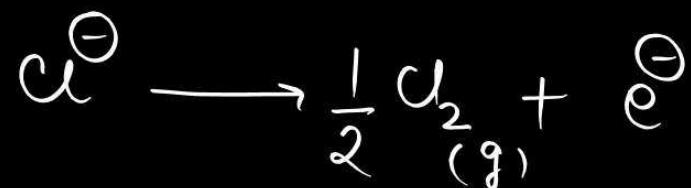
F

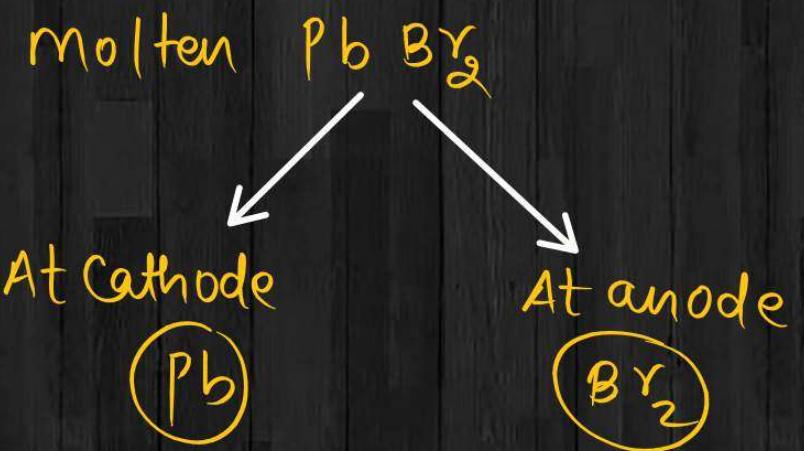


At Cathode :



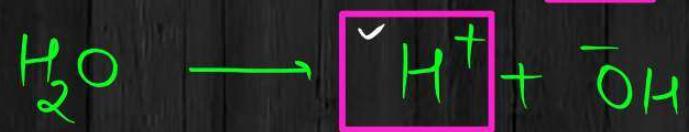
At anode





Preferential discharge Theory (P.D.T)

Aq, NaCl



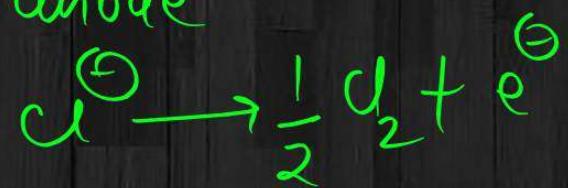
Case ① In the case of cations, that ion will migrate 1st which has greater E°_R (which lie below in E₀s)

Jo neechhe aata Hai, woh jata Hai

At Cathode



At anode



Nature of soln $\rightarrow \text{NaOH}$ (Basic)

case ② for anions



tendency to migrate



S NO OH Cl Br I

Electrolyte
Aq CuSO₄

Electrode
Pt or graphite

Product at Cathode
Cu

Product at Anode
O₂

Aq AgNO₃

Pt or graphite

Ag

O₂

Aq NaOH

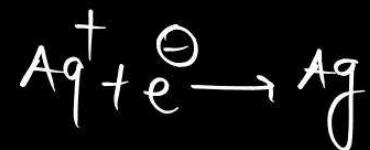
Pt or graphite

H₂

O₂

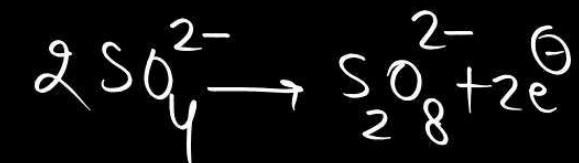
Aq AgNO₃

Ag electrode



Conc H₂SO₄

Pt or graphite



Faradays Law - First law

$\omega \propto Q$ $z =$ electrochemical equivalence

$\omega = z Q$ $Q =$ charge = $i t$

$$\omega = \frac{E \cdot w}{F} Q$$

$$\omega = \frac{Mw}{nfxF} \times Q$$

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

Q. How long should a current of 0.25 Amp be passed through a molten metal salt when it deposit that much wt of metal which is equal to its Electrochemical equivalence?

$$\omega = Z$$

$$it = I$$

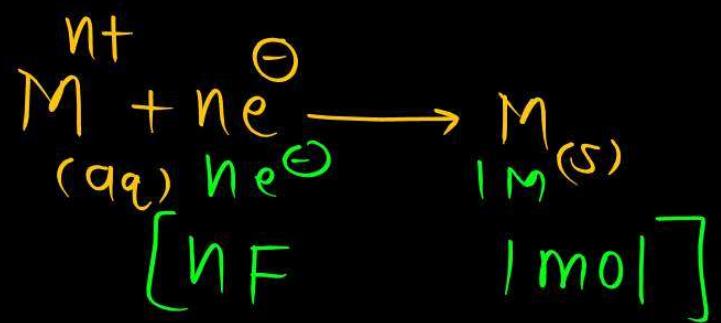
$$\omega = Z \times$$

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

$$Q = I$$

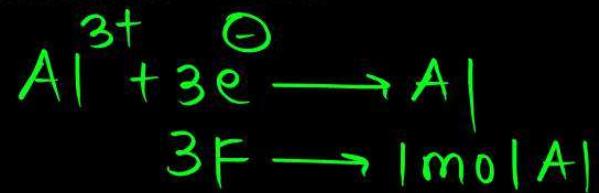
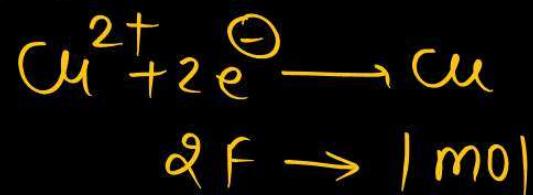
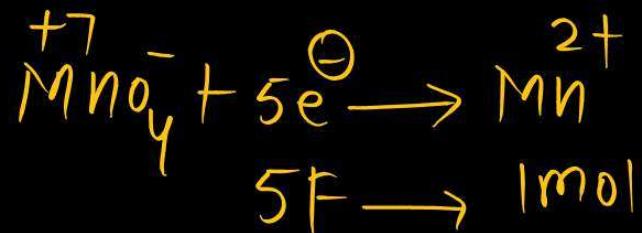
$$t = 4 \text{ sec}$$

Trick to solve ques of F. L in us



charge of 1 mol of e^-
= 1 F
96500

How much change is req for Rxns

1. 1 mol $\text{Al}^{3+} \rightarrow \text{Al}$ 2. 1 mol $\text{Cu}^{2+} \rightarrow \text{Cu}$ 3. 1 mol $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$ 

Resistance conductance resistivity conductivity of a cell



$$\textcircled{1} \quad R = \frac{\rho l}{A} \quad \Omega \text{ (ohm)}$$

l = distance b/w
electrodes

A = Area of cross section

\textcircled{2} Resistivity or specific Resistance
(ρ)

$$\rho = \frac{RA}{l} \quad \text{ohm-cm}$$

($\Omega\text{-cm}$)

③ Conductance (G)

$$G = \frac{1}{R} \text{ } (\Omega)^{-1} \text{ } (\text{ohm})^{-1} \text{ } S$$

Ω mho

④ Specific conductance or conductivity (K)

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

$$K = \frac{l}{RA} \text{ } (\text{ohm})^{-1} \text{ } \text{cm}^{-1} \text{ } S \text{cm}^{-1}$$

$\Omega^{-1} \text{cm}^{-1}$
 V cm^{-1}

⑤ cell constant (σ or q^*)

$$\sigma \text{ or } q^* = \frac{l}{A}$$

Relation b/w K , q^* & R

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

$$R = \frac{l}{K} \times q^*$$

$$q^* = R K$$

Molar conductivity

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

$$K = S \text{ cm}^{-1} \quad \Lambda_m^c = S \text{ cm}^2 \text{ mol}^{-1}$$

$$M = \frac{\text{mol}}{\text{L}}$$

Relation b/w Λ_m^c & Λ_{eq}^c

$$\Lambda_{eq}^c = \frac{\Lambda_m^c}{n.f}$$

Equivalent Conductivity

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

$$K = S \text{ cm}^{-1} \quad N = \text{gm eq/L}$$

$$\Lambda_{eq}^c = S \text{ cm}^2 \text{ gm eq}^{-1}$$

$n.f$ = Total +ve charge

OR

Total -ve charge



Q. If k of 0.1 N KCl is $1.2 \times 10^{-2} \text{ S/cm}$ and $R = 60 \Omega$ find cell constant ?

$$\begin{aligned}G^* &= R k \\&= 60 \times 1.2 \times 10^{-2} \text{ cm}^{-1}\end{aligned}$$

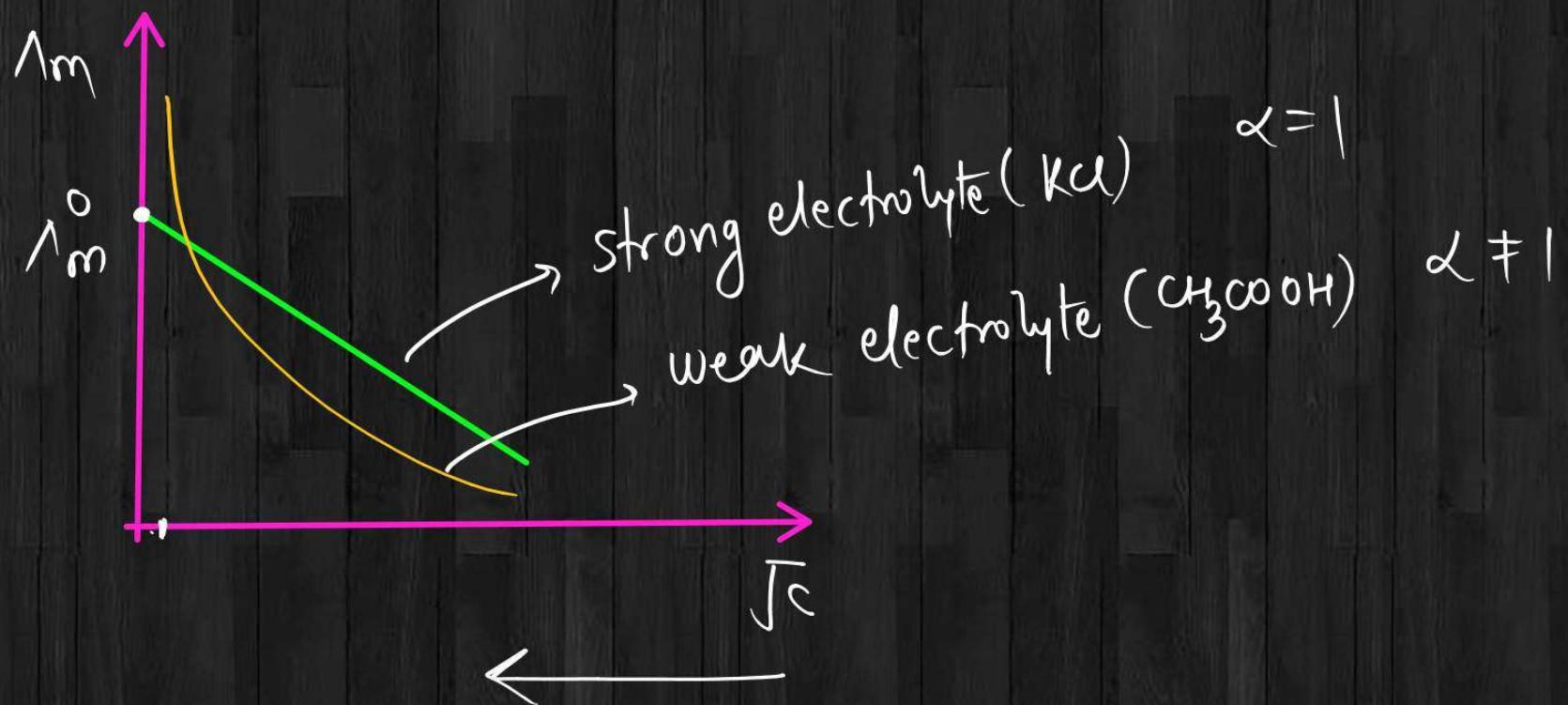
$$\Lambda_{eq}^c = \Lambda_{eq}^0 - A \sqrt{c}$$

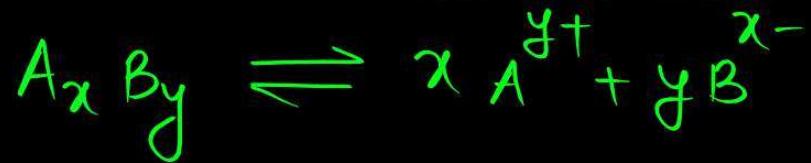
$$\Lambda_m^c = \Lambda_m^0 - A \sqrt{c} \quad A = \text{const} \quad (\text{Nature of electrolyte})$$

Λ_m^c = molar conductivity at concⁿ c

Λ_m^0 or Λ_m^∞ = Limiting molar conductivity ($c \rightarrow 0$; $V \rightarrow \infty$)





KOHLRAUSCH Law


$$\lambda_m^o(A_x B_y) = x \times \lambda_m^o(A^{y+}) + y \times \lambda_m^o(B^{x-})$$

$$\lambda_{eq}^o(A_x B_y) = \lambda_{eq}^o(A^{y+}) + \lambda_{eq}^o(B^{x-})$$

MgCl₂

$$\lambda_m^o(MgCl_2) = 1 \times \lambda_m^o(Mg^{2+}) + 2 \times \lambda_m^o(Cl^-)$$

$$\lambda_{eq}^o(MgCl_2) = \lambda_{eq}^o(Mg^{2+}) + \lambda_{eq}^o(Cl^-)$$

Application of Kohlrausch Law

$$\textcircled{1} \quad \alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

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

$$\textcircled{3} \quad \Lambda_m^0 = \frac{K \times 1000}{S} ; \quad K_{sp} = x^x y^y S^{x+y}$$

$$\textcircled{4} \quad \Lambda_m^0 (\text{CH}_3\text{COOH}) = ? \quad \text{Given: } \Lambda_m^0 \text{CH}_3\text{COONa}, \Lambda_m^0 \text{HCl}, \Lambda_m^0 \text{NaCl}$$

$$\Lambda_m^0 (\text{CH}_3\text{COOH}) = \Lambda_m^0 (\text{CH}_3\text{COONa}) + \Lambda_m^0 (\text{HCl}) - \Lambda_m^0 (\text{NaCl})$$

Q. The conductivity of 10^{-2} M CH_3COOH is $3.9 \times 10^{-5} \text{ S cm}^{-1}$ find K_a & α (Given
 $\Lambda_m^0 (\text{CH}_3\text{COOH}) = 390 \text{ s cm}^2 \text{ mol}^{-1}$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{3.9}{390} = 10^{-2}$$

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

$$\begin{aligned}\Lambda_m^c &= \frac{3.9 \times 1000}{M} \\ &= \frac{3.9 \times 10^{-5} \times 10^3}{10^{-2}} \\ &= 3.9\end{aligned}$$

Q. The conductivity of Saturated solⁿ of $\text{Ba}_3(\text{PO}_4)_2$ is $1.2 \times 10^{-5} \text{ s cm}^{-1}$ and Λ_m^0 of $\text{Ba}_3(\text{PO}_4)_2$ is $1200 \text{ s cm}^2 \text{ mol}^{-1}$ find Ksp?

$$\Lambda_m^0 = \frac{K \times 1000}{S}$$

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

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

$$\begin{aligned} K_{\text{sp}} &= 3^3 \times 2^2 \times S^{3+2} \\ &= 108 \times (10^{-5})^5 \\ &= 108 \times 10^{-25} \end{aligned}$$

Q. Calculate Λ_m^0 (CH_3COOH)

Given	Electrolyte	$\Lambda_m^0 \text{ s cm}^2 \text{ mol}^{-1}$
	CH_3COONa	91
	HCl^+	426
	NaCl^-	126

$$\begin{aligned}\Lambda_m^0 (\text{CH}_3\text{COOH}) &= 91 + 426 - 126 \\ &= 391\end{aligned}$$

Effect of dilution on K and Λ_m

on dilution, K decreases

- Λ_m increases
or
 Λ_{eq}

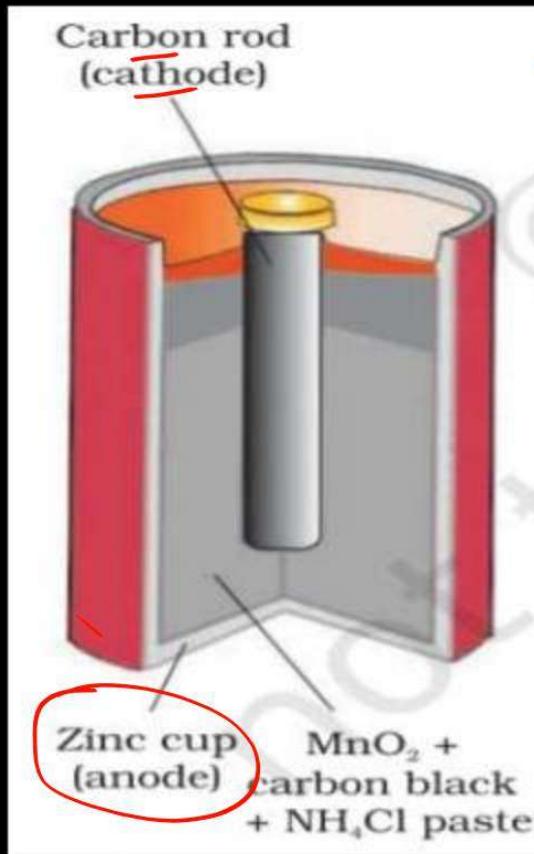
Batteries

Electrochemical cells can be used batteries, Batteries are of two kinds.

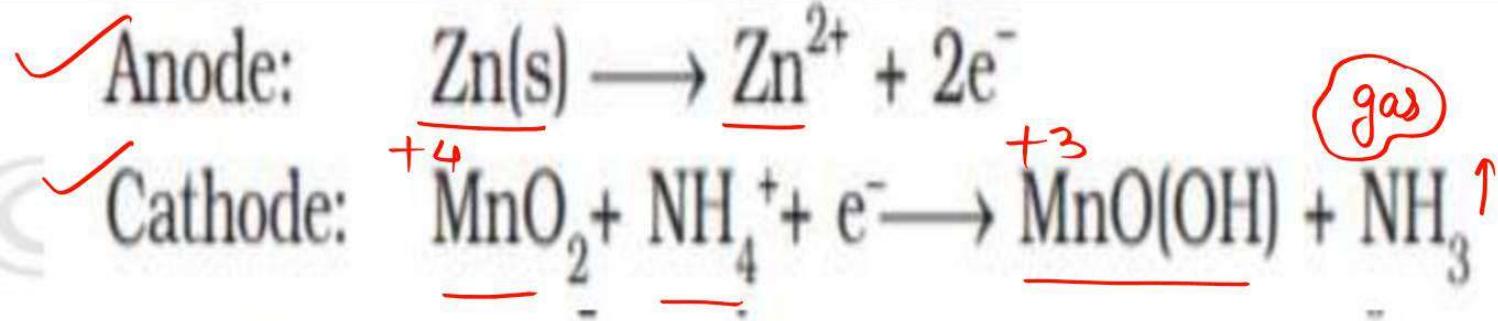
- ❖ Primary battery :
 1. Lechlanche cell
 2. Mercury Cell

- ❖ Secondary battery :
 1. Lead Storage battery
 2. NI-Cd cell

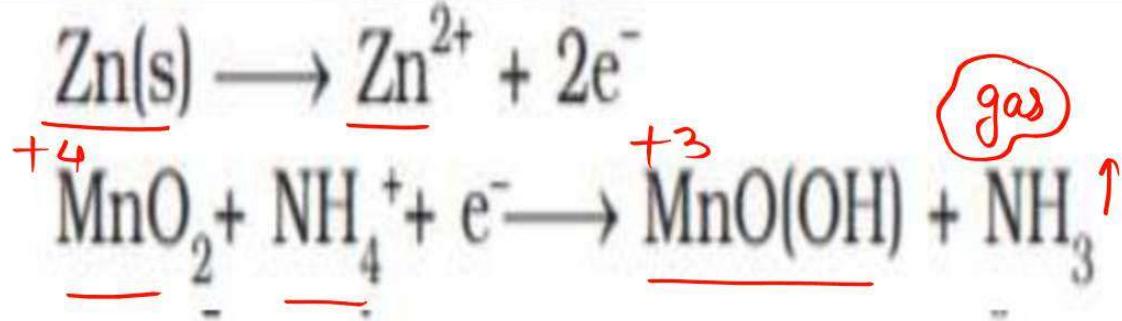
1. Laclanche cell



✓ Anode:



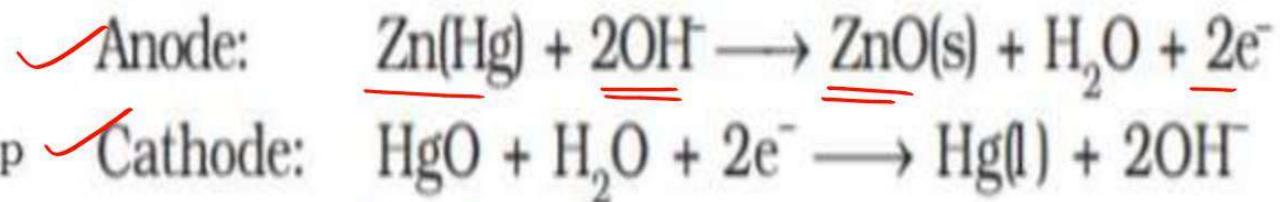
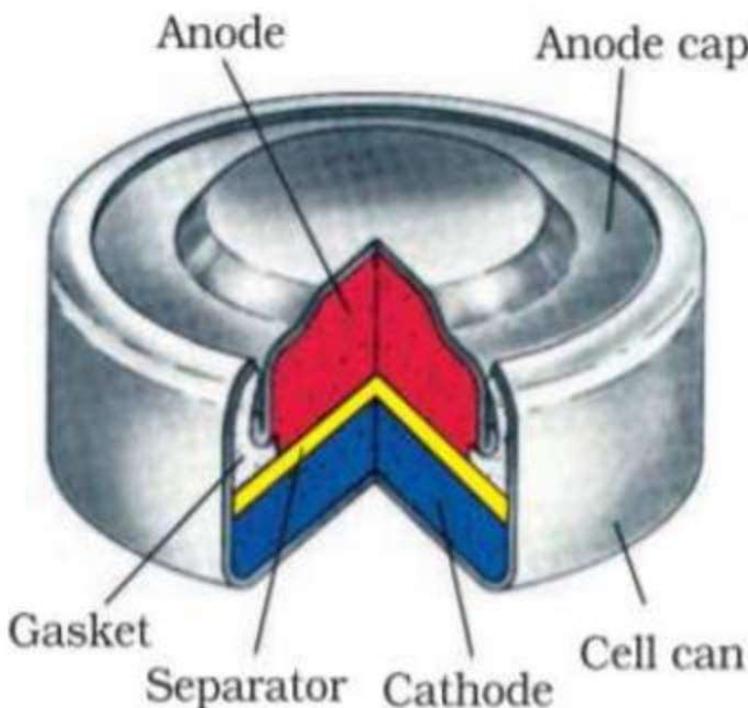
✓ Cathode:



In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

Voltage approx. 1.5 V

2. Mercury cell



The overall reaction is represented by

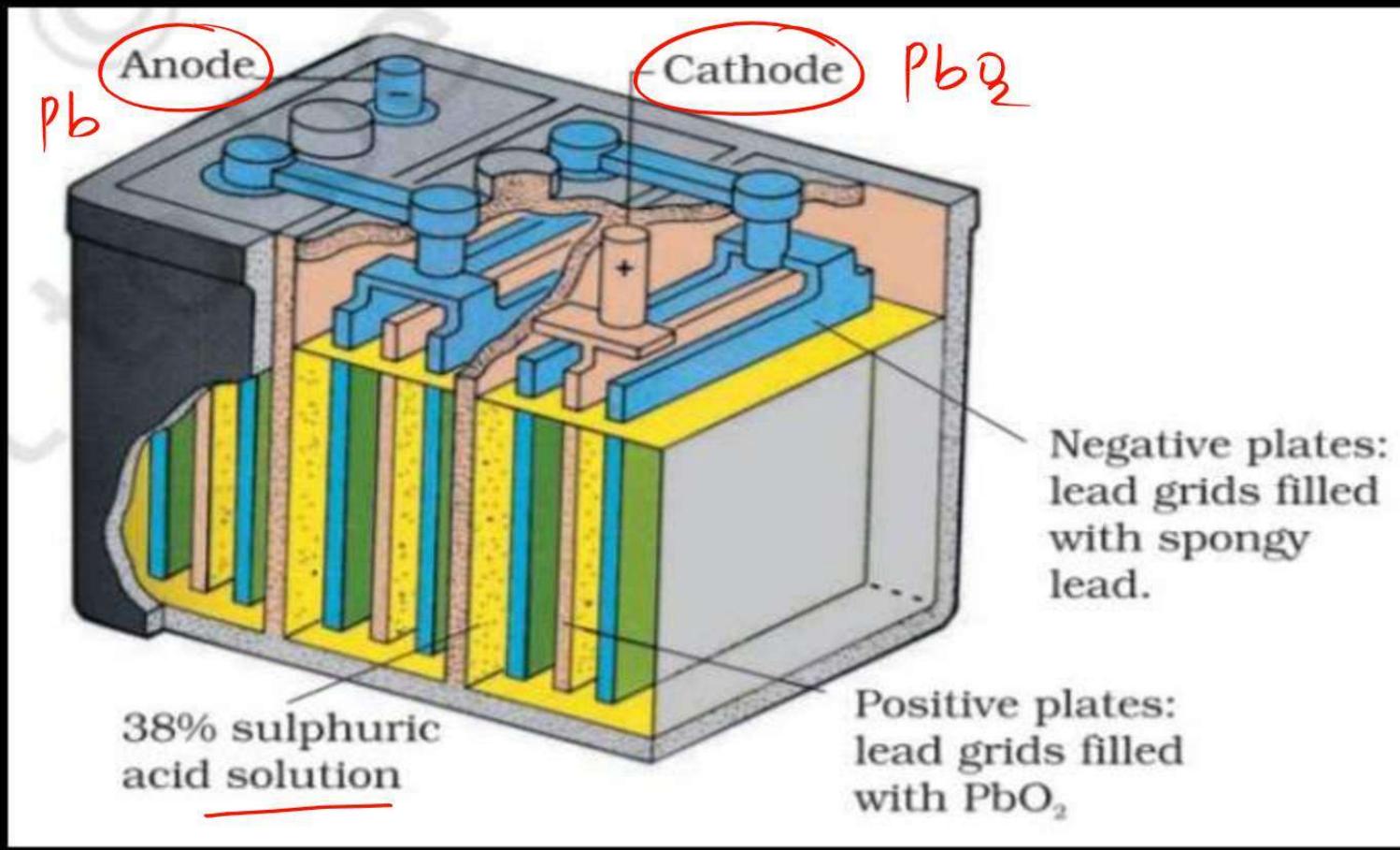


The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

Voltage approx. 1.35 V

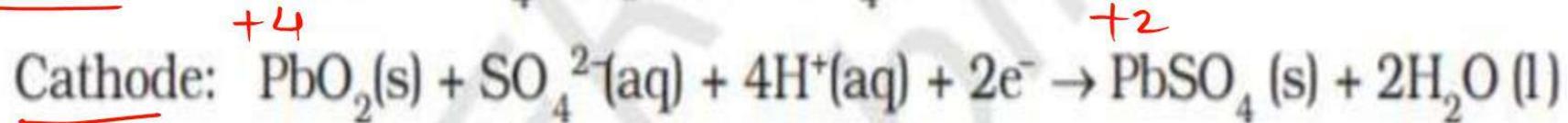
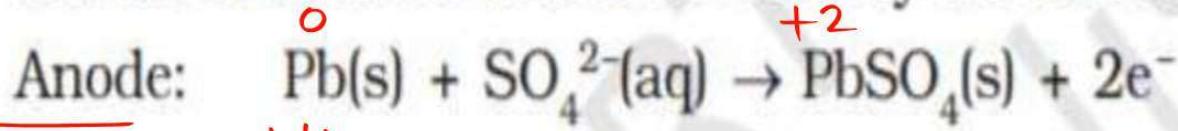


3. Lead Storage battery

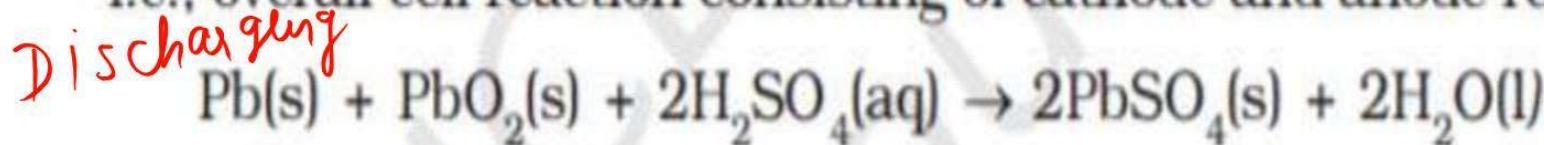


3. Lead Storage battery

The cell reactions when the battery is in use are given below:



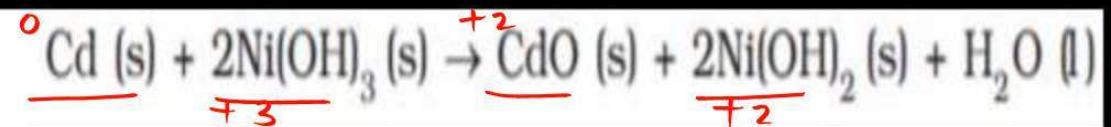
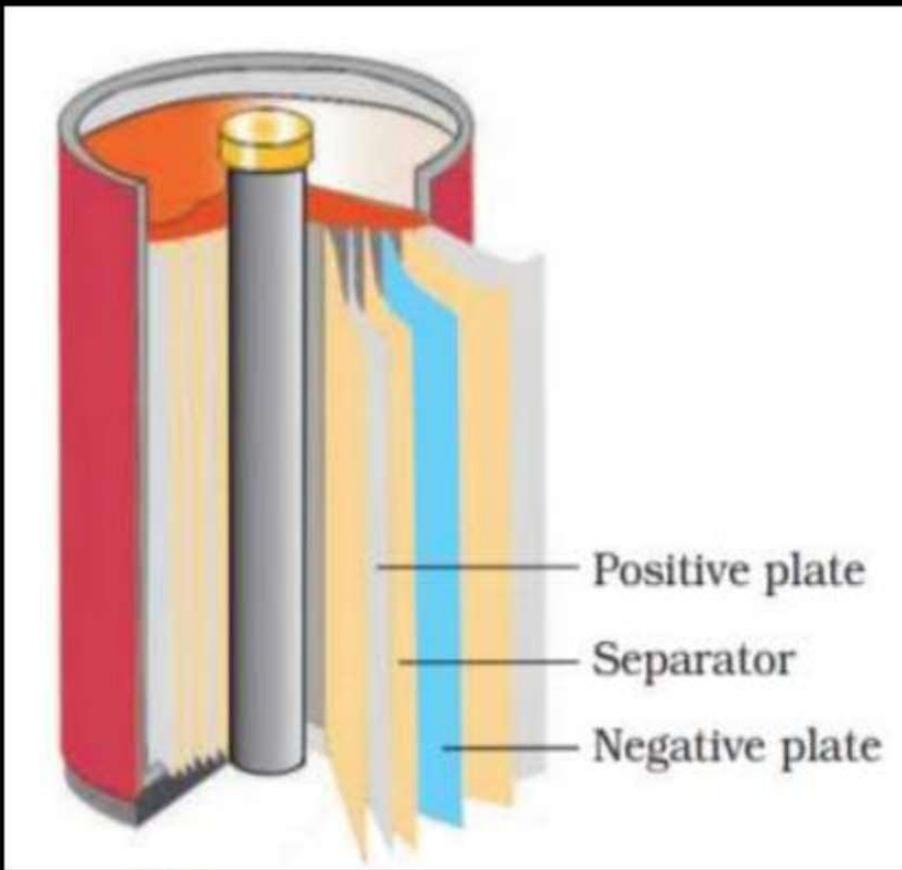
i.e., overall cell reaction consisting of cathode and anode reactions is:



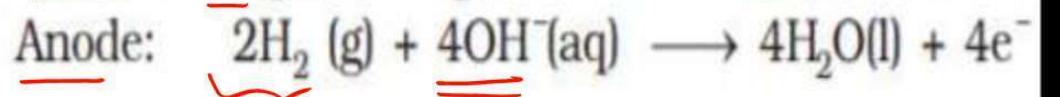
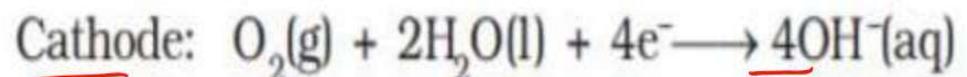
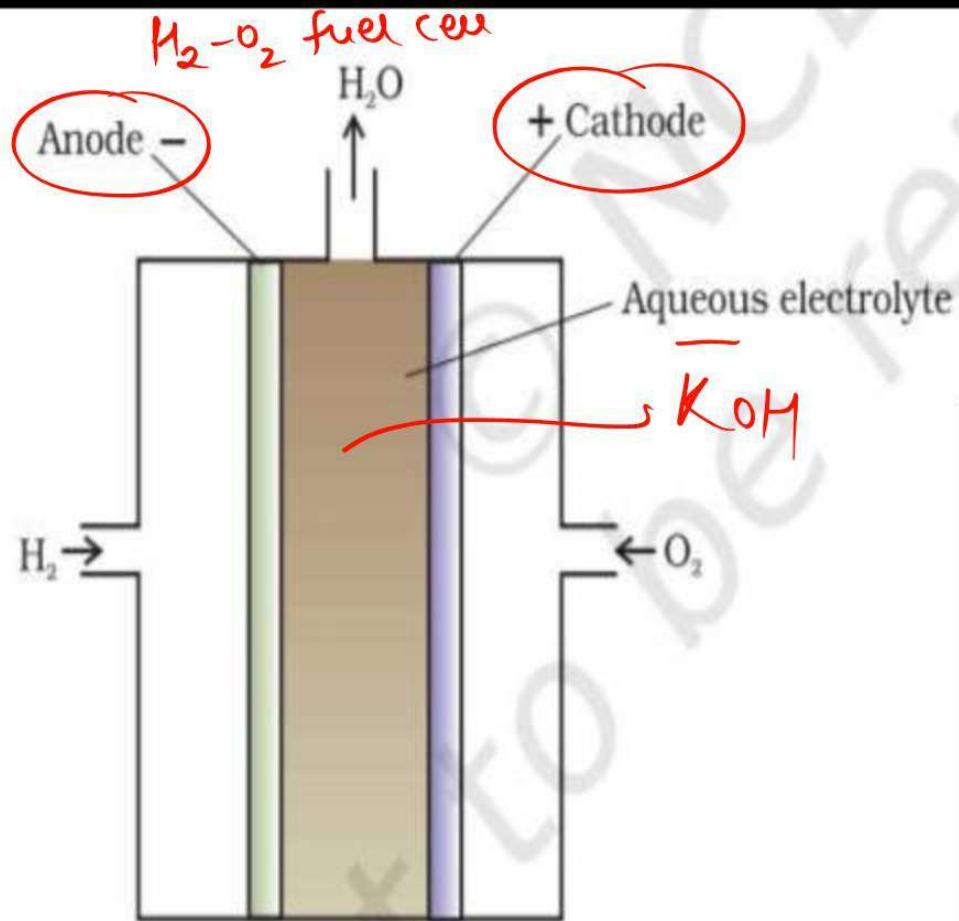
On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.



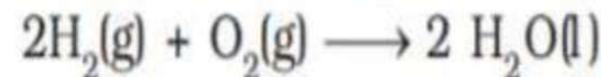
4. Ni-Cd cell



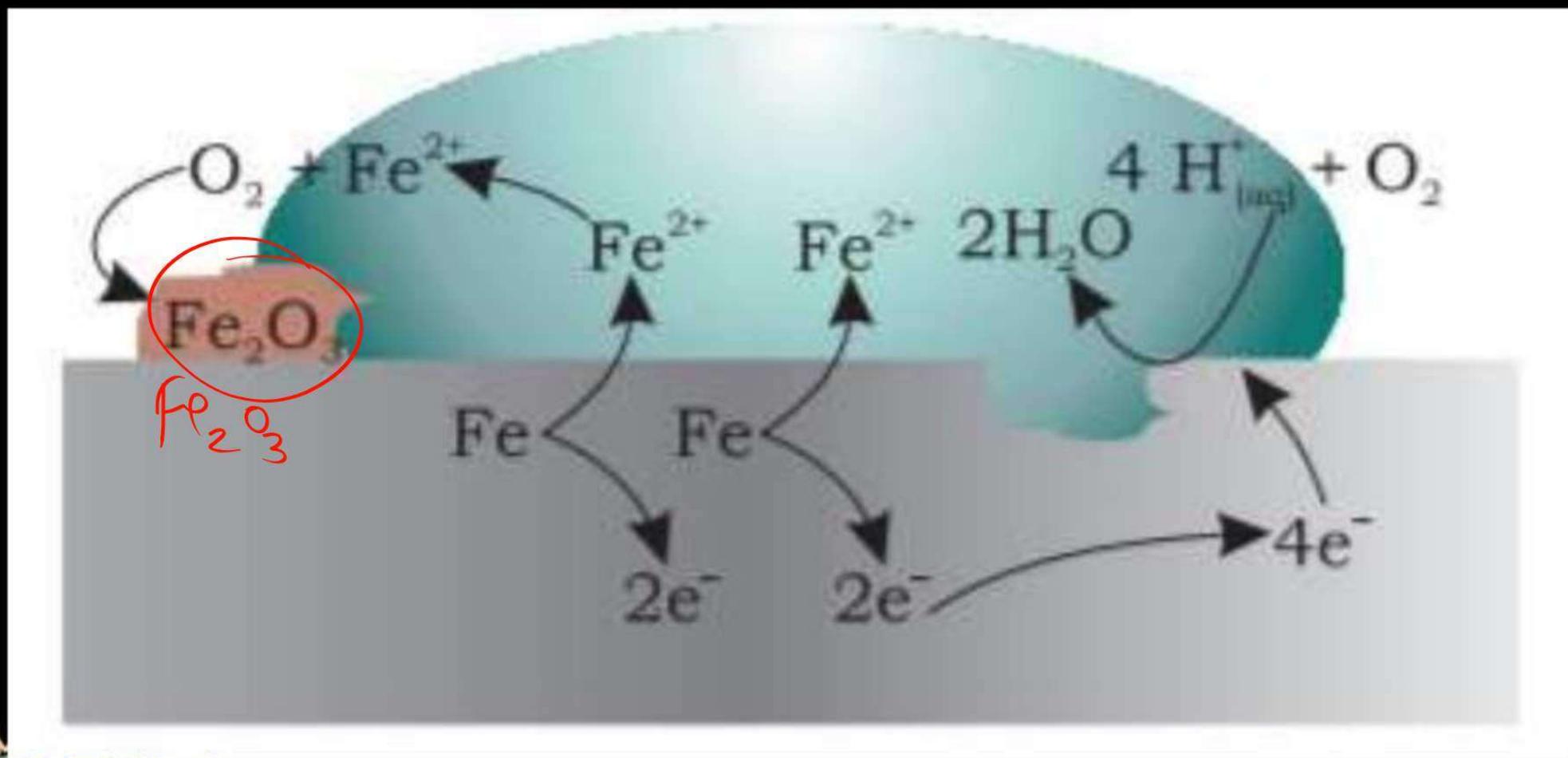
Fuel Cells



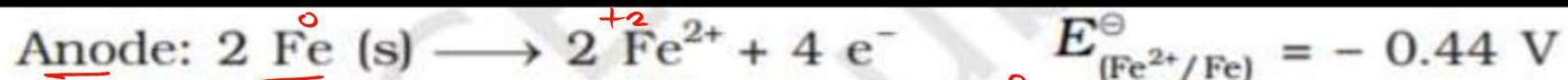
Overall reaction being:



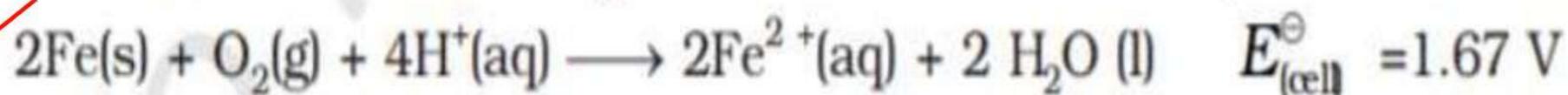
Corrosion



Corrosion



The overall reaction being:



The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) and with further production of hydrogen ions.



Galvanisation

fe coated with zn



Q. Match the items of Column I and Column II.

Column I	Column II
(i) Lead storage battery	(a) Maximum efficiency
(ii) Mercury cell	(b) Prevented by galvanization
(iii) Fuel cell	(c) Gives steady potential
(iv) Rusting	(d) Pb is anode, PbO_2 cathode





P Y Q S

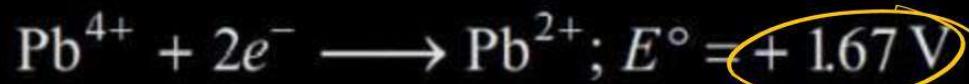


Q.

Given,



$$E_R^\circ \uparrow, R \cdot P \downarrow, O \cdot P \uparrow$$

Oxidising power of the species will increase in the order

(2019 Main, 12 April I)

a.



b.



c.



d.





Q.

Calculate the standard cell potential (in V) of the cell in which following reaction takes place



Given that,

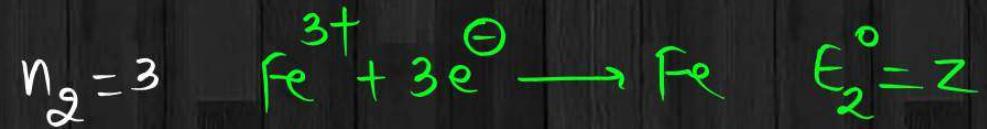
$$\text{Red } E^\circ_{\text{Ag}^+/\text{Ag}} = x \text{ V}$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = y \text{ V}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}} = z \text{ V} \quad (2019 \text{ Main, 8 April II})$$

$$\begin{aligned} E^\circ_{\text{cell}} &= (E^\circ_R)_C - (E^\circ_R)_A \\ &= x - (-2y + 3z) \\ &= x + 2y - 3z \end{aligned}$$

- (a) $x + 2y - 3z$
- (b) $x - y$
- (c) $x + y - z$
- (d) $x - z$



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

$$-n_3FE_3^\circ = +n_1FE_1^\circ - n_2FE_2^\circ$$

$$n_3E_3^\circ = -n_1E_1^\circ + n_2E_2^\circ$$

$$E_3^\circ = -2\gamma + 3\gamma$$



Q.

Given, that $E_{O_2/H_2O}^\ominus = +1.23V$;

$$E_{S_2O_8^{2-}/SO_4^{2-}}^\ominus = 2.05V;$$

$$E_{Br_2/Br^\ominus}^\ominus = +1.09V,$$

$$E_{Au^{3+}/Au}^\ominus = +1.4V$$

$$E_R^\ominus \uparrow, R \cdot p \downarrow, O \cdot p \uparrow$$

The strongest oxidising agent is

(2019 Main, 8 April I)

- (a) Au^{3+} (b) O_2 ~~(c) $S_2O_8^{2-}$~~ (d) Br_2

Solution.



Q.

Consider the following reduction processes:



$E_R^\circ \uparrow, R \cdot P \downarrow, O \cdot P \uparrow$

The reducing power of the metals increases in the order

(2019 Main, 10 Jan I)

- (a) Zn < Mg < Ni < Ca
- (b) Ni < Zn < Mg < Ca
- (c) Ca < Zn < Mg < Ni
- (d) Ca < Mg < Zn < Ni

Solution:

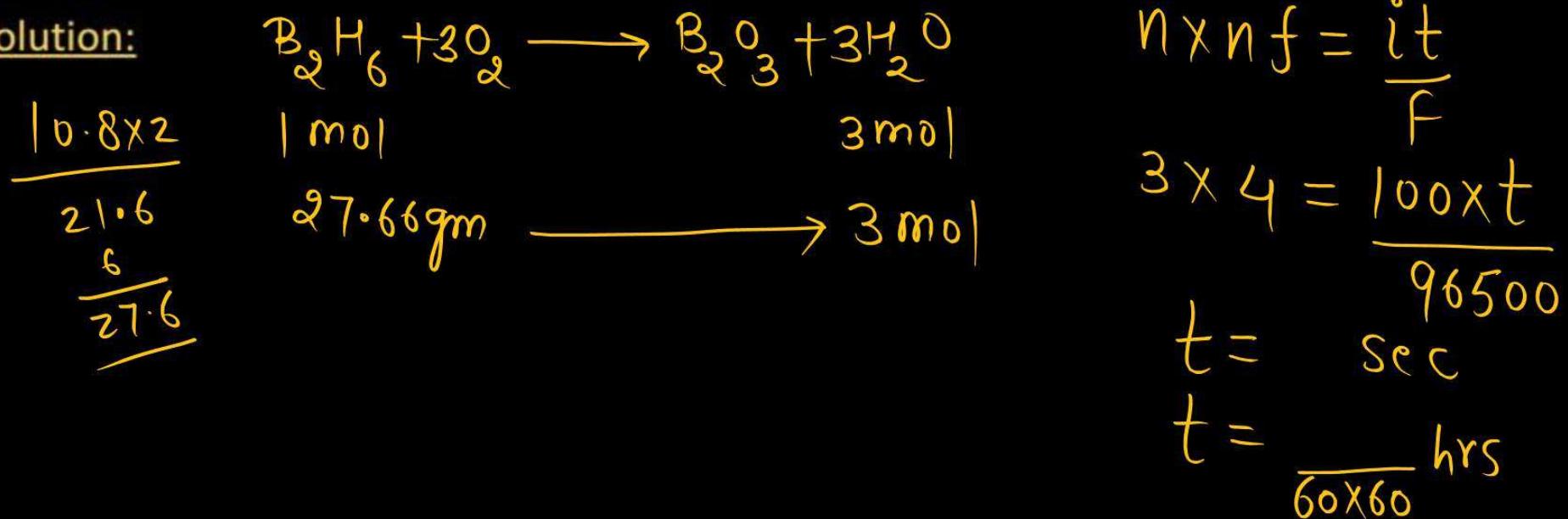


Q.

How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane?
(Atomic weight of $B = 10.8 \mu$) (2018 Main)

- (a) 6.4 hours (b) 0.8 hours (c) 3.2 hours (d) 1.6 hours

Solution:





Q.

Given, $E_{\text{Cl}_2/\text{Cl}^-}^\circ = 1.36 \text{ V}$, $E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V}$

$E_R^\circ \uparrow R \cdot P \downarrow O \cdot P \uparrow$

$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^\circ = 1.33 \text{ V}$, $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^\circ = 1.51 \text{ V}$

Among the following, the strongest reducing agent is

(2017 Main)

(a) Cr

(b) Mn^{2+}

(c) Cr^{3+}

(d) Cl^-

Solution:

$R \cdot A \rightarrow$ oxidises itself

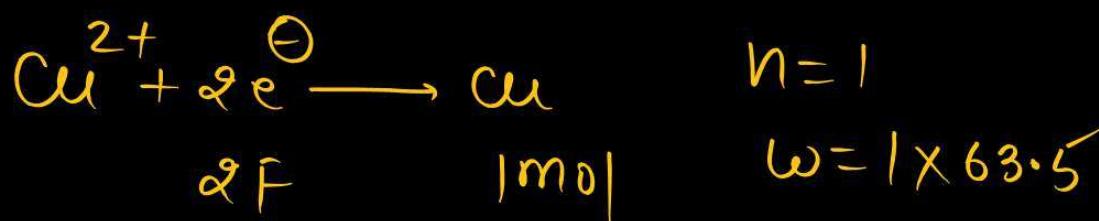


Q.

Two Faraday of electricity is passed through a solution of CuSO_4 . The mass of copper deposited at the cathode is
(at. mass of Cu = 63.5 u) (2015 Main)

- (a) 0 g (b) 63.5 g (c) 2 g (d) 127 g

Solutio...



Q.

Given, $E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = -0.74 \text{ V}$

$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = 1.51 \text{ V}$

$E_R \uparrow, R \cdot P \downarrow, O \cdot P \uparrow$

$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\circ} = 1.33 \text{ V}; E_{\text{Cl}/\text{Cl}^-}^{\circ} = 1.36 \text{ V}$

Reduces
itself

Based on the data given above strongest oxidising agent will be

(2013 Main)

- (a) Cl (b) Cr³⁺ (c) Mn²⁺ (d) MnO₄⁻

Solution:



Q.

Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H₂ gas at the cathode is (1 F = 96500 C mol⁻¹)
(2008, 3M)

- (a) 9.65×10^4 s (b) 19.3×10^4 s
 (c) 28.95×10^4 s (d) 38.6×10^4 s



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

$$0.01 \times 2 = \frac{10 \times 10^{-3} \times t}{96500}$$

Q.

Saturated solution of KNO_3 is used to make ‘salt-bridge’
because

(2001, 1M)



- (a) velocity of K^+ is greater than that of NO_3^-
- (b) velocity of NO_3^- is greater than that of K^+
- (c) velocities of both K^+ and NO_3^- are nearly the same
- (d) KNO_3 is highly soluble in water

Solution:

Q.

The gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C . If the order of reduction potential is $Z > Y > X$, then (1999, 2M)

- (a) Y will oxidise X and not Z
- (b) Y will oxidise Z and not X
- (c) Y will oxidise both X and Z
- (d) Y will reduce both X and Z

Solution:

X
Y
Z



Q.

The standard reduction potential values of three metallic cations, X , Y , Z are 0.52 , -3.03 and -1.18 V respectively. The order of reducing power of the corresponding metals is

- (a) $Y > Z > X$ (b) $X > Y > Z$ (1998, 2M)
 (c) $Z > Y > X$ (d) $Z > X > Y$

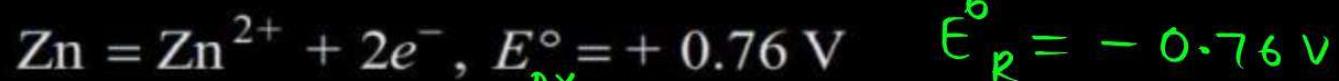
Solution:

$$E^\circ_R \uparrow \quad R.P \downarrow$$



Q.

The standard reduction potentials E° , for the half reactions are as



The emf for the cell reaction, $\text{Fe}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Fe}$ is

- (a) -0.35 V (b) $+0.35 \text{ V}$ (c) $+1.17 \text{ V}$ (d) -1.17 V

Soluti

$$E_{\text{cell}}^\circ = (E_R^\circ)_C - (E_R^\circ)_A$$

$$= -0.41 - (-0.76)$$



Q.

When a lead storage battery is discharged

(1986, 1M)

- (a) SO_2 is evolved
- (b) lead is formed
- (c) lead sulphate is consumed
- (d) sulphuric acid is consumed

Solution:

Q.

A solution containing one mole per litre of each $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , $\text{Hg}_2(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials in volts (reduction potential) are

$$\text{Ag}^+/\text{Ag} = +0.80, \text{Hg}_2^{2+}/2\text{Hg} = +0.79$$

$$\text{Cu}^{2+}/\text{Cu} = +0.34, \text{Mg}^{2+}/\text{Mg} = -2.37$$

With increasing voltage, the sequence of deposition of metals on the cathode will be

(1984, 1M)

(a) Ag, Hg, Cu, Mg

(b) Mg, Cu, Hg, Ag

(c) Ag, Hg, Cu

(d) Cu, Hg, Ag

Q.

Faraday's laws of electrolysis are related to the (1983, 1M)



- (a) atomic number of the cation
- (b) atomic number of the anion
- (c) equivalent weight of the electrolyte
- (d) speed of the cation

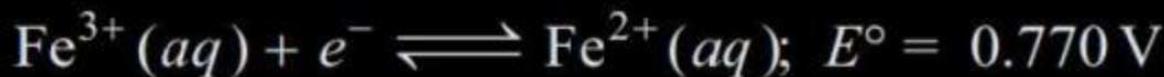
Solution:

Q.

The standard reduction potentials at 298K for the following half cells are given :



$E_R^\circ \uparrow, R \cdot P \downarrow, O \cdot P \uparrow$



Which is the strongest reducing agent?

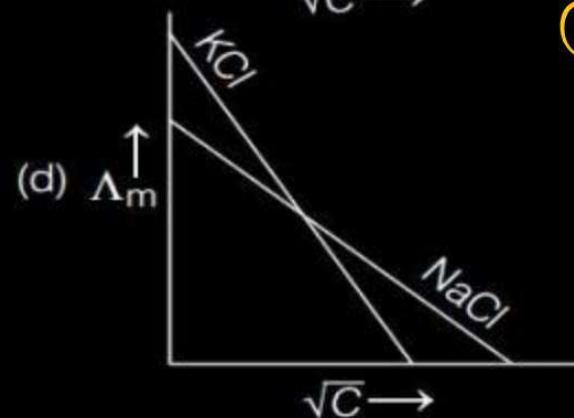
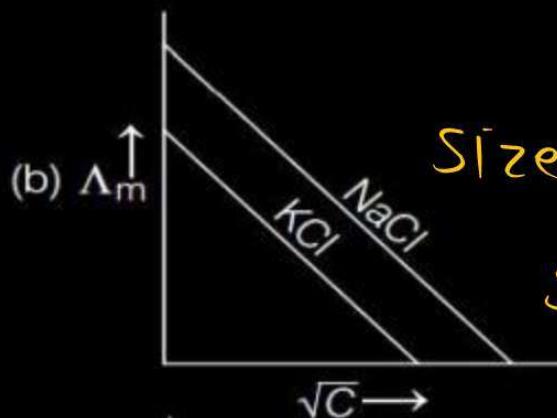
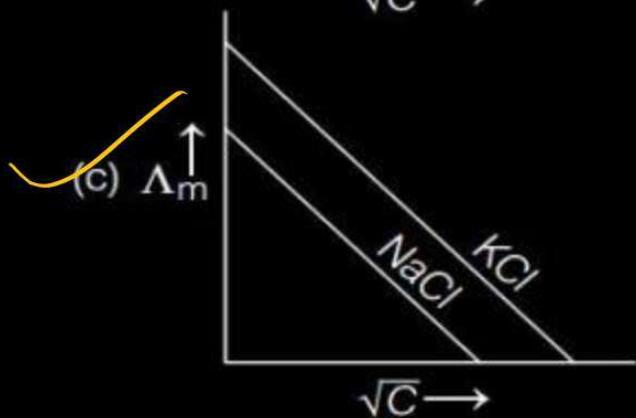
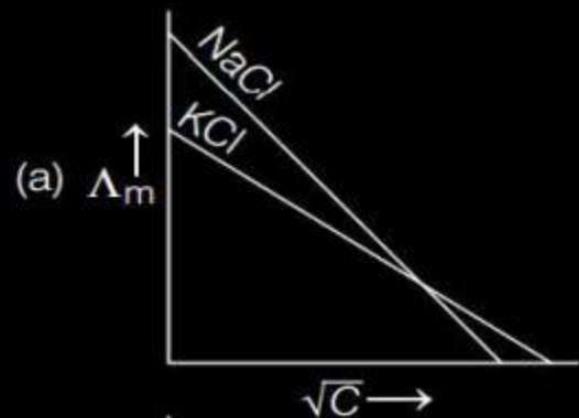
(1981, 1M)

- (a) $\text{Zn}(s)$ (b) $\text{Cr}(s)$ (c) $\text{H}_2(g)$ (d) $\text{Fe}^{2+}(aq)$

Solution:

Q.

Which one of the following graphs between molar conductivity (Λ_m) versus \sqrt{C} is correct? (2019 Main, 10 April II)



$K\alpha$ NaCl
 Size K^+ _(g) > Na^+ _(g)
 Size K^+ _(aq) < Na^+ _(aq)
 Cond. K^+ _(aq) > Na^+ _(aq)



Q. Consider the statements S_1 and S_2 :

- (W) S_1 : Conductivity always increases with decrease in the concentration of electrolyte. $C \downarrow \vee \uparrow$ dilution
- (C) S_2 : Molar conductivity always increases with decrease in the concentration of electrolyte.

The correct option among the following is

(2019 Main, 10 April I)

- (a) S_1 is correct and S_2 is wrong (b) S_1 is wrong and S_2 is correct
(c) Both S_1 and S_2 are wrong (d) Both S_1 and S_2 are correct

Solution:



Q.

The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is



$$E^\circ = 2\text{V at } 298\text{ K}$$

(Faraday's constant, $F = \underline{96000 \text{ C mol}^{-1}}$) (2019 Main, 9 April I)

- (a) 384 (b) 192 (c) -384 (d) -192

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

Solution:

$$= -2 \times 96000 \times 2 \text{ J}$$



Q.

Λ_m° for NaCl, HCl and NaA are 126.4, 425.9 and 100.5 $S\ cm^{-2}\ mol^{-1}$, respectively. If the conductivity of 0.001 M HA is $5 \times 10^{-5} S\ cm^{-1}$, degree of dissociation of HA is

(2019 Main, 12 Jan II)

(a) 0.25

(b) 0.50

(c) 0.75

(d) 0.125

$$\text{Solution: } \alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

$$\alpha = \frac{50}{400} = \frac{1}{8}$$

$$\Lambda_m^\circ = \frac{K \times 1000}{M} = \frac{5 \times 10^{-5} \times 10^3}{10^{-3}} = 50$$

$$\Lambda_m^\circ = 400$$

$$\begin{aligned} & \frac{425.9}{100.5} \\ & \frac{526.4}{126.4} \\ & \underline{400.0} \end{aligned}$$

Q.

Given the equilibrium constant (K_C) of the reaction :



is 10×10^{15} , calculate the E_{cell}° of this reaction at 298 K.

$$\left[2.303 \frac{RT}{F} \text{ at } 298 \text{ K} = 0.059 \text{ V} \right]$$

(2019 Main, 11 Jan II)

- (a) 0.4736 V (b) 0.04736 mV
 (c) 0.4736 mV (d) 0.04736 V

Solution:

$$-nF E_{\text{cell}}^{\circ} = -RT \ln K$$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \times 2.3 \log_{10} K$$

$$= \frac{0.06}{n} \log K$$

$$= \frac{0.06}{2} \log 10^{16}$$

Q.

For the cell, $\text{Zn}(s) \mid \text{Zn}^{2+}(aq) \parallel M^{x+}(aq) \mid M(s)$, different half cells and their standard electrode potentials are given below.

$M^{x+}(aq)/M(s)$	$\text{Au}^{3+}(aq)/\text{Au}(s)$	$\text{Ag}^+(aq)/\text{Ag}(s)$	$\text{Fe}^{3+}(aq)/\text{Fe}^{2+}(aq)$	$\text{Fe}^{2+}(aq)/\text{Fe}(s)$
$E^\circ_{M^{x+}/M}/V$	1.40	0.80	0.77	-0.44

If $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, which cathode will give a maximum value of E°_{cell} per electron transferred? (2019 Main, 11 Jan I)

- (a) $\frac{\text{Ag}^+}{\text{Ag}}$
- (b) $\frac{\text{Fe}^{2+}}{\text{Fe}}$
- (c) $\frac{\text{Au}^{3+}}{\text{Au}}$
- (d) $\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}}$

Solution:

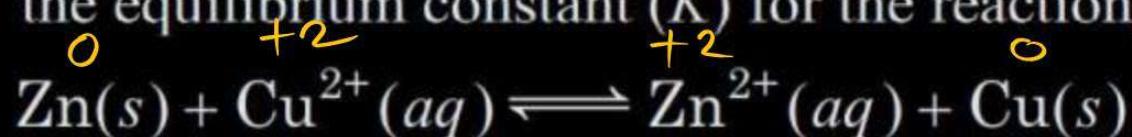
$$\begin{aligned}E_{\text{cell}}^{\circ} &= (E_R^{\circ})_C - (E_R^{\circ})_A \\&= (E_R^{\circ})_C - (-0.76)\end{aligned}$$

$$E_{\text{cell}}^{\circ} = (E_R^{\circ})_C + 0.76$$



Q.

If the standard electrode potential for a cell is 2V at 300 K,
the equilibrium constant (K) for the reaction,



at 300 K is approximately

($R = 8 \text{ JK}^{-1} \text{ mol}^{-1}$, $F = 96000 \text{ C mol}^{-1}$) (2019 Main, 9 Jan II)

(a) ~~e^{-160}~~

(b) e^{160}

~~(c) e^{-80}~~

(d) e^{320}

$$\ln K = \frac{4 \times 2.3}{0.06}$$

Solution:

$$E_{\text{cell}}^{\circ} = \frac{0.06}{n} \log_{10} K$$

$$\mathcal{Q} = \frac{0.06}{2} \log_{10} K$$

$$\frac{4}{0.06} \approx \log K$$

$$\frac{4}{0.06} = \frac{\ln K}{2.3}$$

Q.

Galvanisation is applying a coating of

(2016 Main)

- (a) Cr
- (b) Cu
- (c) Zn
- (d) Pb

Solution:





Q.

The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ , respectively. The correct relationship between λ_C and λ_∞ is given as (where, the constant B is positive) (2014 Main)

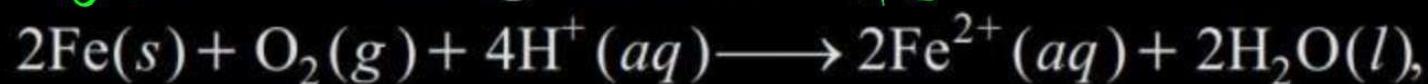
- (a) $\lambda_C = \lambda_\infty + (B) C$ (b) $\lambda_C = \lambda_\infty - (B) C$
~~(c) $\lambda_C = \lambda_\infty - (B) \sqrt{C}$~~ (d) $\lambda_C = \lambda_\infty + (B) \sqrt{C}$

Solution:



Q.

Consider the following cell reaction,



$$\epsilon_{cell} = 1.67 - \frac{0.06}{4} \log Q \quad E^\circ = 1.67 \text{ V}$$

At $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$, $P(\text{O}_2) = 0.1 \text{ atm}$ and $\text{pH} = 3$, the cell potential at 25°C is (2011)

- (a) 1.47 V
- (b) 1.77 V
- (c) 1.87 V
- (d) 1.57 V

$$Q = \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1}$$

Solution:



Q.



The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is (2004, 1M)

(a) $10^{0.32/0.059}$

(b) $10^{0.32/0.0295}$

(c) $10^{0.26/0.0295}$

(d) $10^{0.32/0.295}$

Solution:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.06}{2} \log 10$$

$$0.2905 = E_{\text{cell}}^\circ - 0.03$$

$$E_{\text{cell}}^\circ =$$



$$Q = \frac{0.1}{0.01} = 10$$

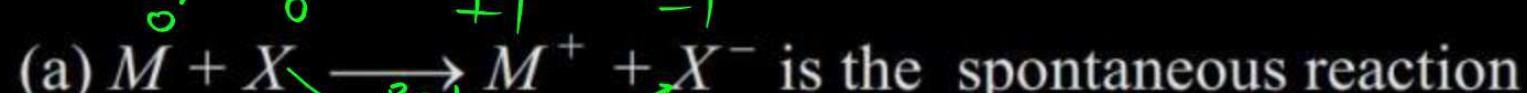
$$E_{\text{cell}}^\circ = + \frac{0.06}{2} \log k$$



Q.

For the electrochemical cell, $(M|M^+) \parallel (X^-|X)$, $E^\circ(M^+/M) = 0.44$ V and $E^\circ(X/X^-) = 0.33$ V.

From this data one can deduce that (2000, 1M)



(c) $E_{\text{cell}}^\circ = 0.77$ V

(d) $E_{\text{cell}}^\circ = -0.77$ V

Solution:

$$\begin{aligned}E_{\text{cell}}^\circ &= (E_R^\circ)_C - (E_R^\circ)_A \\&= 0.33 - (0.44) \\&= -1\text{e}\end{aligned}$$

$$\Delta G^\circ > 0$$