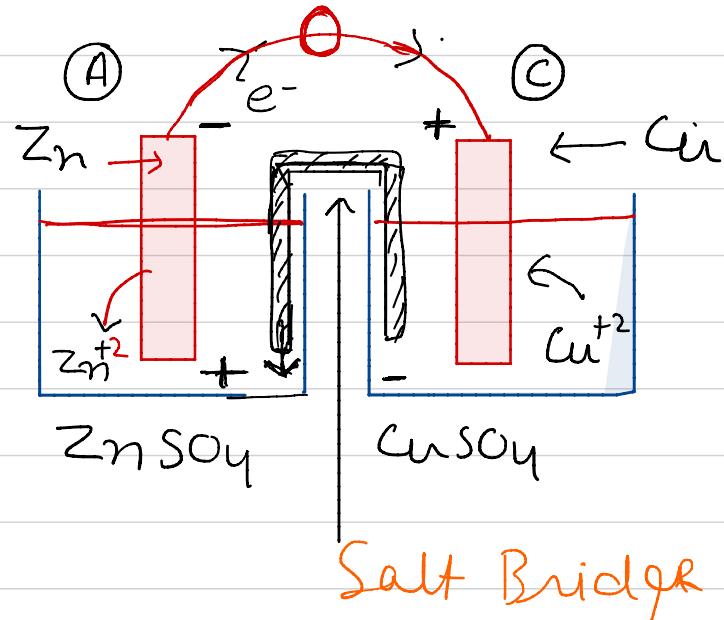


Electrochemistry :- Cell  $\xrightarrow{\text{Electrolytic Cell}}$

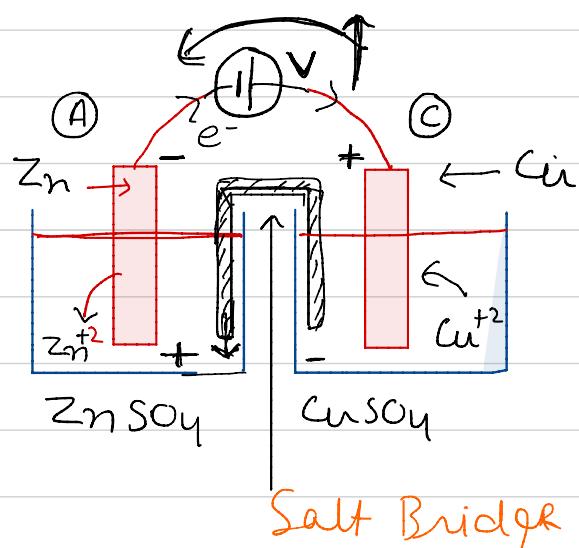
① Galvanic cell :- Convert chemical energy into electrical energy

eg: Zn - Cu Cell  $\Rightarrow$  Spontaneous rxn  $\Rightarrow G \downarrow$

on Daniell cell =  $\omega_{\text{electrical}}$

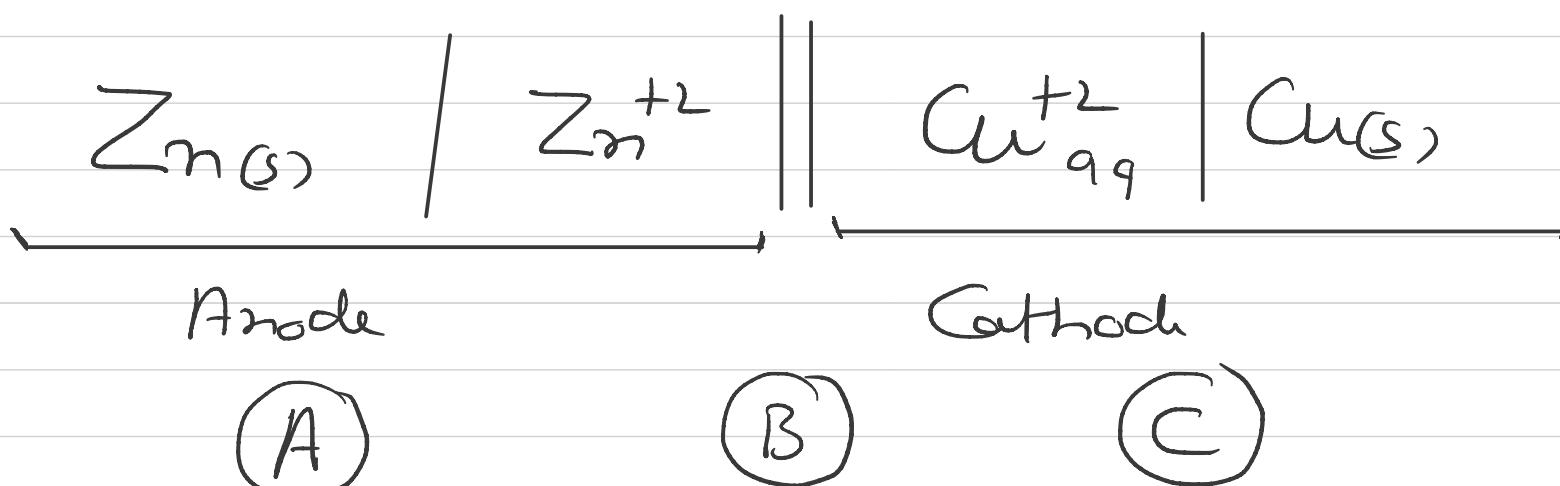


- Charges on Cathode and anode are +ve and -ve, flow of  $e^-$  take place from Anode to Cathode in external circuit.
  - Potential develop b/w  $10^3$  due to difference of charge is called as liquid junction potential. which is opposite to cell potential.



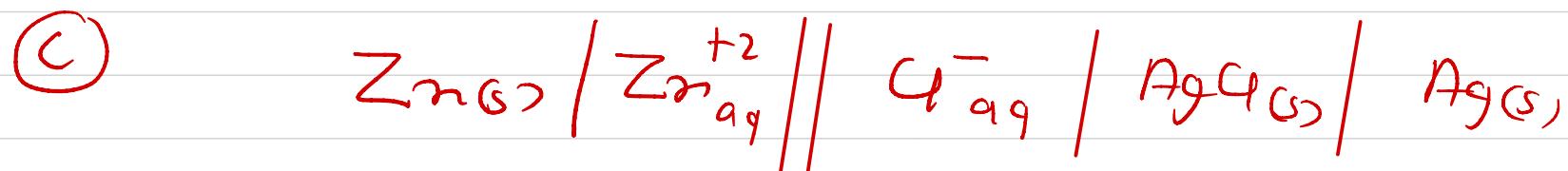
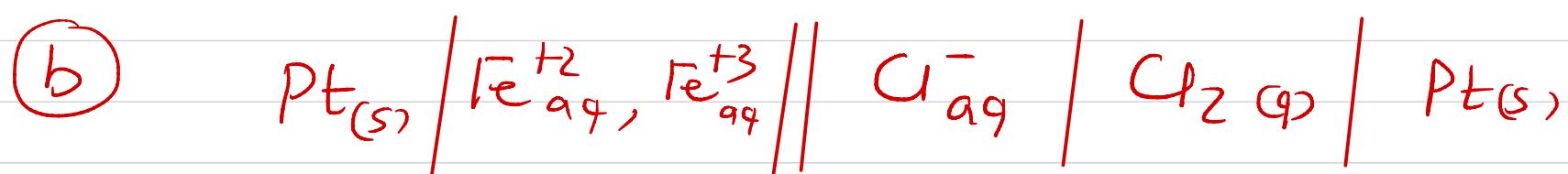
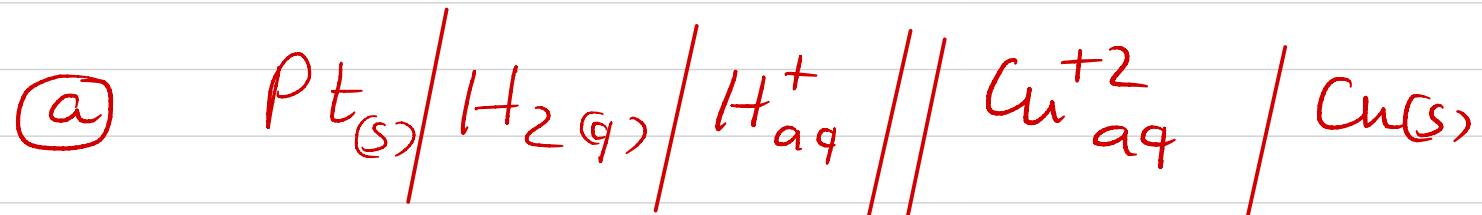
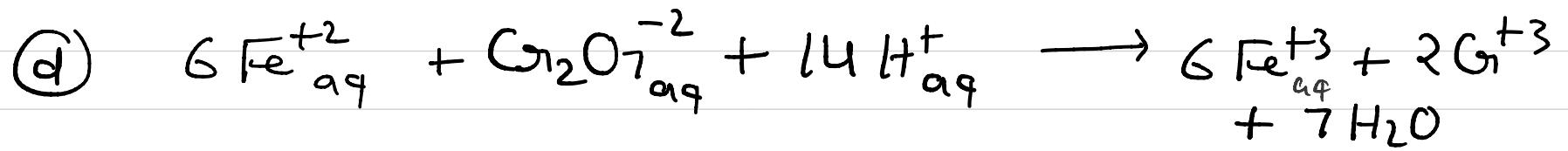
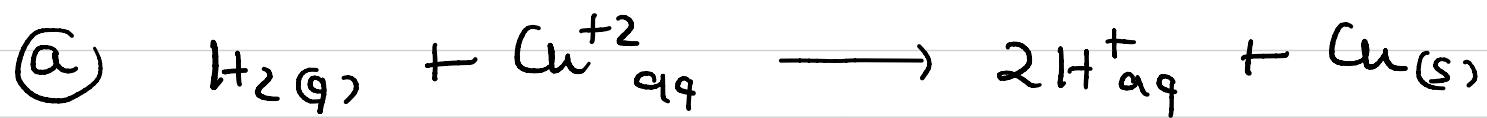
- Salt bridge provide opposite ions to solution and minimize liquid junction potential.
  - Salt bridge contains strong electrolyte with agar-agar paste or gelatin.

Cell notation :-

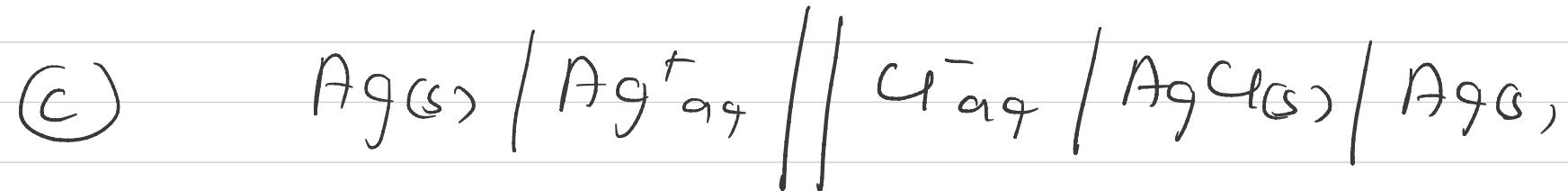
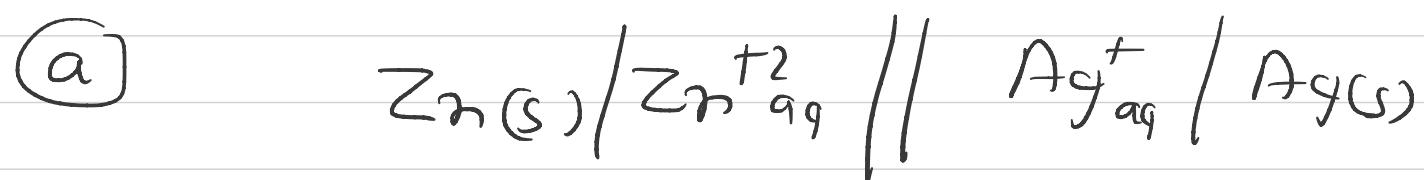
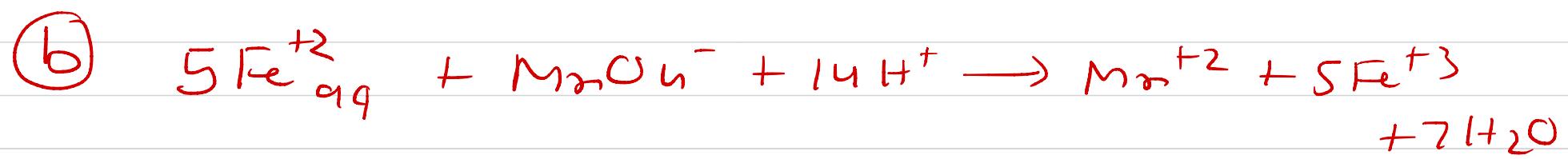


- Rule :-
- ① Right half represent Cathode and Left half represent anode.
  - ② Salt bridge equally divide Cell into Cathode and Anode and is represented by  $\parallel$ .
  - ③ At Cathode / Anode all the components involved are represented.
  - ④ Ions are represented close to salt bridge. Components with same phase are separated by , and with different phase are separated by /.
  - ⑤ If there is no solid electrode present then represent Pt electrode for current.
  - ⑥ Conc<sup>2</sup> or pressure of components are represented in just right of it within first brackete ( ).

Problem:- Write cell notation from given cell rxn?



Prob: Write cell notation from cell given



Electrode Potential: Tendency of electrode to take  $e^-$  wrt. Standard H-electrode is called its electrode potential. Standard electrode potential of H is taken as zero.

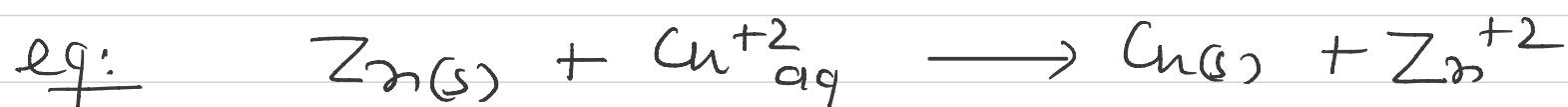
Cell Potential ( $E_{\text{cell}}$ ): Tendency of cathode to accept  $e^-$  wrt anode is called as cell potential.

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

$$(RP)_{\text{Cathode}} \quad (RP)_{\text{Anode}}$$

Under standard condition

$$E_{\text{cell}}^{\circ} = E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ} = (SRP)_{\text{Cathode}} - (SRP)_{\text{Anode}}$$



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{Cu^{+2}/Cu}^{\circ} - E_{Zn^{+2}/Zn}^{\circ} = (+0.34) - (-0.76) \\ &= 1.10 \text{ V} \end{aligned}$$

### Electrochemical Series :-

Electrode	$E_{\text{volt}}^{\circ} (\text{SRP})$
$Ag^+ / Ag$	+ 0.80
$Cu^{+2} / Cu$	+ 0.34
$H^+ / H_2$	0
$Zn^{+2} / Zn$	- 0.76

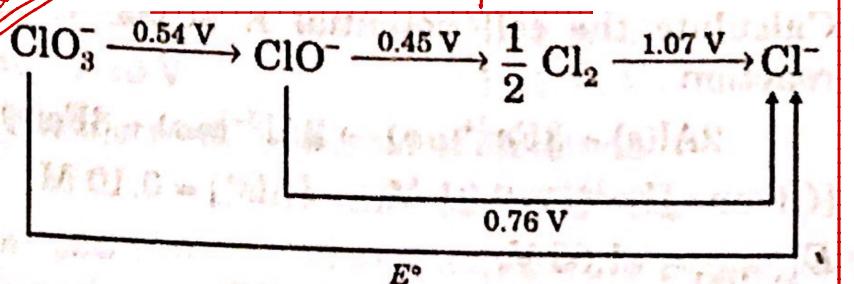
$$E_{\text{cell}}^{\circ} = 1.10$$

→ ECS shows relative tendency of electrode to take  $e^-$  under standard condition.

→ Standard electrode potential of H-electrode is taken as zero.

→ Electrodes having more tendency to take  $e^-$  than hydrogen are given +ve value of EP. While having less tendency are given -ve values.

## Latimer diagram



$$E^o = \frac{n_1 E_1^o + n_2 E_2^o + n_3 E_3^o}{n}$$

$$E^\circ = \frac{4 \times 0.54 + 1 \times 0.45 + 1 \times 1.07}{6}$$

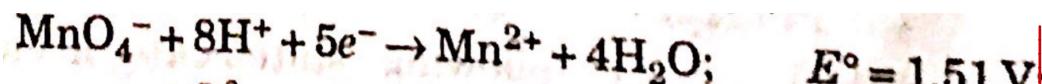
$$= 0.6 \checkmark$$

The  $E^\circ$  in the given figure is :

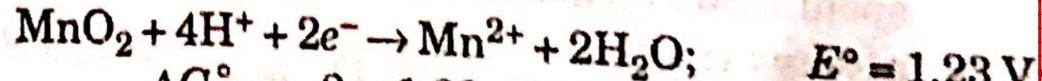


B

Bob:



$$\Delta G_1^\circ = -5 \times 1.51 \times F$$



$$\Delta G_2^{\circ} = -2 \times 1.23 \times F$$

$E^\circ_{\text{MnO}_4^- \mid \text{MnO}_2}$  is :

- (a) 1.70 V      (b) 0.91 V  
 (c) 1.37 V      (d) 0.548 V

$$E^o = \frac{n_1 E_1^o - n_2 E_2^o}{n_1 + n_2}$$

$$= \frac{5 \times 1.51 - 2 \times 1.23}{3}$$

170

A

For the reduction of  $\text{NO}_3^-$  ion in an aqueous solution,  $E^\ominus$  is 0.96 V.  $E^\ominus$  for some metal ions are given as:

- i.  $\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Fe}(\text{s}), E^\ominus = -0.04 \text{ V}$
  - ii.  $\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}(\text{s}), E^\ominus = 0.86 \text{ V}$
  - iii.  $\text{V}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{V}(\text{s}), E^\ominus = -1.19 \text{ V}$
  - iv.  $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s}), E^\ominus = 1.40 \text{ V}$

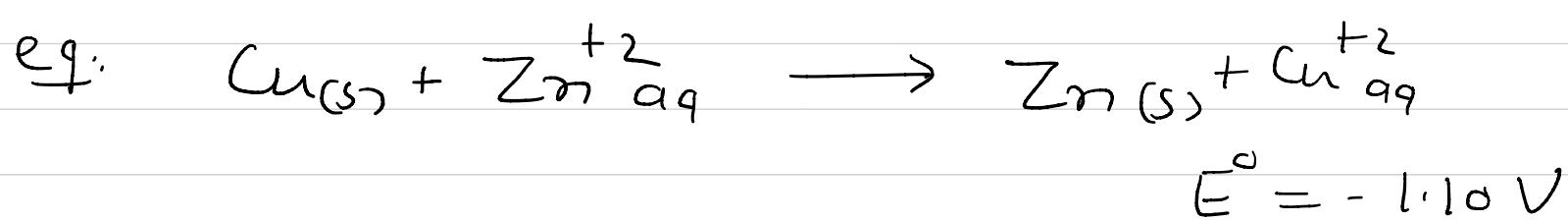
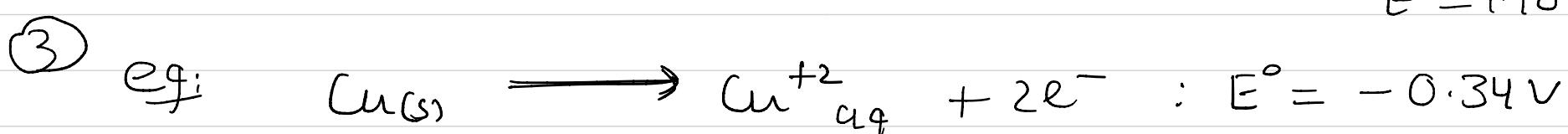
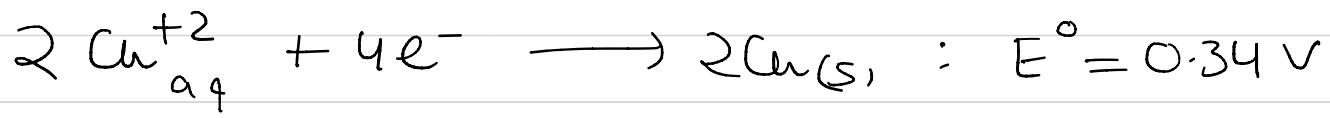
The pair of metals that is oxidized by  $\text{NO}_3^-$  in aqueous solution is:

- a. Fe and Au      b. Hg and Fe  
c. Fe and V      d. V and Hg

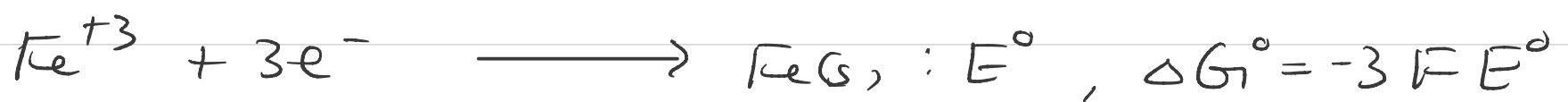
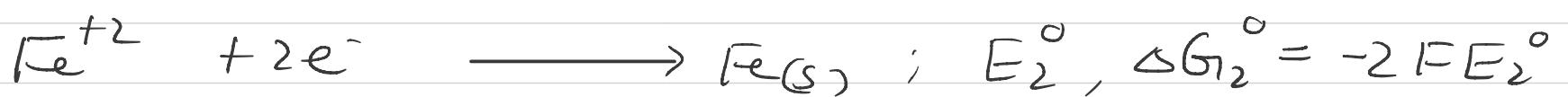
**Sol.**(

## Properties of electrode Potential :-

① Electrode Potential is intensive in nature.



④ Electrode potential is not additive in nature.

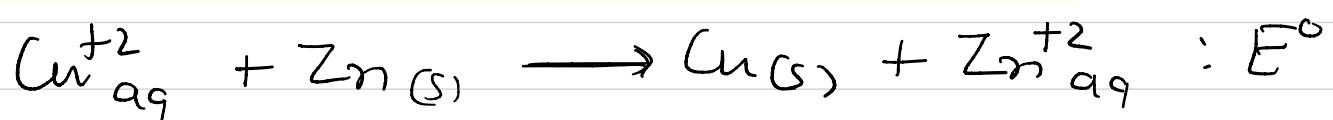
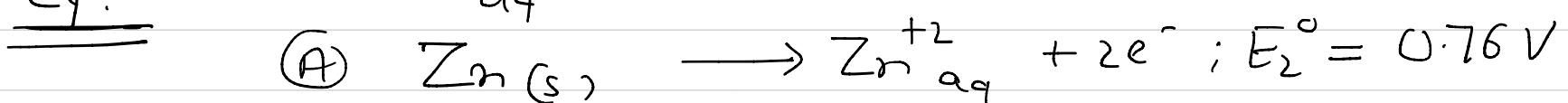
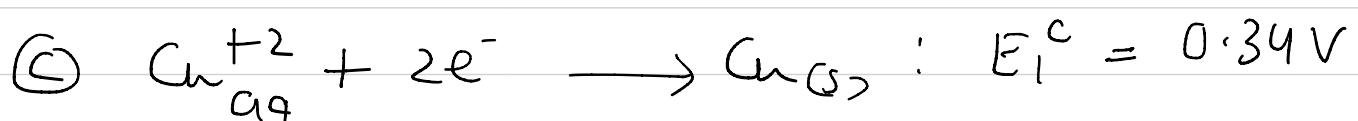


$$E^\circ = E_1^\circ + E_2^\circ \times$$

$$\begin{aligned} \Delta G^\circ &= \Delta G_1^\circ + \Delta G_2^\circ \\ -3 \times F E^\circ &= -F E_1^\circ - 2 \times F E_2^\circ \Rightarrow E^\circ = \left( \frac{E_1^\circ + 2E_2^\circ}{3} \right) \end{aligned}$$

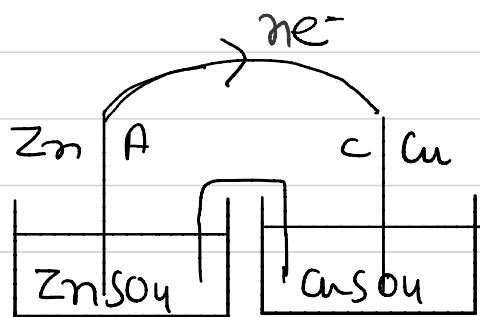
Note:

$$E^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n}$$



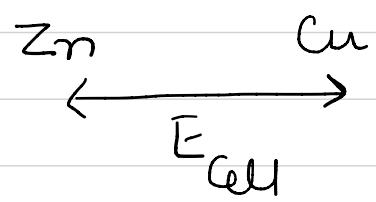
$$E^\circ = \frac{2 \times E_1^\circ + 2 \times E_2^\circ}{2} = E_1^\circ + E_2^\circ = \underline{\underline{1.10 \text{ V}}}$$

Calculation of  $\Delta G_f$  and Cell Potential in Galvanic cell :-



$$\omega = q \times v$$

$$\omega = (nF) E_{\text{cell}} = \text{Electrical work}$$



$$G_f \downarrow \Rightarrow \omega \uparrow$$

$$\Rightarrow -\Delta G_f \geq \omega$$

for reversible process

$$(-\Delta G_f) = \omega = nFE_{\text{cell}}$$

$$\Delta G_f = -nFE_{\text{cell}}$$

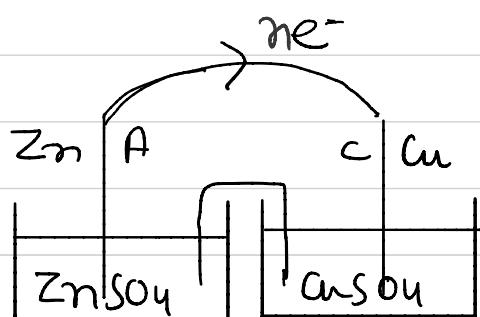
Under standard condition

$$\Delta G_f^\circ = -nFE_{\text{cell}}^\circ$$

Where  $F$  = Faraday = Charge present on 1 mole  $e^-$   
 $= 96500 \text{ C}$

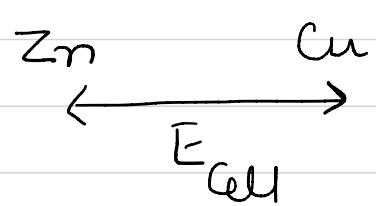
# Electrochemistry TOL\_TOV 21-22(1)

Calculation of  $\Delta G_f$  and Cell Potential in Galvanic cell :-



$$\omega = q \times v$$

$$\omega = (nF) E_{\text{cell}} = \text{Electrical work}$$



$$G_f \downarrow \Rightarrow \omega \uparrow$$

$$\Rightarrow -\Delta G_f \geq \omega$$

for reversible process

$$(-\Delta G_f) = \omega = nFE_{\text{cell}}$$

$$\Delta G_f = -nFE_{\text{cell}}$$

Under standard condition

$$\Delta G_f^\circ = -nFE_{\text{cell}}^\circ$$

Where  $F$  = Faraday = Charge present on 1 mole e<sup>-</sup>  
= 96500 C

# Cell rxn:



$$\Delta G_f = \Delta G_f^\circ + RT \ln Q$$

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + 2.303RT \log Q$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{nF} \log Q \quad \text{new inst'n Eqn}$$

at Room Temp  $T = 298 \text{ K}$

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500} = 0.0591$$

at 298 K

$$\bar{E}_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$$

if  $\Delta G_r = -\text{ve} \Rightarrow \bar{E}_{\text{cell}} = +\text{ve} \Rightarrow \text{Spontaneous}$

$\Delta G_r = +\text{ve} \Rightarrow \bar{E}_{\text{cell}} = -\text{ve} \Rightarrow \text{Non-Spontaneous}$

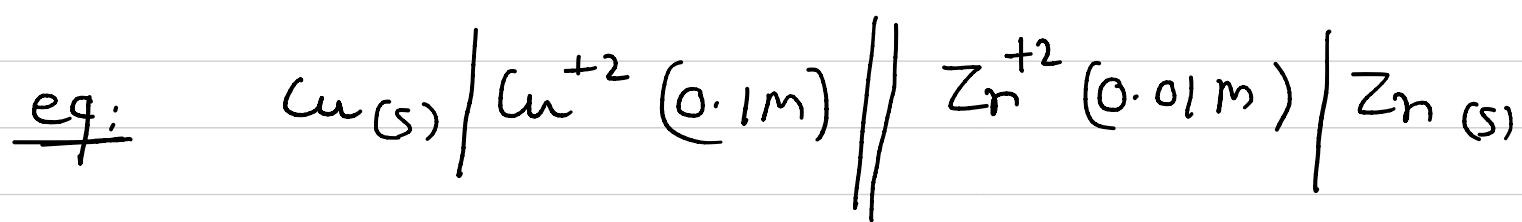
$\Delta G_r = 0 \Rightarrow \bar{E}_{\text{cell}} = 0 \Rightarrow \text{at Equib}$

$$Q = K_{\text{eq}}$$

$$0 = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K_{\text{eq}}$$

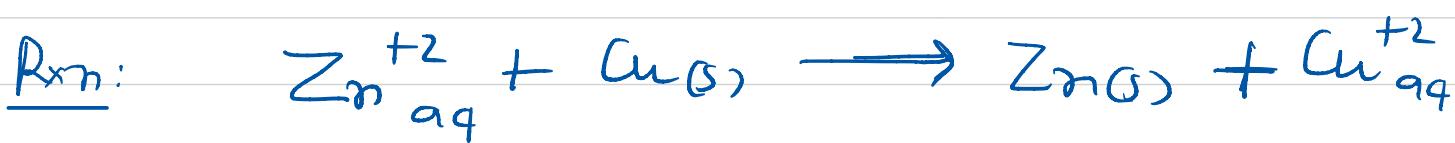
$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_{\text{eq}}$$

{ Cell size  $n$   
Q , n  
 $E_{\text{cell}}^{\circ}$   
 $\bar{E}_{\text{cell}}$



given  $\frac{2.303 RT}{F} = 0.06$

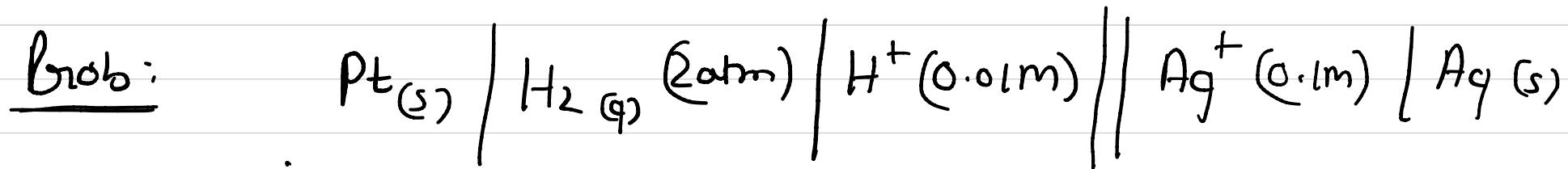
Calculate  $E_{\text{cell}}^{\circ}$  ?



$$Q = \frac{[\text{Cu}^{+2}]}{[\text{Zn}^{+2}]} = \frac{0.1}{0.01} = 10, \quad n=2$$

$$E_{\text{Cell}}^{\circ} = (-0.76) - (0.34) = -1.10 \text{ V}$$

$$E_{\text{Cell}} = -1.10 \text{ V} - \frac{0.06}{2} \log 10 = \underline{-1.13 \text{ V}}$$



given  $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.8 \text{ V}$

$$\frac{2.303 RT}{F} = 0.06 \quad (\text{calculate } E_{\text{cell}} = ?)$$



$$Q = \frac{(10^{-2})^2}{(10^{-1})^2 \times 2} = \frac{1}{2} \times 10^{-2} ; \quad n=2$$

$$E_{\text{Cell}}^{\circ} = 0.8 - 0 = 0.8 \text{ V}$$

$$E_{\text{Cell}} = 0.8 - \frac{0.06}{2} \log \left( \frac{1}{2} \times 10^{-2} \right)$$

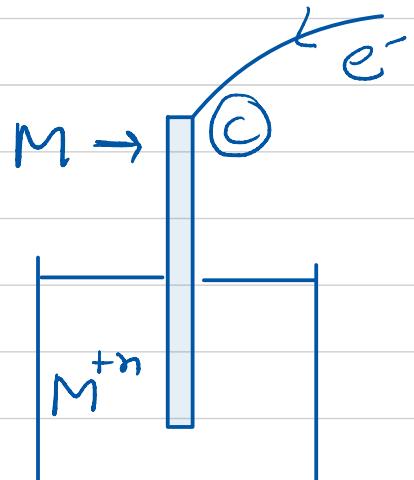
$$= 0.8 - 0.03 [-0.3 - 2] = 0.8 + 0.03 \times 2.3$$

$$= 0.869$$

## Different type of half cell :

### ① Metal / metal ion half cell:

e.g:  $Zn/Zn^{+2}$ ,  $Cu/Cu^{+2}$ ,  $Ag/Ag^+$  etc



$$Q = \frac{1}{[M^{+n}]}$$

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

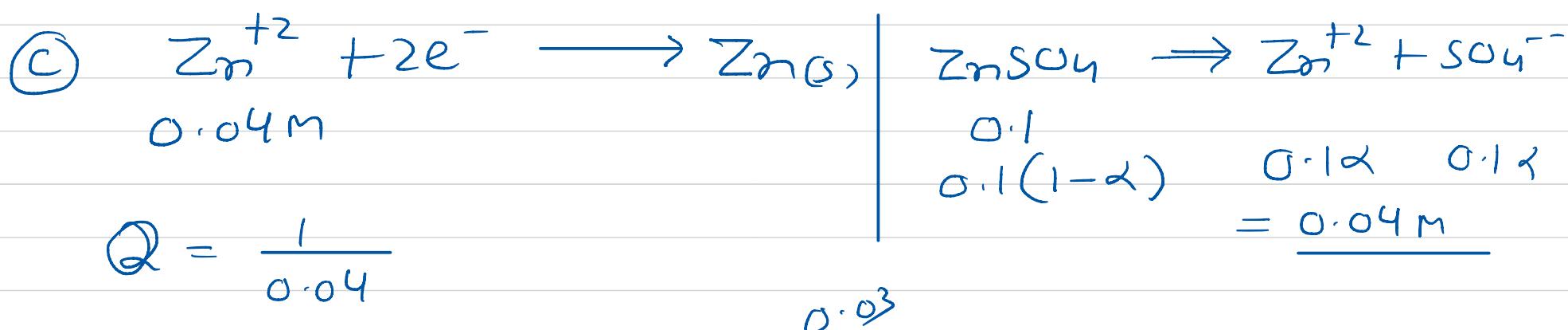
# for Active metals, we use metal amalgam - metal ion half cell



With metal amalgam metal reduces its activity.

Prob: Zn electrode is dipped into 0.1M  $ZnSO_4$  sol.  
if degree of ionization of  $ZnSO_4$  is 60%. then  
Calculate reduction potential of Zn electrode

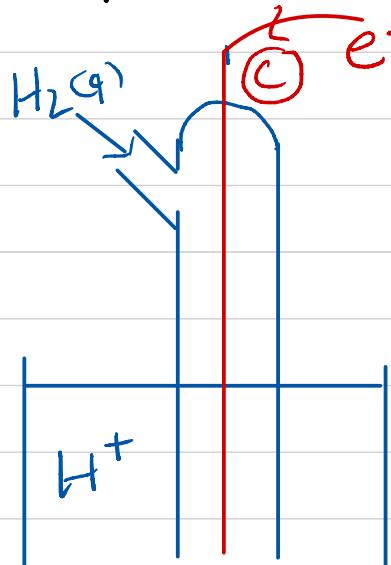
$$E^\circ_{Zn^{+2}/Zn} = -0.76 \text{ V} \quad \frac{2.303 R F}{F} = 0.06$$



$$E_{Zn^{+2}/Zn} = -0.76 - \frac{0.06}{2} \log \left( \frac{10^2}{4} \right)$$

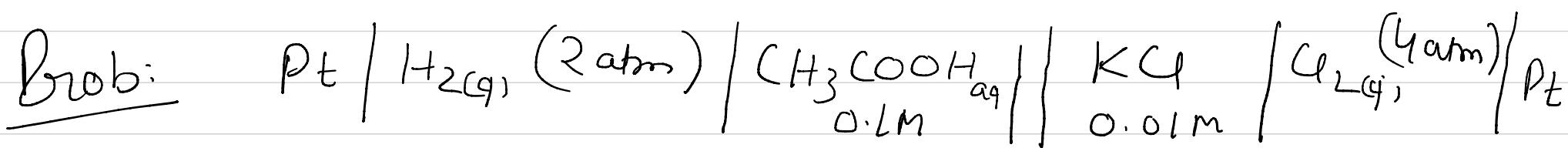
$$= -0.76 - 0.03 [2 - 0.6] = -0.802$$

② Gas | Gas ion half cell :-



$$Q = \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$

$$E_{\text{H}^+/\text{H}_2} = E_{\text{H}^+/\text{H}_2}^\circ - \frac{0.0591}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+]^2}$$



Given  $\frac{2.303RT}{F} = 0.06$ ,  $E_{\text{Cl}_2/\text{Cl}^-}^\circ = 1.36 \text{ V}$

Calculate  $E_{\text{cell}}$  )  $K_a(\text{CH}_3\text{COOH}) = 10^{-5}$



$$Q = \frac{(10^{-3})^2 \times (10^{-2})^2}{2 \times 4} = \frac{10^{-10}}{8}; n=2$$

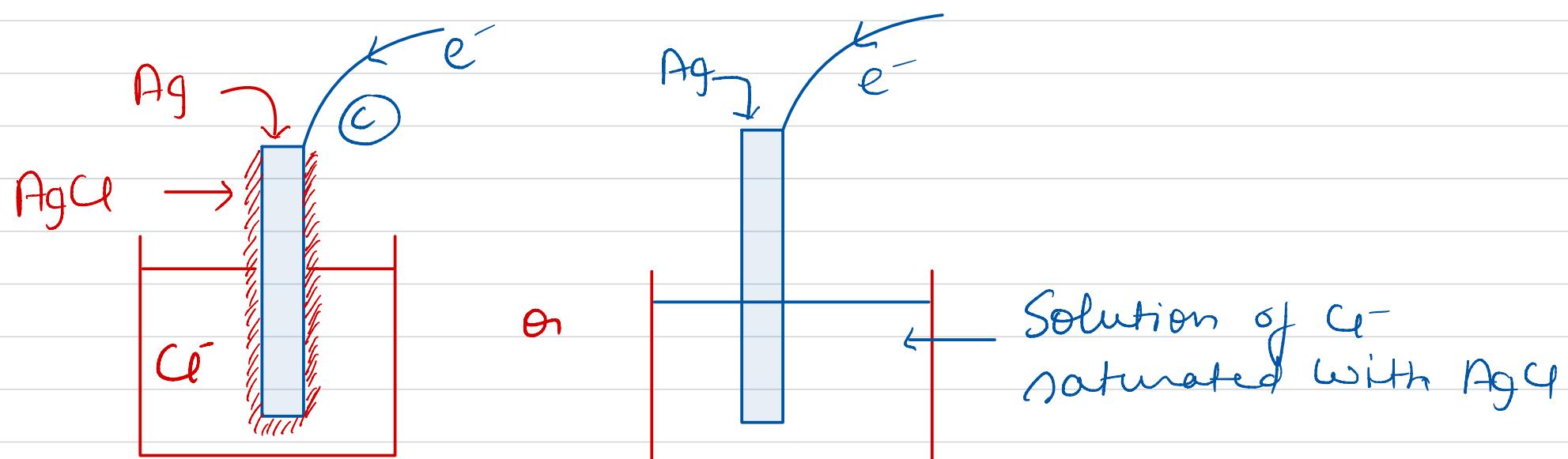
$$E_{\text{cell}}^\circ = (1.36 - 0) = 1.36$$

$$E_{\text{cell}} = 1.36 - \frac{0.06}{2} \log \frac{10^{-10}}{8}$$

$$= 1.36 - 0.03[-10 - 0.9] = \underline{1.687}$$

### ③ Metal Insoluble Salt Anion Half cell :

e.g.  $\text{Ag}/\text{AgCl}/\text{Cl}^-$ ,  $\text{Ag}/\text{Ag}_2\text{S}/\text{S}^-$  etc



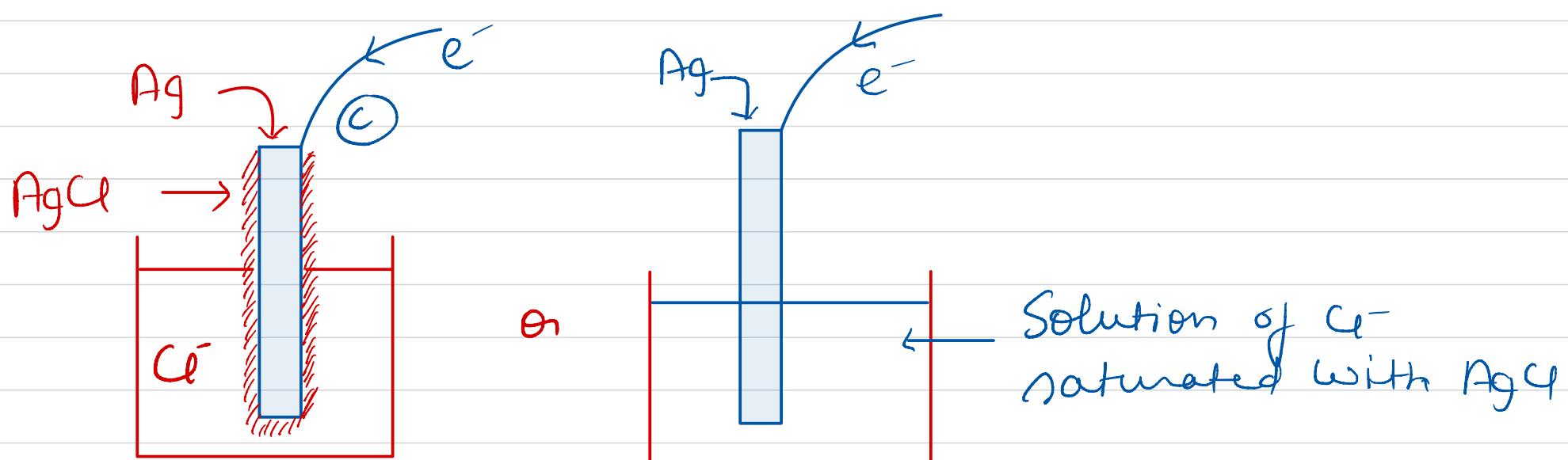
$$Q = [\text{Cu}^-]$$

$$E_{\text{Ag}_4/\text{Ag}/\text{Cu}^-} = E_{\text{AgCl}/\text{Ag}/\text{Cl}^-}^{\circ} - \frac{0.0891}{1} \log[\text{Cu}^-]$$

# Electrochemistry TOL\_TOV 21-22(2)

### ③ Metal Insoluble Salt Anion Half Cell:

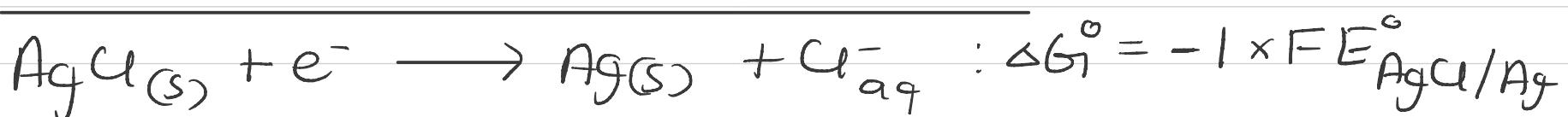
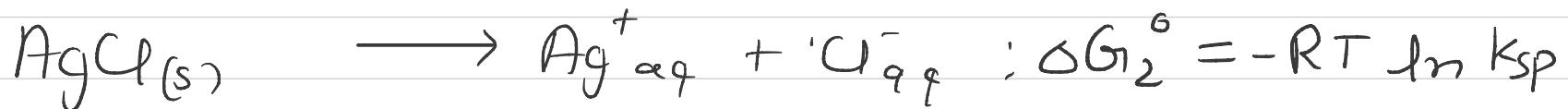
e.g.  $\text{Ag}/\text{AgCl}/\text{Cl}^-$ ,  $\text{Ag}/\text{Ag}_2\text{S}/\text{S}^-$  etc



$$Q = [\text{Cl}^-]$$

$$E_{\text{AgCl}/\text{Ag}/\text{Cl}^-} = E_{\text{AgCl}/\text{Ag}/\text{Cl}^-}^\circ - \frac{0.0591}{F} \log Q$$

$$\# \quad E_{\text{AgCl}/\text{Ag}}^\circ \neq E_{\text{Ag}^+/\text{Ag}}^\circ$$



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

$$-1 \times F E_{\text{AgCl}/\text{Ag}}^\circ = -1 \times F E_{\text{Ag}^+/\text{Ag}}^\circ - RT \ln K_{sp}$$

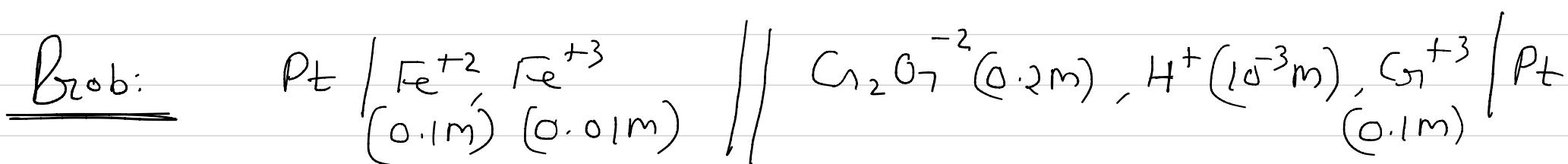
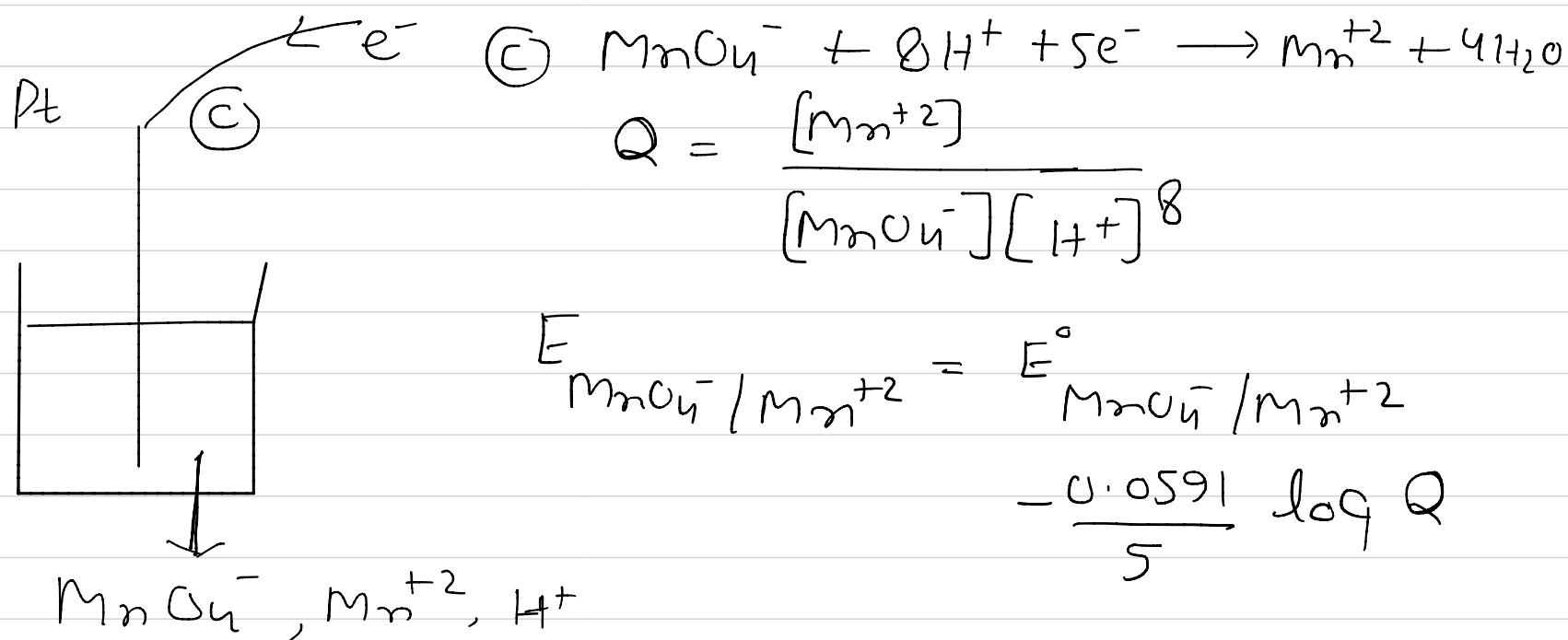
$$E_{\text{AgCl}/\text{Ag}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{RT}{F} \times 2.303 \log K_{sp}$$

$$E_{\text{AgCl}/\text{Ag}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{0.0591}{F} \log K_{sp}$$

at Room Temp.

#### ④ Oxidation - Reduction Half cell (Redox Half cell)

Eq: Pt / Fe<sup>+2</sup>, Fe<sup>+3</sup> , Pt / MnO<sub>4</sub><sup>-</sup>, Mn<sup>+2</sup>, H<sup>+</sup>



Given  $\frac{2.303 RT}{F} = 0.06$ ,  $\log 2 = 0.3$

$$E^\circ_{\text{Fe}^{+2}/\text{Fe}^{+3}} = -0.77 \text{ V}, \quad E^\circ_{\text{Cr}_2\text{O}_7^{-2}/\text{Cr}^{+3}} = 1.33 \text{ V}$$



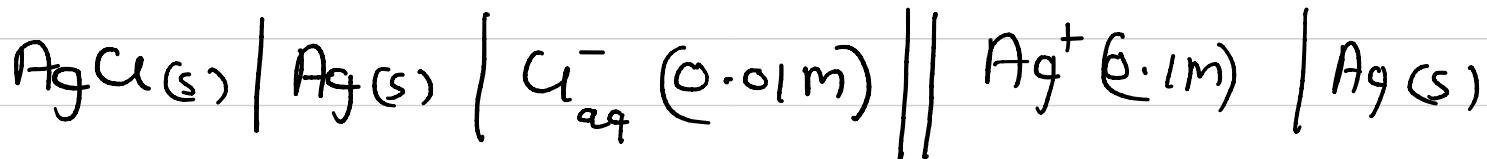
$$Q = \frac{(10^{-2})^6 \times (10^{-1})^2}{0.2 \times (10^{-3})^{14} (10^{-1})^6} = \frac{10^{-12}}{0.2 \times 10^{-42} \times 10^{-4}} = \left(\frac{10^{35}}{2}\right)$$

$$n = 6$$

$$E^\circ_{\text{cell}} = 1.33 - (0.77) = 0.56$$

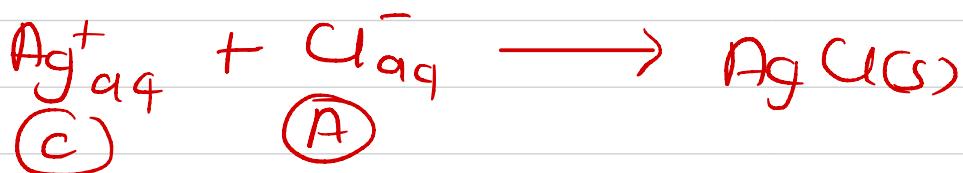
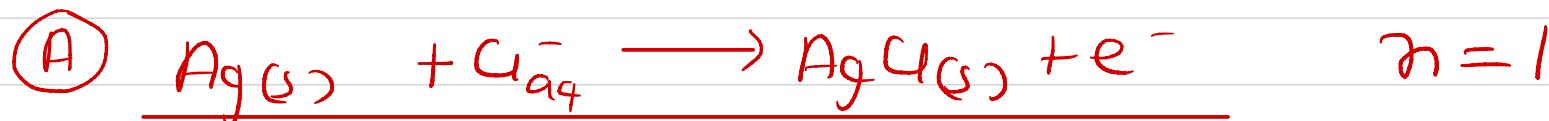
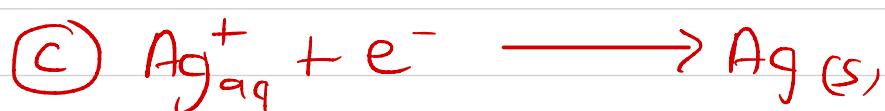
$$E_{\text{cell}} = 0.56 - \frac{0.06}{6} \log \frac{10^{35}}{2} = 0.56 - [35 - 0.3] \times 0.01 = 0.213$$

Problem:- Calculate  $E_{\text{cell}}$  ?



given  $\frac{2.303 RT}{F} = 0.06$ ,  $K_{\text{sp}} (\text{AgCl}) = 10^{-10}$

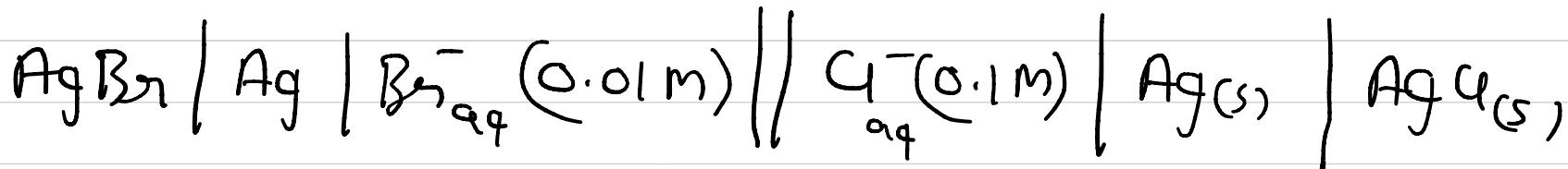
#  $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = 0.8 \text{ V}$



$$E_{\text{cell}}^{\circ} = E^{\circ}_{\text{Ag}^{+}/\text{Ag}} - [E^{\circ}_{\text{Ag}^{+}/\text{Ag}} + 0.06 \log 10^{-10}] = 0.6 \text{ V}$$

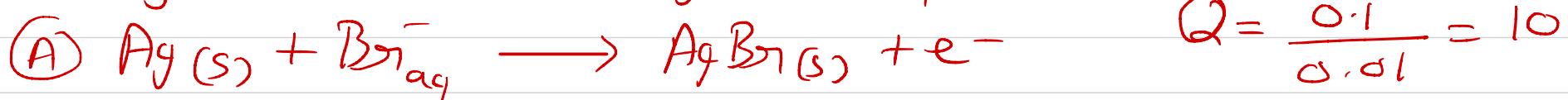
$$E_{\text{cell}} = 0.6 - \frac{0.06 \log 10^3}{1} = 0.42$$

Prob: Calculate  $E_{\text{cell}}$



given  $\frac{2.303 RT}{F} = 0.06$ ,  $K_{\text{sp}} (\text{AgCl}) = 10^{-10}$

$$K_{\text{sp}} (\text{AgBr}) = 10^{-13}$$



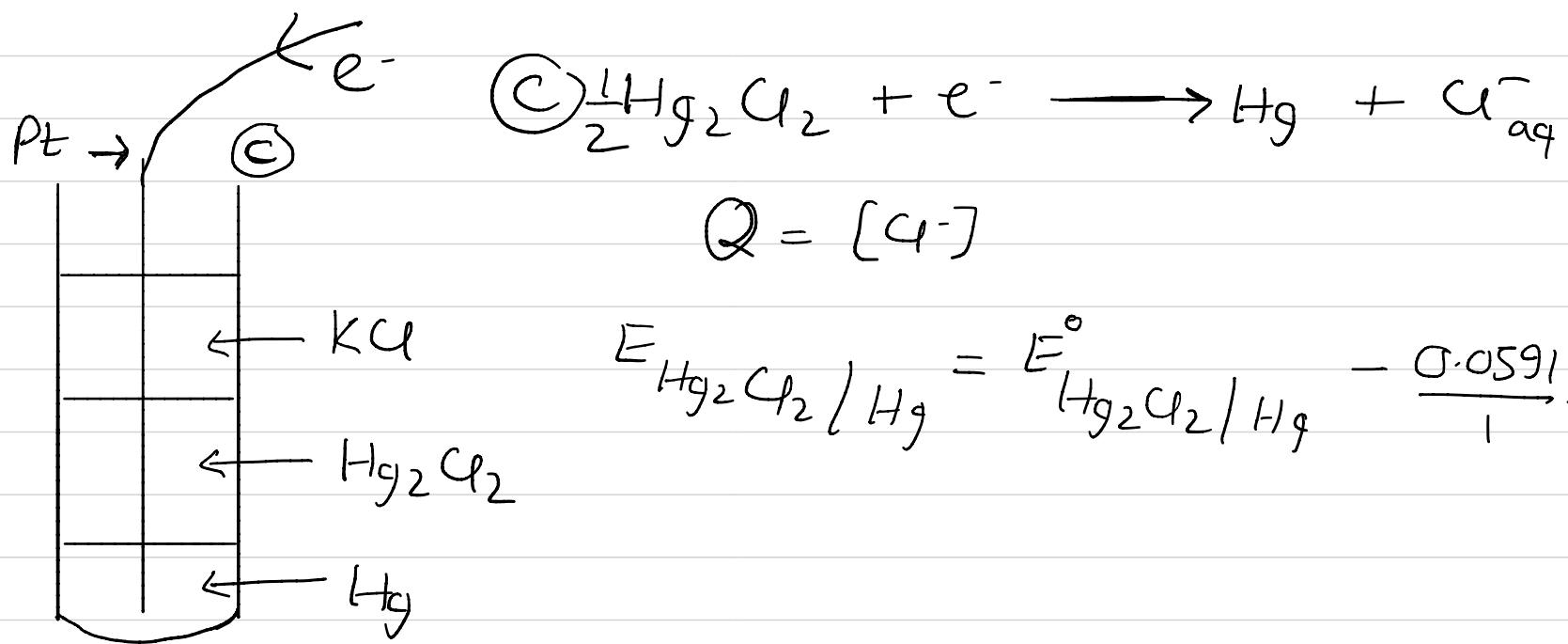
$$E_{\text{cell}}^{\circ} = (E^{\circ}_{\text{Ag}^{+}/\text{Ag}} + 0.06 \log 10^{-10}) - (E^{\circ}_{\text{Ag}^{+}/\text{Ag}} + 0.06 \log 10^{-13})$$

$$= 0.06 [-10 + 13] = 0.18$$

$$E_{\text{cell}} = 0.18 - \frac{0.06}{1} \log 10 = 0.12$$

### Calomel half cell :-

e.g.  $\text{Hg} \mid \text{Hg}_2\text{Cl}_2 \mid \text{KCl}$

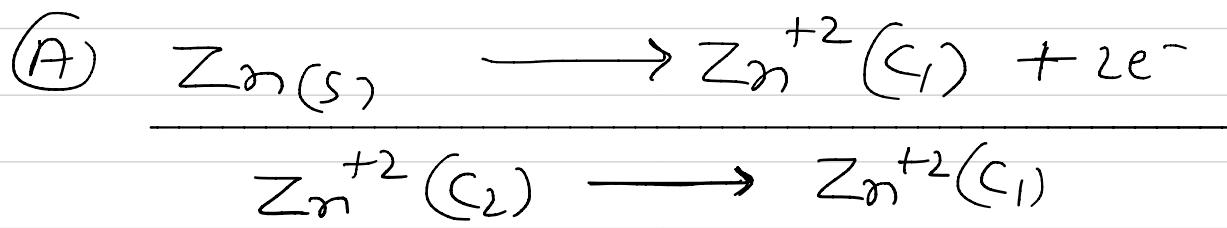
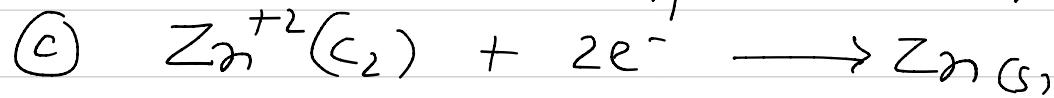
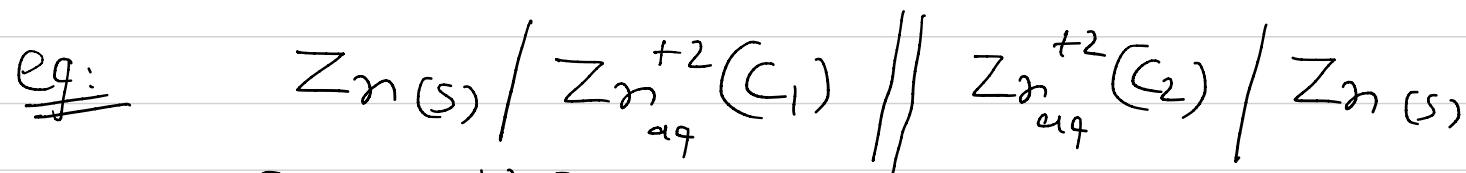


Concentration Cell :- Cathode and Anode are identical, only

diff is in press of gas or in concn of electrolyte.

① Electrolyte Conc<sup>n</sup> Cell :-

# Difference in conc<sup>n</sup> of electrolyte



$$Q = \left(\frac{C_1}{C_2}\right) : n=2, E_{cell}^o = 0$$

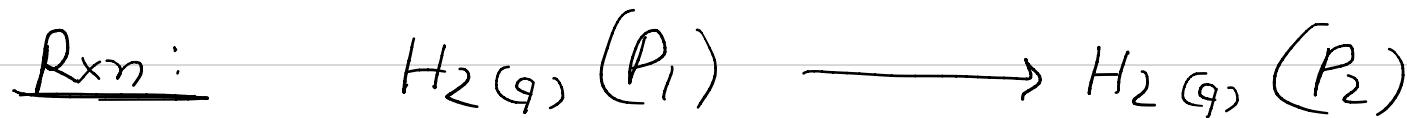
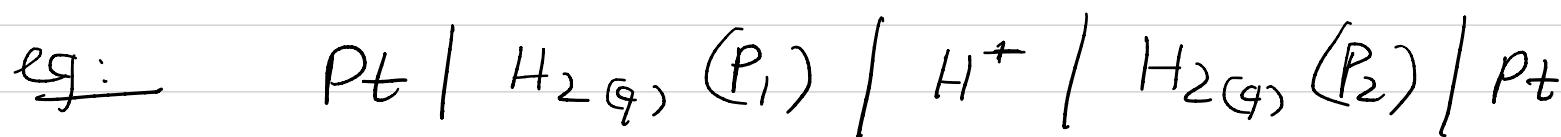
$$E_{cell} = 0 - \frac{0.0591}{2} \log\left(\frac{C_1}{C_2}\right)$$

$\Rightarrow C_2 > C_1$  for cell to be spontaneous

② Electrode Conc<sup>n</sup> Cell :-



# Difference in pressure of gas at electrode



$$Q = \left(\frac{P_2}{P_1}\right) : n=2 ; E_{cell}^o = 0$$

$$E_{cell} = 0 - \frac{0.0591}{2} \log\left(\frac{P_2}{P_1}\right)$$

$\Rightarrow P_1 > P_2$  for cell to be spontaneous.

# Electrochemistry TOL\_TOV 21-22(3)

Calculation of  $\Delta S^\circ$  and  $\Delta H^\circ$  for cell rxn:

$$dG^\circ = V \cdot dP - S \cdot dT$$

at const P

$$dG^\circ = -S \cdot dT$$

$$\delta G^\circ = -\left(\frac{\partial G^\circ}{\partial T}\right)_P$$

$$(\Delta S)^\circ = -\left[\frac{\partial (\Delta G^\circ)}{\partial T}\right]_P$$

$$\Delta G^\circ = -nFE^\circ$$

$$(\Delta S)^\circ = nF \left(\frac{\partial E^\circ}{\partial T}\right)_P$$

Where  $\left(\frac{\partial E^\circ}{\partial T}\right)_P$  = Temp coeff.

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$$

$$-nFE^\circ = \Delta H^\circ - T \times nF \left(\frac{\partial E^\circ}{\partial T}\right)_P$$

$$\Delta H^\circ = -nFE^\circ + nFT \left(\frac{\partial E^\circ}{\partial T}\right)_P$$

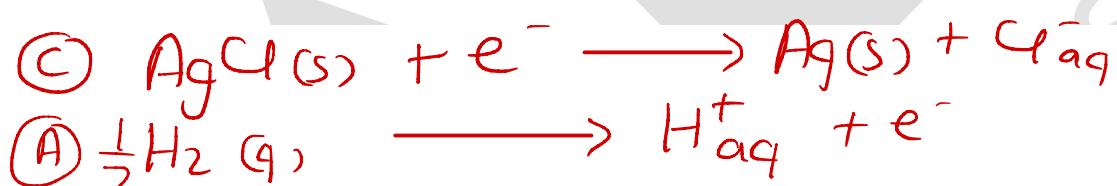
7. The standard potential of the following cell is 0.23 V at 15°C & 0.21 V at 35°C



$$= E^\circ_{\text{AgCl}/\text{Ag}} - 0 \Rightarrow E^\circ_{\text{AgCl}/\text{Ag}} = 0.22 \text{ V}$$

- (i) Write the cell reaction.
- (ii) Calculate  $\Delta H^\circ, \Delta S^\circ$  for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.
- (iii) Calculate the solubility of AgCl in water at 25°C. Given standard reduction potential of the  $\text{Ag}^+|\text{Ag}$  couple is 0.80 V at 25°C. [JEE 2001]

7. Ans.  $\Delta H^\circ = -49987 \text{ J mol}^{-1}, \Delta S^\circ = -96.5 \text{ J mol}^{-1} \text{ K}^{-1}, s = 1.47 \times 10^{-5} \text{ M}$



$$\left( \frac{\partial E}{\partial T} \right)_P = \frac{0.21 - 0.23}{20} = -10^{-3}$$



#  $\Delta S^\circ = nF \left( \frac{\partial E}{\partial T} \right)_P = 1 \times 96500 \times (-10^{-3}) = -96.5 \text{ J/K}$

$$\Delta H^\circ = -nFE^\circ + nFT \left( \frac{\partial E}{\partial T} \right)_P = -1 \times 96500 \times 0.22 + 1 \times 96500 \times 298 \times -10^{-3}$$

$$\Delta H^\circ = -21230 - 28757 = -49987 \text{ J/mol}$$

#  $E^\circ_{\text{AgCl}/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} + \frac{0.0591}{1} \log K_{\text{sp}} = 0.22$

$$0.0591 \log(s)^2 = 0.22 - 0.8 = -0.58$$

$$\log(s) = \frac{-0.58}{0.0591 \times 2} = 4.906$$

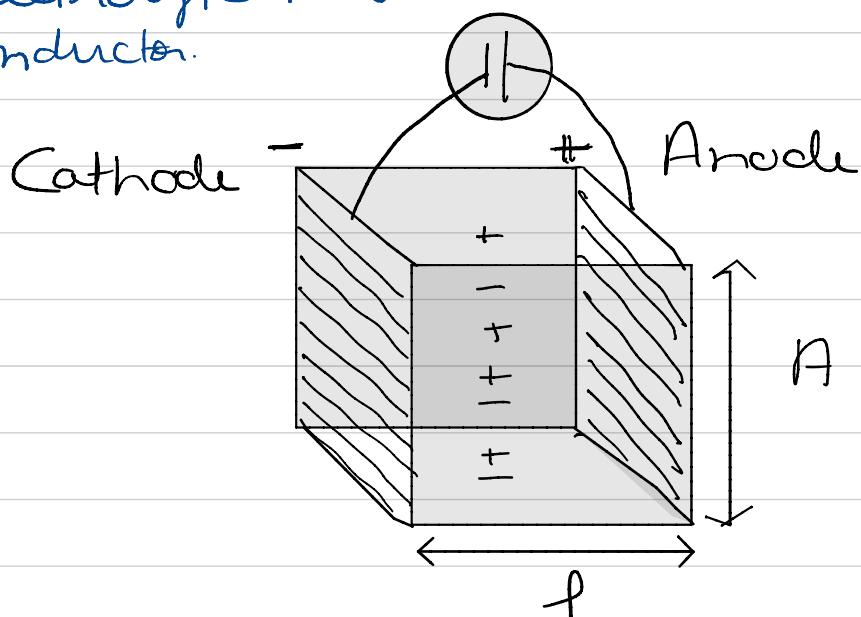
$$(s) = 10^{-4.906}$$

# Conduction in electrolytes:-

$T \uparrow \Rightarrow$  conduction in electrolyte ↑

Electrolyte follow same law as in metallic conductor.

Conduction is metal ↓



$$\left(\frac{l}{A}\right) = \text{Cell const} = G^*$$

$$① V = iR$$

$$② i = i_+ + i_-$$

$$③ R = \rho \times \left(\frac{l}{A}\right)$$

Where  $l$  = distance b/w electrode (cm)

$A$  = Cross sectional area of electrode ( $\text{cm}^2$ )

$R$  = Resistance of Solution ( $\Omega$ )

$\rho$  = Resistivity ( $\Omega \cdot \text{cm}$ )

$i$  = total current in  $\text{sol}^3$

## ④ Conductance (C) :-

$$C = \left(\frac{l}{R}\right) \quad \text{or mho or Siemen}$$

## ⑤ Sp conductance (or Conductivity) $K$ :-

Conductance of  $1\text{cm}^3$  soln (where  $l=1\text{cm}$ ,  $A=1\text{cm}^2$ ) is called sp conductance

$$K = \left(\frac{1}{\rho}\right) \quad \text{or } \text{mho cm}^{-1}$$

$$R = \rho \times \left(\frac{l}{A}\right) \Rightarrow \frac{1}{\rho} = \frac{1}{R} \times \frac{A}{l}$$

$$\Rightarrow K = C \times \left(\frac{l}{A}\right)$$

## ⑥ Molar Conductance ( $\Lambda_m$ or $\lambda_m$ ) :-

Conductance of solution having 1 mole of electrolyte is called as molar conductance.

$$\# \quad \Delta m = K \times V$$

$$\boxed{\Delta m = K \times \frac{1000}{M}} \quad \text{or } \text{mole}^{-1} \text{cm}^2/\text{mole}$$

where  $K = \text{mho cm}^{-1}$

$$M \times V_{lit} = \text{mole} = 1$$

$$V_{lit} = \left(\frac{l}{M}\right)$$

$$V_{\text{cm}^3} = \frac{1000}{M}$$

$$\lambda_m = \frac{1}{1000 M}$$

$$\# \quad \Lambda_m = k (n^{-1} m^{-1}) \times V (m^3) = n^{-1} m^2 / \text{mol}$$

$$\Lambda_m = k \times \frac{1}{1000 M}$$

Equivalent Conductance ( $\Lambda_{eq}$  or  $\Lambda_{\epsilon q}$ ) :-

Conductance of solution having 1 eq of electrolyte is called as eq conductance

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

$$k = n^{-1} \text{cm}^{-1}$$

$$\Lambda_{eq} = n^{-1} \text{cm}^2 / \epsilon_q$$

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

$$k = n^{-1} \text{m}^{-1}$$

$$\Lambda_{eq} = n^{-1} \text{m}^2 / \epsilon_q$$

$$\# \quad N = M \times n\text{-factor}$$

$$\Lambda_{eq} = k \times \frac{1000}{M \times n\text{-factor}}$$

$$\Lambda_m = \Lambda_{eq} \times n\text{-factor}$$

A cell whose resistance, when filled with 0.1 M – KCl is  $200 \Omega$ , is measured to be  $6400 \Omega$ , when filled with 0.003 M – NaCl solution. What is the molar conductance of NaCl solution, in  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  if the molar conductance of 0.1 M – KCl is  $120 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ ?

- (a) 41.67      ~~mole~~  
(c) 125      (b) 250  
(d) 375

**Ans:** c

$$\lambda_m = k \times \frac{1000}{m} = \left( C \times \frac{1}{A} \right) \times \frac{1000}{m}$$

$$\frac{\lambda_{m_1}}{\lambda_{m_2}} = \frac{C_L}{C_2} \times \frac{M_2}{M_1}$$

$$\frac{\lambda_m(\text{NaCl})}{120} = \frac{1 \times 200}{6400 \times 1} \times \frac{0.1}{0.003}$$

$$\Delta m(\text{NaCl}) = \frac{120}{32} \times \frac{100}{10}$$

The molar conductivity of 0.10 M solution of  $\text{MgCl}_2$  is 100 mho  $\text{cm}^2 \text{mol}^{-1}$ , at 25°C. A cell with electrodes that are 1.50  $\text{cm}^2$  in surface area and 0.50 cm apart is filled with 0.10 M –  $\text{MgCl}_2$  solution. How much current will flow when the potential difference between the electrodes is 5 volts?



**Ans: c**

$$V = i R$$

$$\Delta m = k \times \frac{1000}{m}$$

$$= C \times \frac{1}{A} \times \frac{1000}{m}$$

$$L_{\text{eq}} = \frac{L}{R} \times \left( \frac{0.5}{1.5} \right)^p \times \frac{1000}{0.1}$$

$$R = \frac{100}{3} \text{ m}$$

$$5 = j * \frac{100}{3} \Rightarrow j = 0.15 \text{ amp}$$

Resistance of 0.2 M solution of an electrolyte is  $50 \Omega$ . The specific conductance of the solution is  $1.4 \text{ S m}^{-1}$ . The resistance of 0.5 M solution of the same electrolyte is  $280 \Omega$ . The molar conductivity of 0.5 M solution of the electrolyte (in  $\text{S m}^2 \text{ mol}^{-1}$ ) is

- (a)  $5 \times 10^{-3}$       (b)  $5 \times 10^3$   
 (c)  $5 \times 10^2$       (d)  $5 \times 10^{-4}$

Ans: d

$$K = C \times \left(\frac{1}{n}\right)$$

$$14 = \frac{1}{50} \times \left(\frac{1}{A}\right) \Rightarrow \left(\frac{1}{A}\right) = 70$$

$$\Rightarrow K = \frac{1}{280} \times 7\phi = \left(\frac{1}{4}\right) r^{-l} m^{-l}$$

for 0.5M net

$$\Delta m = k \times \frac{1}{1000 \text{ M}}$$

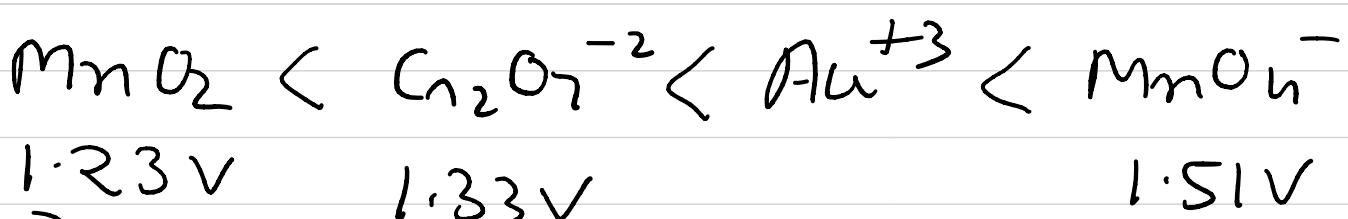
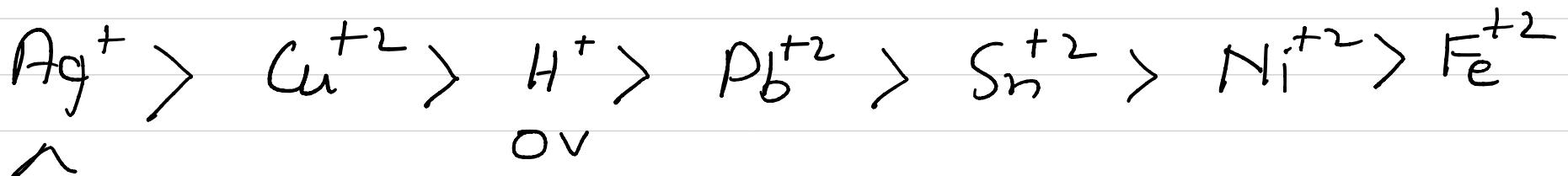
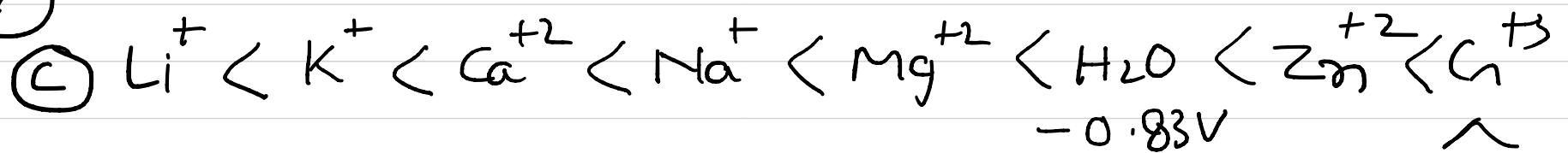
$$= \frac{1}{4} \times \frac{1}{1000 \times 0.5}$$

$$= 5 \times 10^{-4} \text{ N}^{-1}\text{m}^2/\text{mol}$$

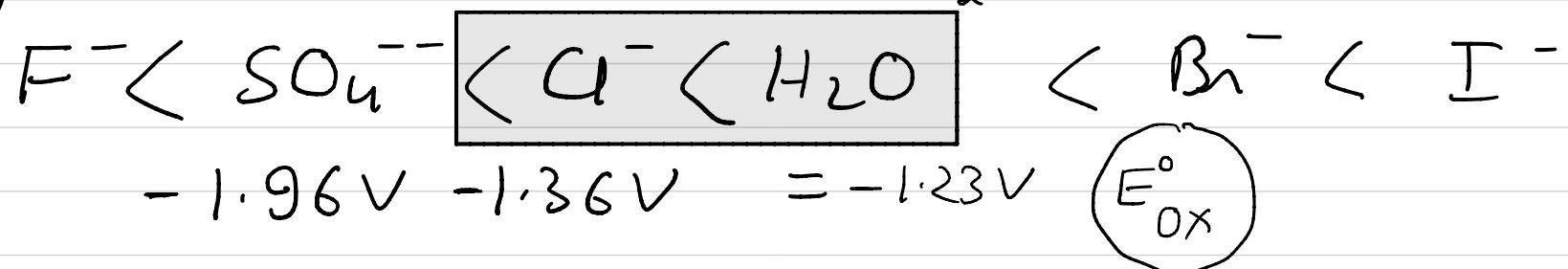
# Electrochemistry TOL\_TOV 21-22(4)

Order of reduction at Cathode and Oxidation at Anode  
Under Standard condition.

⑦



(A)

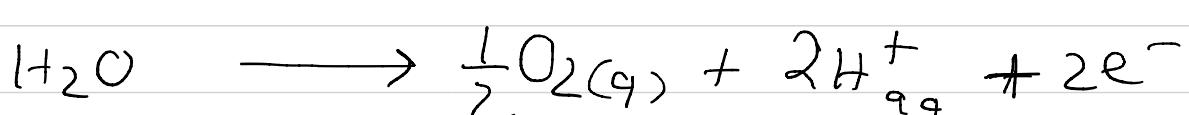
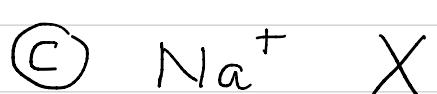


# in aq soln of  $\text{Cl}^-$ , oxidation of  $\text{Cl}^-$  take place before  $\text{H}_2\text{O}$

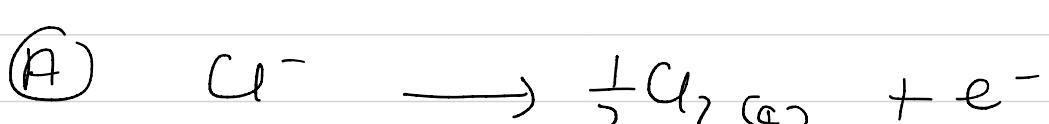
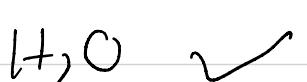
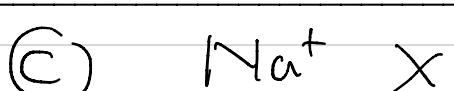
# in diluted aq soln of  $\text{Cl}^-$ , oxidation of  $\text{H}_2\text{O}$  take place before  $\text{Cl}^-$

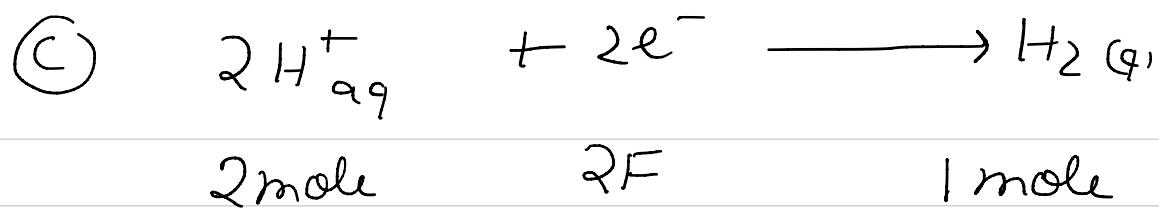
⑧ Electrolysis of different electrolytic Solution :-

① aq diluted NaCl Using Pt



② aq Conc<sup>n</sup> NaCl Using Pt





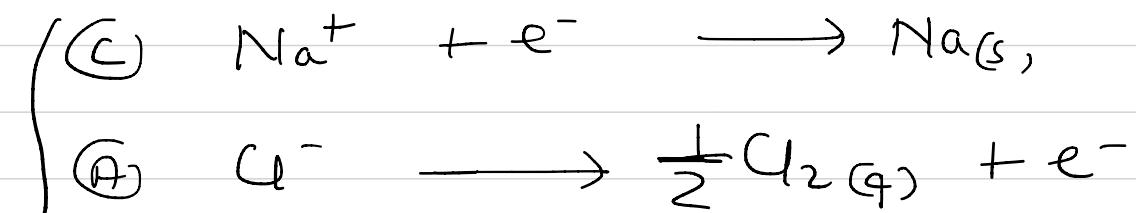
### Q) Current efficiency ( $\eta$ )

$$\eta = \frac{m_{\text{Actual}}}{m_{\text{theoretical}}} = \frac{Q_{\text{Actual}}}{Q_{\text{theoretical}}} = \frac{i_{\text{Actual}}}{i_{\text{theoretical}}}$$

Prob:

Calculate volume of  $\text{Cl}_2(\text{g})$  produced at NTP when 40 amp current is passed for 9.65 min. from molten NaCl solution. (given current efficiency is 80%).

Soln:



$$\text{No of F} = \frac{(40 \times 9.65 \times 60)}{96500} \times 0.8 = \frac{24 \times 0.8}{100}$$

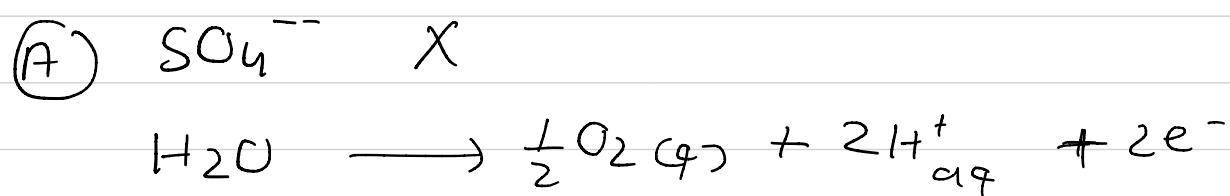
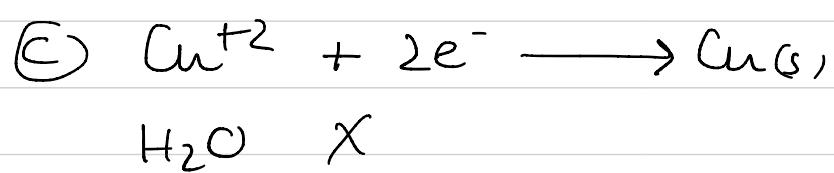
$$n_{\text{Cl}_2} = \frac{1}{2} \times \frac{24 \times 0.8}{100} \text{ mole}$$

$$V_{\text{Cl}_2} = \frac{1}{2} \times \frac{24 \times 0.8}{100} \times 22.4$$

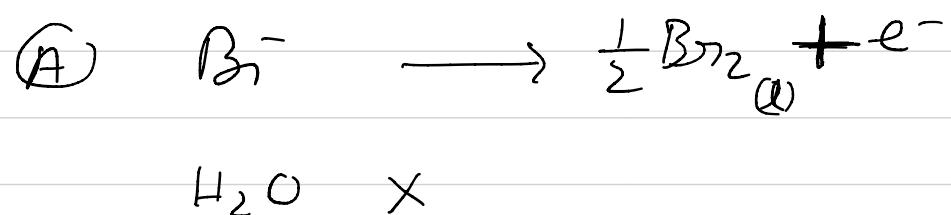
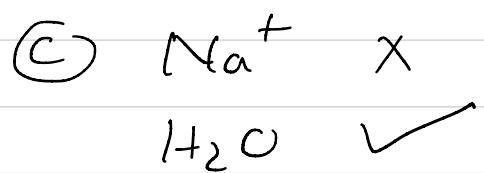
$$= 2.15 \text{ lit}$$

$$\# \quad n_{\text{Cl}_2} \times 2 = \left( \frac{40 \times 9.65 \times 60}{96500} \right) \times 0.8$$

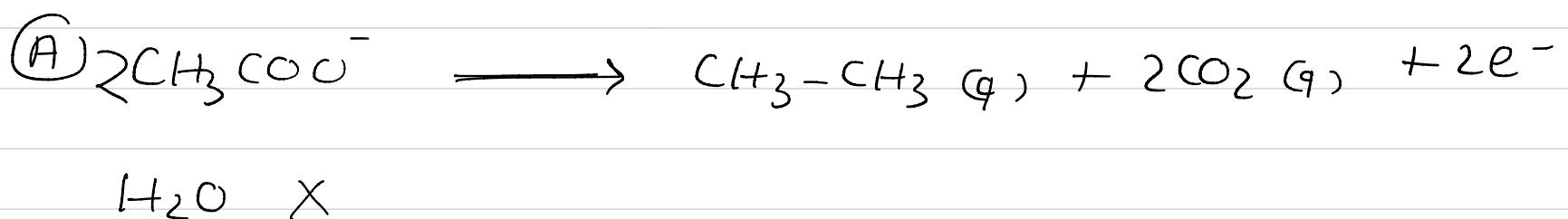
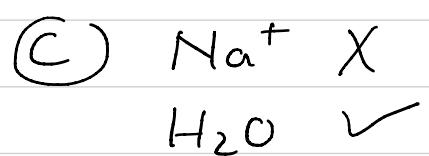
③ aq  $\text{CuSO}_4$  Using Pt



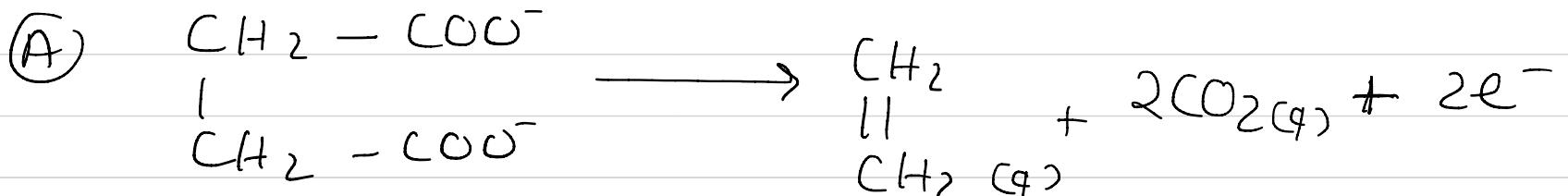
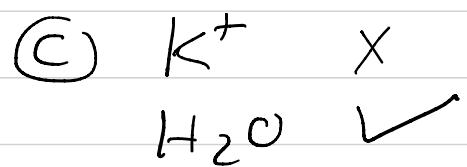
④ aq  $\text{NaBr}$  Using Pt



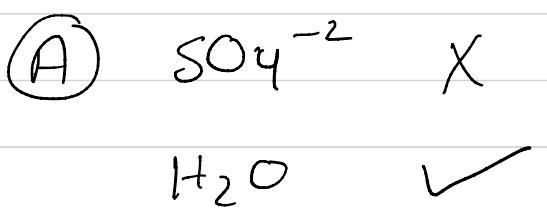
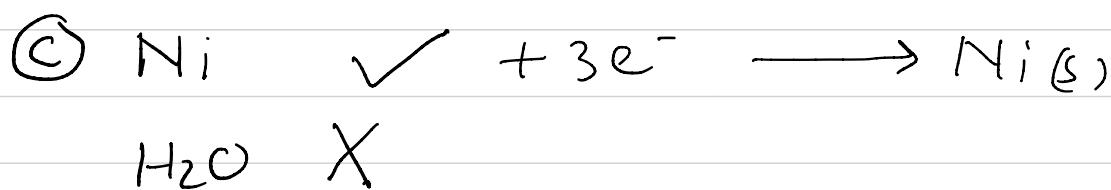
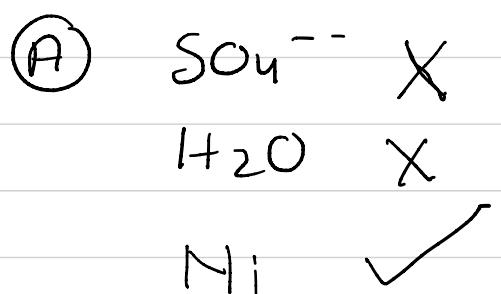
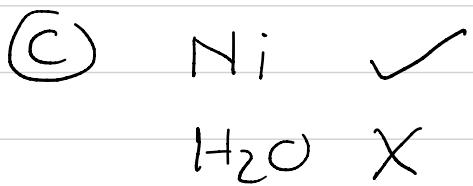
⑤ aq  $\text{CH}_3\text{COONa}$  Using Pt



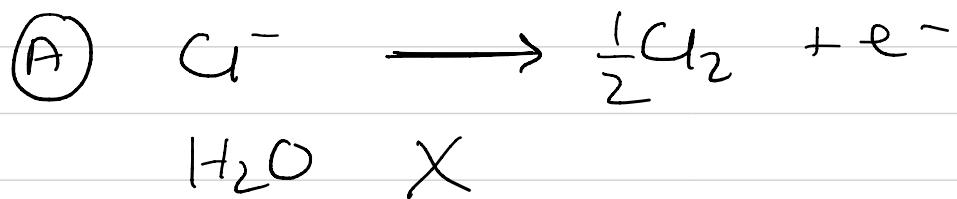
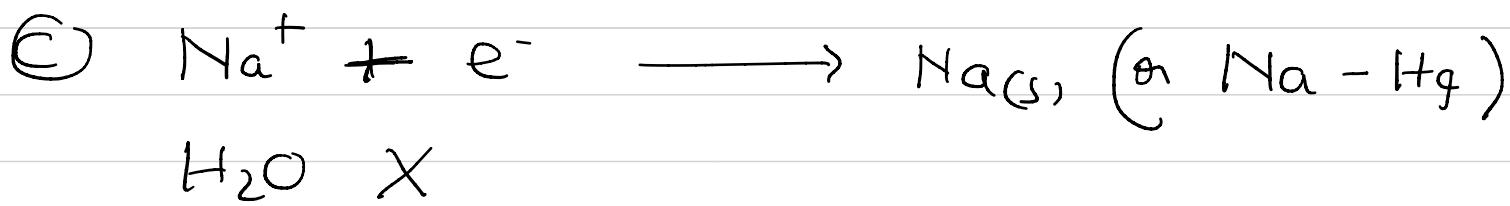
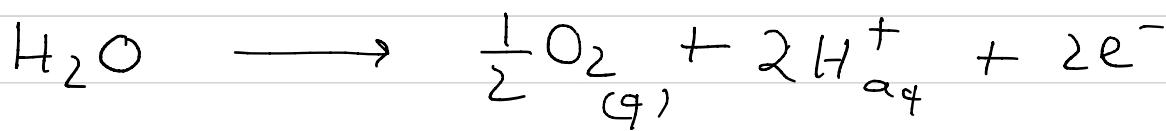
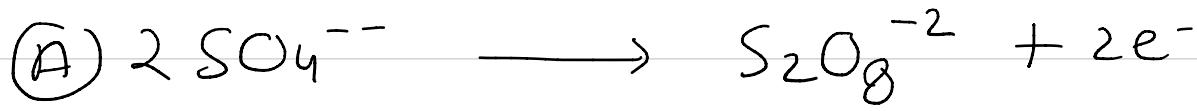
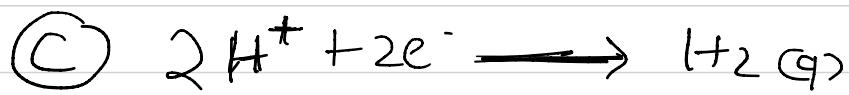
⑥ aq  $\begin{array}{c} \text{CH}_2-\text{COOK} \\ | \\ \text{CH}_2-\text{COOK} \end{array}$  Using Pt



(7)

aq NiSO<sub>4</sub> Using Pt(8) aq (Ni) (SO<sub>4</sub>) Using Ni electrode

\* (9)

aq NaCl Using Hg electrode(10) aq H<sub>2</sub>SO<sub>4</sub> Using Pt electrode

\* Normally oxidation of H<sub>2</sub>O take place but in Case of highly concn soln both H<sub>2</sub>O and SO<sub>4</sub><sup>2-</sup> will oxidize.

## Effect of dilution :-

① Sp conductance :-

$$\text{Dilution} \uparrow \Rightarrow K \downarrow$$

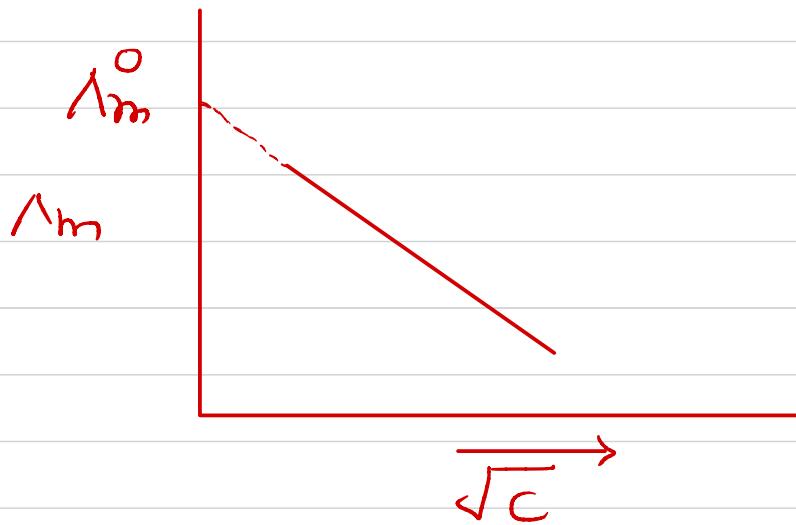
② Conductance :-

$$\text{Dilution} \uparrow \Rightarrow C \downarrow$$

③ Molar Conductance ( $\Lambda_m$  or  $\lambda_m$ ) :-

a) Strong Electrolyte :-

Debye huckle rule



$$\Lambda_m = \Lambda_m^0 - b\sqrt{C}$$

Where

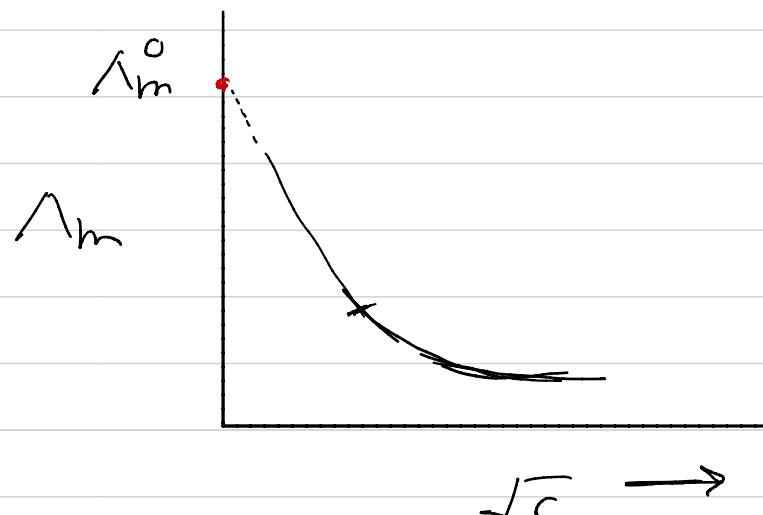
$\Lambda_m$  = molar conductance

$\Lambda_m^0$  = Limiting molar conductance

$b$  = Const for electrolyte

$C$  = Conc of electrolyte

b) Weak Electrolyte :-



At 25°C, the molar conductance at infinite dilution for HCl solution is  $4.25 \times 10^{-2} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$ , while its specific conductance is  $382.5 \Omega^{-1} \text{m}^{-1}$ . If the degree of dissociation is 90%, the molarity of solution is

- (a) 0.9 M
- (b) 1.0 M
- (c) ~~0.1 M~~  $\Rightarrow$  10 M
- (d) 1.1 M

Ans: C

A big irregular shaped vessel contained water, conductivity of which was  $2.56 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1}$ . 585 g of NaCl was then added to the water and conductivity after the addition of NaCl, was found to be  $3.06 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1}$ . The molar conductivity of NaCl at this concentration is  $1.5 \times 10^{-2} \text{ S}^{-1} \text{m}^2 \text{mol}^{-1}$ . The capacity of vessel if it is fulfilled with water, is

- (a)  $3 \times 10^4 \text{ l}$
- (b) 30 l
- (c)  $3 \times 10^8 \text{ l}$
- (d)  $3 \times 10^5 \text{ l}$

$$\Lambda_m = 382.5 \times \frac{1}{1000 \times M}$$

$$0.9 = \frac{\Lambda_m}{\Lambda_m^\circ} \Rightarrow \Lambda_m = 0.9 \times 4.25 \times 10^{-2}$$

$$M = \frac{382.5}{1000 \times 0.9 \times 4.25 \times 10^{-2}} \\ = 10 \text{ mol/l}$$

$$\cdot K_{H_2O} = 2.56 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1} \\ K_{Solv}(NaCl) = 3.06 \times 10^{-3} = K_{NaCl} + K_{H_2O} \\ \Rightarrow K_{NaCl} = (3.06 - 2.56) \times 10^{-3} \\ = 5 \times 10^{-4} \text{ S}^{-1} \text{m}^{-1}$$

$$\Lambda_m = \frac{k \times 1}{1000 M} \\ 1.5 \times 10^{-2} = 8 \times 10^{-4} \times \frac{1}{1000 M} \\ 3 \times 10^{-4} = \frac{1}{M} = \frac{V(l)}{10} \\ V(l) = 3 \times 10^5 \text{ lit}$$

Ans: d

The conductivity of saturated solution of  $Ba_3(PO_4)_2$  is  $1.2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ . The limiting equivalent conductivities of  $BaCl_2$ ,  $K_3PO_4$  and  $KCl$  are 160, 140 and  $100 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ , respectively. The solubility product of  $Ba_3(PO_4)_2$  is

- (a)  $10^{-5}$
- (b)  $1.08 \times 10^{-23}$
- (c)  $1.08 \times 10^{-25}$
- (d)  $1.08 \times 10^{-27}$

Ans: b

## Kohlrausche's Law :

In infinite diluted soln, each ion migrate independently and show max<sup>m</sup> molar conductance  
 Molar conductance of electrolyte is sum of molar conductance of ions.

e.g.:

$$\Lambda_m^\circ(\text{NaCl}) = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-)$$

$$\Lambda_m^\circ(\text{CaCl}_2) = \Lambda_m^\circ(\text{Ca}^{+2}) + 2\Lambda_m^\circ(\text{Cl}^-)$$

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{COO}^-) + \Lambda_m^\circ(\text{H}^+)$$

$$\Lambda_m^\circ(\text{H}_3\text{PO}_4) = 3 \cdot \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{PO}_4^{---})$$

#

$$\Lambda_m = \Lambda_{eq}^\circ \times n\text{-factor}$$

e.g. (a)  $1 \times \Lambda_{eq}^\circ(\text{NaCl}) = 1 \times \Lambda_{eq}^\circ(\text{Na}^+) + \Lambda_{eq}^\circ(\text{Cl}^-)$

$$\Lambda_{eq}^\circ(\text{NaCl}) = \Lambda_{eq}^\circ(\text{Na}^+) + \Lambda_{eq}^\circ(\text{Cl}^-)$$

(b)  $\Lambda_{eq}^\circ(\text{CH}_3\text{COOH}) = \Lambda_{eq}^\circ(\text{CH}_3\text{COO}^-) + \Lambda_{eq}^\circ(\text{H}^+)$

(c)  $2 \times \Lambda_{eq}^\circ(\text{CaCl}_2) = 2 \times \Lambda_{eq}^\circ(\text{Ca}^{+2}) + 2 \times \Lambda_{eq}^\circ(\text{Cl}^-)$

$$\Lambda_{eq}^\circ(\text{CaCl}_2) = \Lambda_{eq}^\circ(\text{Ca}^{+2}) + \Lambda_{eq}^\circ(\text{Cl}^-)$$

(d)  $\Lambda_{eq}^\circ[\text{Ba}_3(\text{PO}_4)_2] = \Lambda_{eq}^\circ(\text{Ba}^{+2}) + \Lambda_{eq}^\circ(\text{PO}_4^{---})$

$$\Lambda_m^\circ[\text{Ba}_3(\text{PO}_4)_2] = 3\Lambda_m^\circ(\text{Ba}^{+2}) + 2\Lambda_m^\circ(\text{PO}_4^{---})$$

## Application:-

① Calculation of limiting molar conductance of weak electrolyte using strong electrolyte

$$\text{eq: } \Lambda_m^\circ(\text{CH}_3\text{COOH}) = ? = \Lambda_m^\circ(\text{CH}_3\text{COO}^-) + \Lambda_m^\circ(\text{H}^+)$$

$$② \Lambda_m^\circ(\text{NaCl}) = \alpha c = \Lambda_m^\circ(\text{Na}^+) + \Lambda_m^\circ(\text{Cl}^-)$$

$$③ \Lambda_m^\circ(\text{CH}_3\text{COONa}) = \gamma = \Lambda_m^\circ(\text{CH}_3\text{COO}^-) + \Lambda_m^\circ(\text{Na}^+)$$

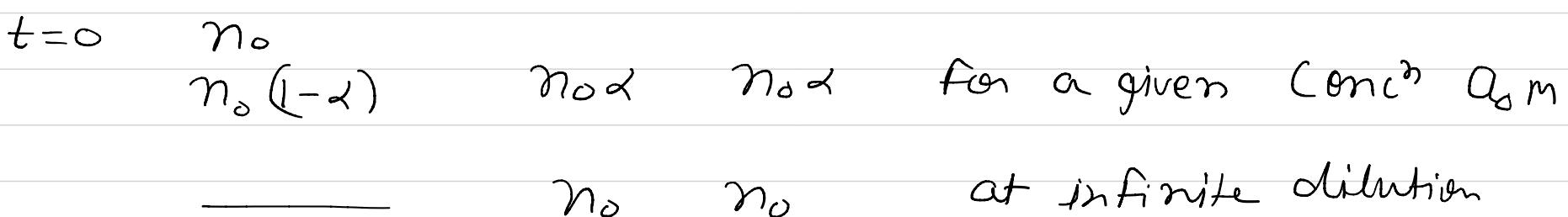
$$④ \Lambda_m^\circ(\text{HCl}) = Z = \Lambda_m^\circ(\text{H}^+) + \Lambda_m^\circ(\text{Cl}^-)$$

$$③ + ④ - ②$$

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = (\gamma + Z - \alpha c)$$

② Degree of ionization of weak electrolyte :-

$\text{HA} \Rightarrow \text{weak Electrolyte}$



# molar conductance  $\propto$  No of ions

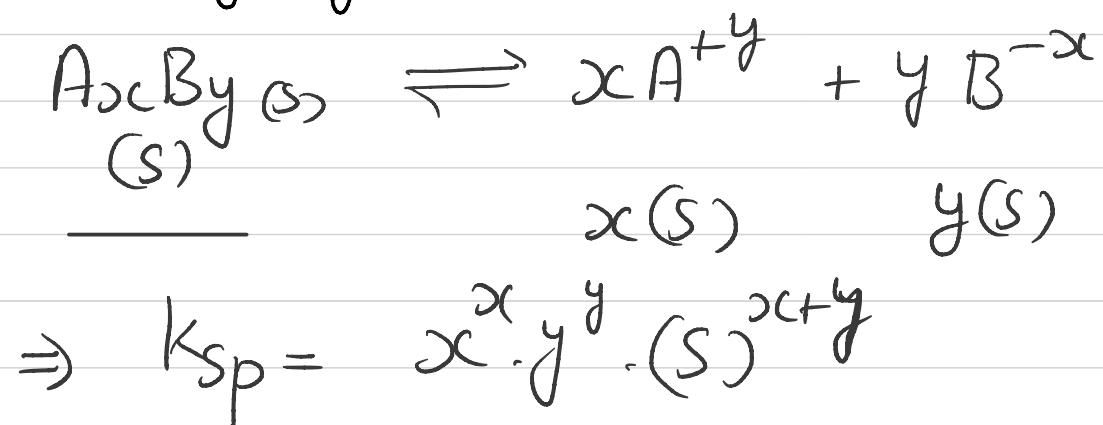
$$\Lambda_m \propto n_0\alpha + n_0\alpha \quad \text{--- (i)}$$

$$\Lambda_m^\circ \propto n_0 + n_0 \quad \text{--- (ii)}$$

$$\boxed{\frac{\Lambda_m}{\Lambda_m^\circ} = \alpha} = \frac{\Lambda_{\text{eq}}}{\Lambda_{\text{eq}}^\circ}$$

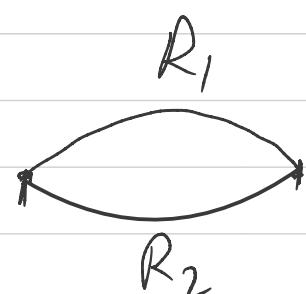
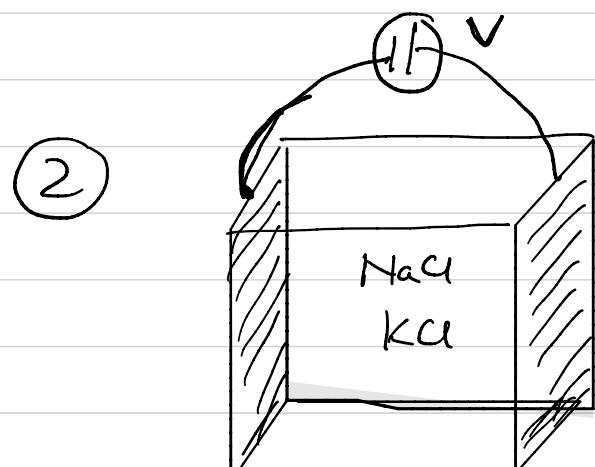
$\Rightarrow$  for diluted soln

### ③ Solubility of Slightly soluble ionic compound :-



ⓐ Saturated Solution of Slightly Soluble ionic compound is taken as infinitely diluted because concn of ions are almost zero.

$$1_m = 1_m^\circ = x \cdot 1_m^\circ (\text{A}^{+y}) + y \cdot 1_m^\circ (\text{B}^{-x})$$



$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

$$C = C_1 + C_2$$

$$C_{soln} = C_{KCl} + C_{NaCl} + C_{H_2O}$$

$$C_{H_2O} \approx 0$$

$$C_{soln} = C_{KCl} + C_{NaCl}$$

# For Slightly soluble compound

$$C_{soln} = C_{A_{x,y}B_y} + C_{H_2O}$$

$$K_{soln} = K_{A_{x,y}B_y} + K_{H_2O}$$

$$\Rightarrow K_{A_{x,y}B_y} = K_{soln} - K_{H_2O}$$

#  $1_m = K \times \frac{1000}{(S)}$

$$1_m^\circ = K_{A_{x,y}B_y} \times \frac{1000}{(S)}$$

↑

## 5. SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably right and compact and its voltage should not vary appreciably during the use.

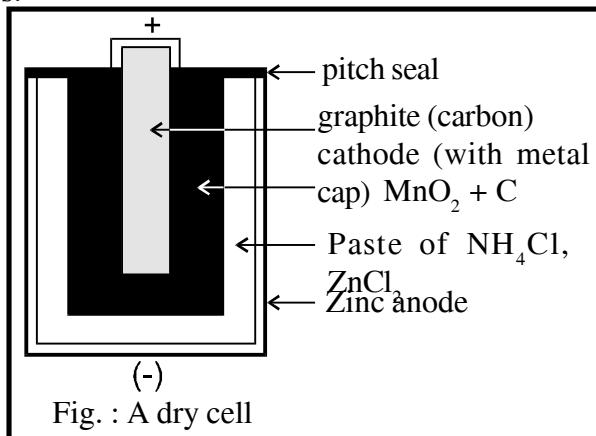
There are mainly two types of cells :

(i) primary cells and (ii) secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again.(For example, lead storage battery, nickel- cadmium storage cell.)

### 5.1 Primary Batteries

#### 5.1.1 Dry cell or Leclanche cell :

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.) : In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered  $\text{MnO}_2$  and carbon. The space between the electrodes is filled with a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ . The electrode reactions are complex, but they can be written approximately as follows.

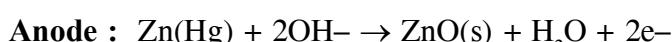


- **Anode**  $\text{Zn(s)} \longrightarrow \text{Zn}^{+2} + 2\text{e}^-$
- **Cathode**  $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \longrightarrow \text{MnO(OH)} + \text{NH}_3$

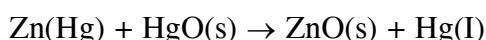
In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with  $\text{Zn}^{2+}$  to form  $\text{Zn}(\text{NH}_3)_4^{2+}$  ion. The cell has a potential of nearly 1.5 V.

#### 5.1.2 Mercury cell :

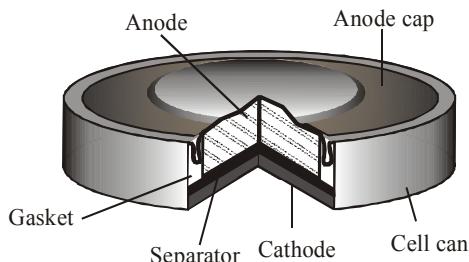
Mercury cell, suitable for low current devices like hearing aids, watches, etc. consists of zinc & mercury amalgam as anode and a paste of  $\text{HgO}$  and carbon as the cathode. The electrolyte is a paste of  $\text{KOH}$  and  $\text{ZnO}$ . The electrode reactions for the cell are given below:



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.



Commonly used mercury cell.

The reducing agent is zinc and the oxidising agent is mercury (II) oxide.

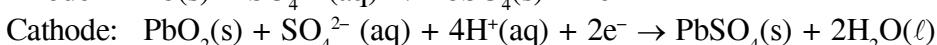
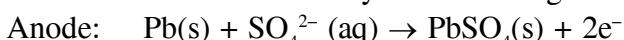
## 5.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

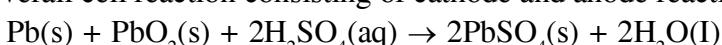
### 5.2.1 Lead storage cell :

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide ( $\text{PbO}_2$ ) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

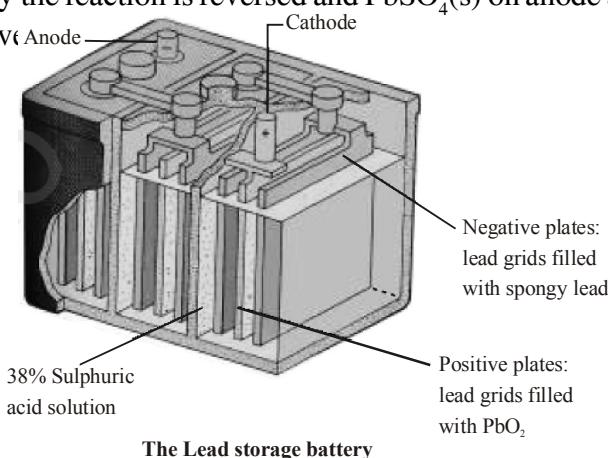
The cell reactions when the battery is in use are given below:



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

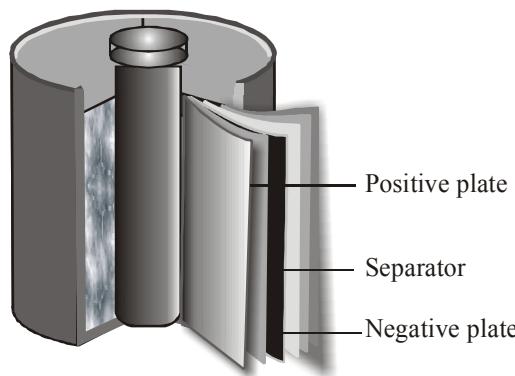


On charging the battery the reaction is reversed and  $\text{PbSO}_4(\text{s})$  on anode and cathode is converted into Pb and  $\text{PbO}_2$ , respectively.



### 5.2.2 Nickel-cadmium cell :

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

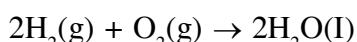


### 5.3 FUEL CELLS

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

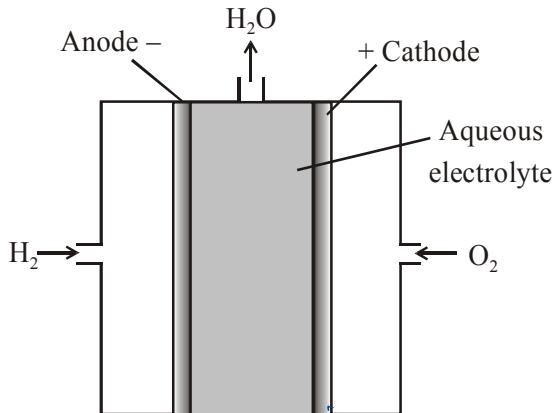


Overall reaction being:



The cell runs continuously as long as the reactions are supplied. Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental

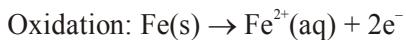
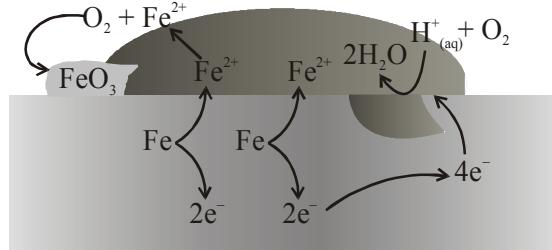
basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.



Fuel cell using  $\text{H}_2$  and  $\text{O}_2$  produces electricity

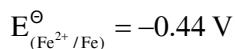
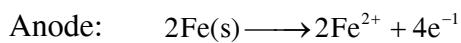
## 6. CORROSION :

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction

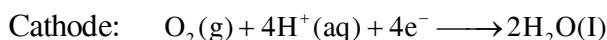


Atmospheric

### Corrosion of iron in atmosphere

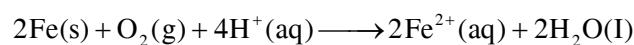


Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of  $\text{H}^+$  (which is believed to be available from  $\text{H}_2\text{CO}_3$  formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction



$E_{H^+|O_2|H_2O} = 1.23 \text{ V}$

The overall reaction being:

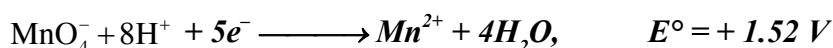


$E_{\text{cell}}^\ominus = 1.67 \text{ V}$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ( $Fe_2O_3 \cdot xH_2O$ ) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.). Which corrodes itself but saves the object.

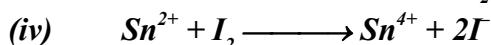
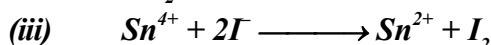
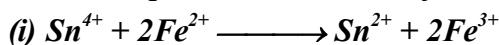
**Ex.1**  $E^\ominus$  of some oxidants are given as :



(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below.



**Sol.** (a) More the  $E^\ominus_{OP}$ , more is the tendency for oxidation. Therefore, since maximum  $E^\ominus_{OP}$  stands for :



$\therefore$  Strongest reductant :  $Sn^{2+}$

and weakest oxidant :  $Sn^{4+}$

(b) More +ve is  $E^\ominus_{RP}$ , more is the tendency for reduction. Therefore, since maximum  $E^\ominus_{RP}$  stands for :



$\therefore$  Strongest oxidant :  $MnO_4^-$

and weakest reductant :  $Mn^{2+}$

**Note :-** Stronger is oxidant, weaker is its conjugate reducant and vice-versa.

(c) For (i)  $E^\ominus_{\text{Cell}} = E^\ominus_{OP_{Fe^{2+}/Fe^{3+}}} + E^\ominus_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1$

$Fe^{2+}$  oxidizes and  $Sn^{4+}$  reduces in change.

# ELECTRO- THEORY -ENG

At 25°C, the molar conductance at infinite dilution for HCl solution is  $4.25 \times 10^{-2} \Omega^{-1} \text{m}^2 \text{mol}^{-1}$ , while its specific conductance is  $382.5 \Omega^{-1} \text{m}^{-1}$ . If the degree of dissociation is 90%, the molarity of solution is

- (a) 0.9 M
- (b) 1.0 M
- (c) ~~0.1 M~~  $\Rightarrow$  10 M
- (d) 1.1 M

Ans: C

A big irregular shaped vessel contained water, conductivity of which was  $2.56 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1}$ . 585 g of NaCl was then added to the water and conductivity after the addition of NaCl, was found to be  $3.06 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1}$ . The molar conductivity of NaCl at this concentration is  $1.5 \times 10^{-2} \text{ S}^{-1} \text{m}^2 \text{mol}^{-1}$ . The capacity of vessel if it is fulfilled with water, is

- (a)  $3 \times 10^4 \text{ l}$
- (b) 30 l
- (c)  $3 \times 10^8 \text{ l}$
- (d)  $3 \times 10^5 \text{ l}$

Ans: d

The conductivity of saturated solution of  $\text{Ba}_3(\text{PO}_4)_2$  is  $1.2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ . The limiting equivalent conductivities of  $\text{BaCl}_2$ ,  $\text{K}_3\text{PO}_4$  and  $\text{KCl}$  are 160, 140 and  $100 \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$ , respectively. The solubility product of  $\text{Ba}_3(\text{PO}_4)_2$  is

- (a)  $10^{-5}$
- (b)  $1.08 \times 10^{-23}$
- (c)  $1.08 \times 10^{-25}$
- (d)  $1.08 \times 10^{-27}$

$$\Lambda_m = \frac{382.5}{1000 \times M}$$

$$0.9 = \frac{\Lambda_m}{\Lambda_m^\circ} \Rightarrow \Lambda_m = 0.9 \times 4.25 \times 10^{-2}$$

$$M = \frac{382.5}{1000 \times 0.9 \times 4.25 \times 10^{-2}} = 10 \text{ mol/l}$$

$$\begin{aligned} K_{\text{H}_2\text{O}} &= 2.56 \times 10^{-3} \text{ S}^{-1} \text{m}^{-1} \\ K_{\text{Solv}}(\text{NaCl}) &= 3.06 \times 10^{-3} = K_{\text{NaCl}} + K_{\text{H}_2\text{O}} \\ \Rightarrow K_{\text{NaCl}} &= (3.06 - 2.56) \times 10^{-3} \\ &= 5 \times 10^{-4} \text{ S}^{-1} \text{m}^{-1} \end{aligned}$$

$$\begin{aligned} \Lambda_m &= \frac{k \times 1}{1000 M} \\ 1.8 \times 10^{-2} &= 8 \times 10^{-4} \times \frac{1}{1000 M} \\ 3 \times 10^{-4} &= \frac{1}{M} = \frac{V(l)}{10} \\ V(l) &= 3 \times 10^5 \text{ lit} \end{aligned}$$

$$\begin{aligned} \Lambda_m^\circ [\text{Ba}_3(\text{PO}_4)_2] &= \Lambda_{\text{eq}}^\circ (\text{Ba}^{2+}) \\ &\quad + \Lambda_{\text{eq}}^\circ (\text{PO}_4^{3-}) \\ &= 160 + 140 - 100 = 200 \end{aligned}$$

$$\begin{aligned} \Lambda_m [\text{Ba}_3(\text{PO}_4)_2] &= 200 \times 6 \\ &= 1.2 \times 10^{-5} \times \frac{1000}{(S)} \end{aligned}$$

$$(S) = 10^{-5} \text{ M}$$

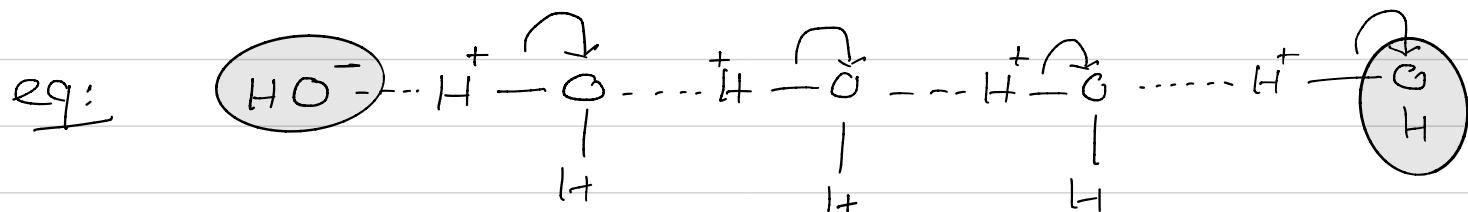
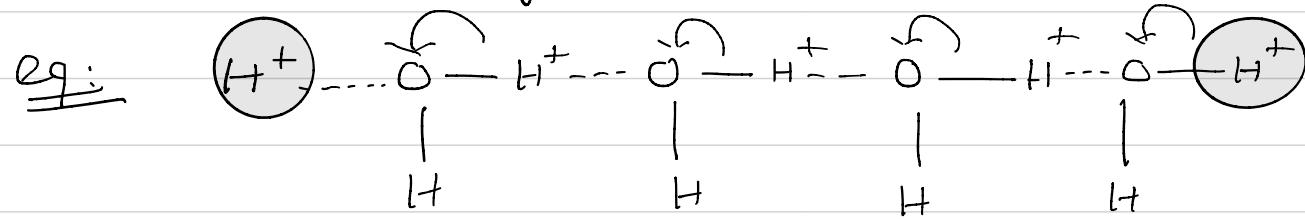
$$\begin{aligned} K_{\text{SP}} &= 3^3 \times 2^2 (S)^{3+2} \\ &= 108 \times 10^{-25} \\ &= 1.08 \times 10^{-23} \text{ M} \end{aligned}$$

Ans: b

## Conductometric titration :-

Conductometric titration :- Measurement of eq pt by calculating conductance of soln is called conductometric titration.  
It is more accurate than indicator based titration.

# grotthuss type of conduction

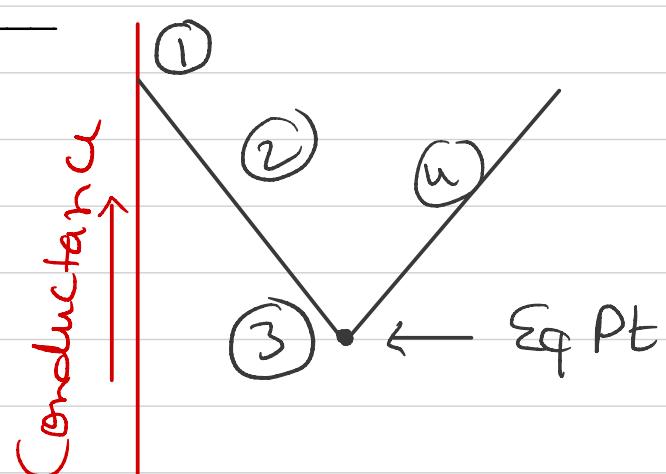
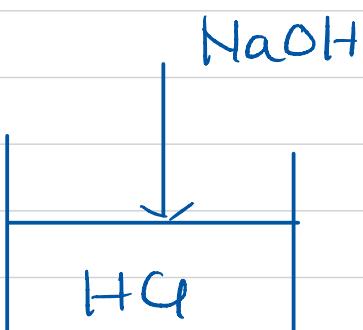


H<sup>+</sup> / OH<sup>-</sup> have higher conductance value compare to other ions.

Conductance value of ions do not affect due to dilution during titration.

Example of Conductometric titration :-

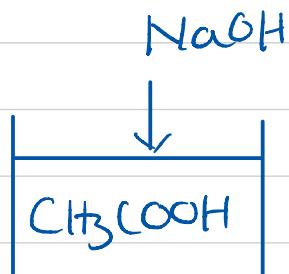
① titration of HCl Using NaOH :-



V<sub>NaOH</sub>

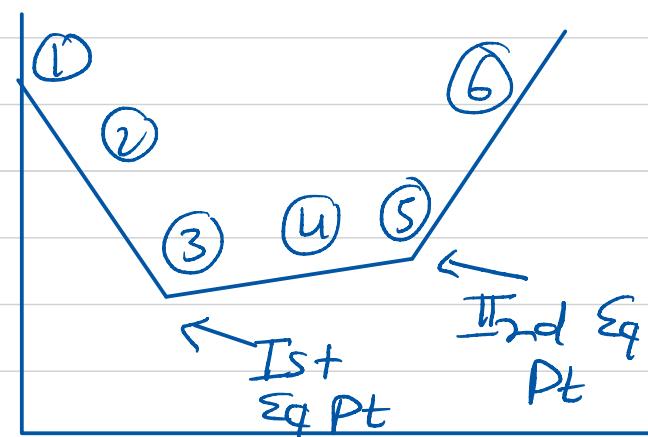
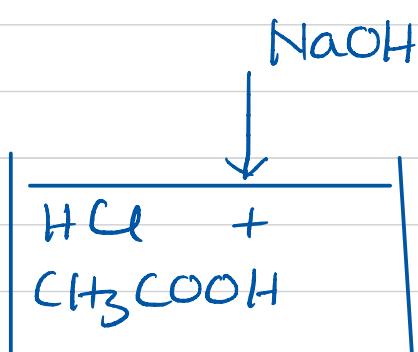
- ① HCl
- ② HCl + NaCl
- ③ NaCl
- ④ NaCl + NaOH

## ② titration of $\text{CH}_3\text{COOH}$ with $\text{NaOH}$ :-



- ①  $\text{CH}_3\text{COOH}$
- ②  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- ③  $\text{CH}_3\text{COONa}$
- ④  $\text{CH}_3\text{COONa} + \text{NaOH}$

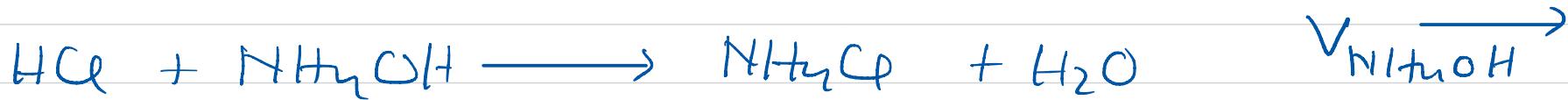
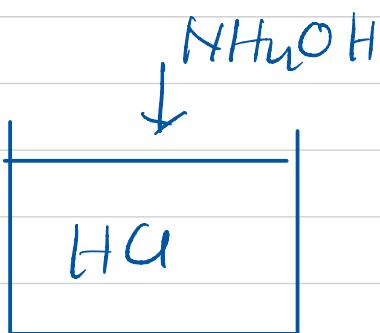
## ③ Titration of mix of ( $\text{HCl} + \text{CH}_3\text{COOH}$ ) with $\text{NaOH}$ :-



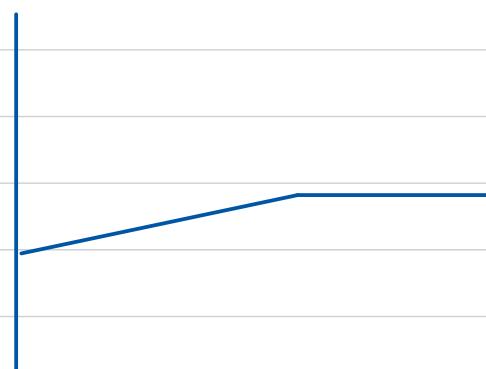
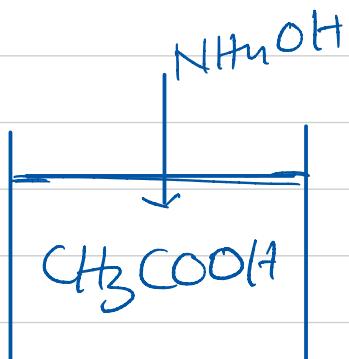
$\rightarrow \text{V}_{\text{NaOH}}$

- ①  $\text{HCl} + \text{CH}_3\text{COOH}$
- ②  $\text{HCl} + \text{NaCl} + \text{CH}_3\text{COOH}$
- ③  $\text{NaCl} + \text{CH}_3\text{COOH}$
- ④  $\text{NaCl} + \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- ⑤  $\text{NaCl} + \text{CH}_3\text{COONa}$
- ⑥  $\text{NaCl} + \text{CH}_3\text{COONa} + \text{NaOH}$

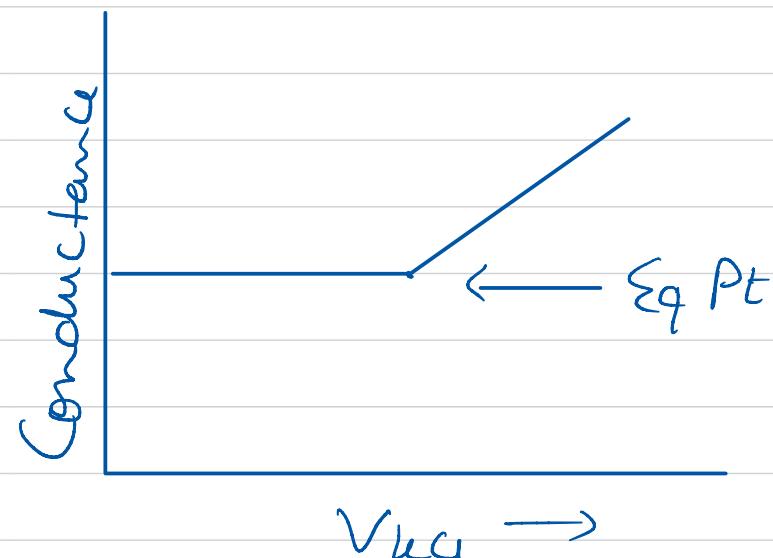
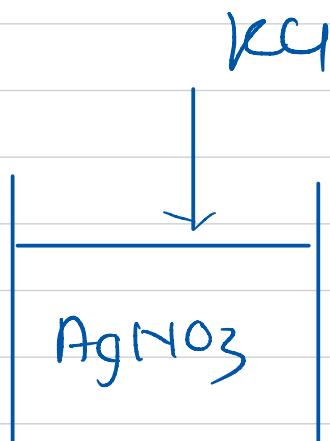
④ titration of HCl Using NH<sub>2</sub>OH :-



⑤ titration of CH<sub>3</sub>COOH using NH<sub>2</sub>OH :-



⑥ titration of AgNO<sub>3</sub> with KCl :-  $C_{\text{Ag}^+} = C_{\text{K}^+}$



6. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List-I. The variation in conductivity of these reactions is given in List-II. Match List-I with List-II and select the correct answer using the code given below the lists : **[JEE-Adv. 2013]**

**List-I**

- (P)  $(C_2H_5)_3N + CH_3COOH$  (1)  
 X            Y
- (Q)  $KI(0.1M) + AgNO_3(0.01M)$  (2)  
 X            Y
- (R)  $CH_3COOH + KOH$  (3)  
 X            Y
- (S)  $NaOH + HI$  (4)  
 X            Y

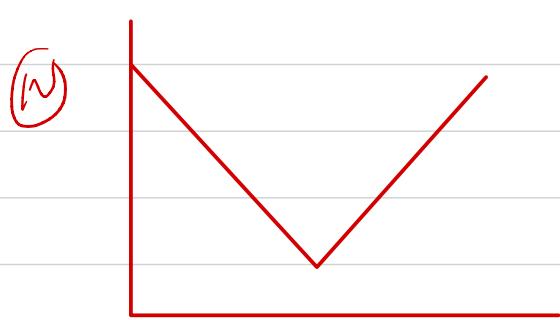
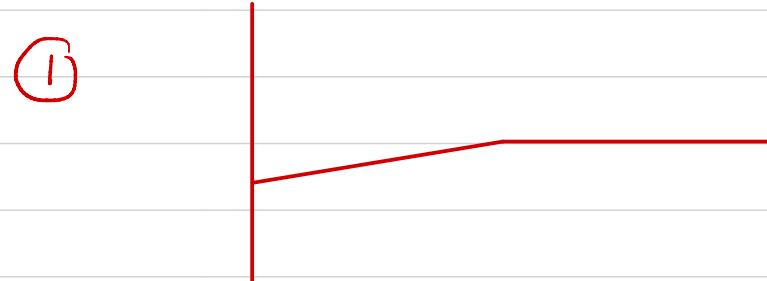
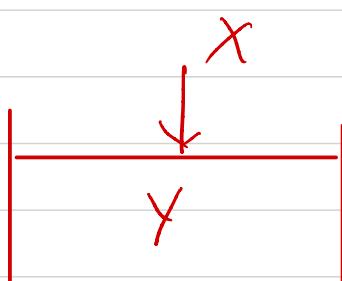
**List-II**

- Conductivity decreases and then increases
- Conductivity decreases and then does not change much
- Conductivity increases and then does not change much
- Conductivity does not change much and then increases

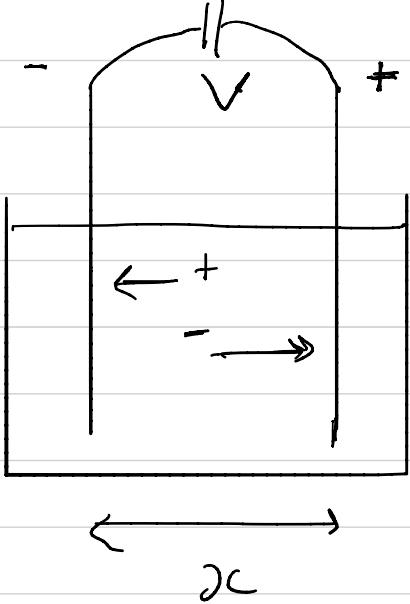
**Codes :**

	P	Q	R	S
(A)	3	4	2	1
(C)	2	3	4	1

	P	Q	R	S
(B)	4	3	2	1
(D)	1	4	3	2



## Ionic mobility ( $\mu$ ) :-



Speed of ions under unit potential gradient is called as ionic mobility ( $\mu$ ).

$$\mu = \frac{V}{\left(\frac{V}{d}\right)}$$

Where  $V$  = Speed of ion

$V$  = Potential diff

$d$  = distance b/w electrode

$\mu$  = ionic mobility

$\lambda_m \propto \mu$

Where

$$\lambda_m = Z F \mu$$

$Z$  = Charge on ion

$F$  = Faraday

# Electrochemistry TOL\_TOV 21-22(6)