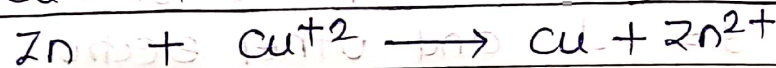
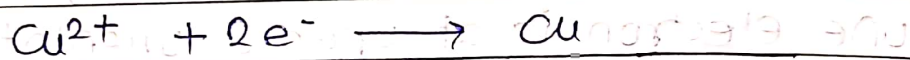
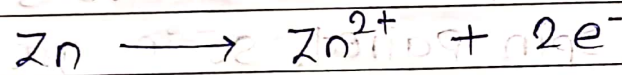


## 5. Electromotive Force.

15 02 2025  
D D M M Y Y Y Y

If electrical energy is converted into chemical energy is called electrolysis, electrochemical cell. If chemical energy is converted into electrical energy is called electrochemical.

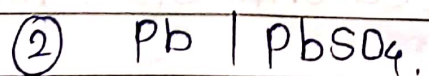
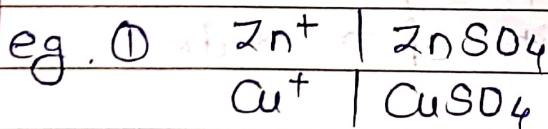
	Oxidation	Reduction
Organic	+ O <sub>2</sub>	+ H <sub>2</sub>
Inorganic	↑ charge	↓ charge
physical	Loss of electron	Gain of electron



### IUPAC Rwe for cell representation.

1) Oxidation is always occurs on anode and hence it is right on - extern left on side, and cathod is represent extern right hand side.

2) Single vertical line (|) shows phase boundary within half cell.

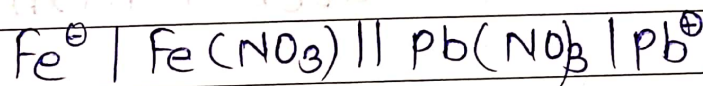
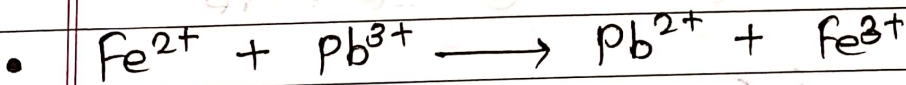
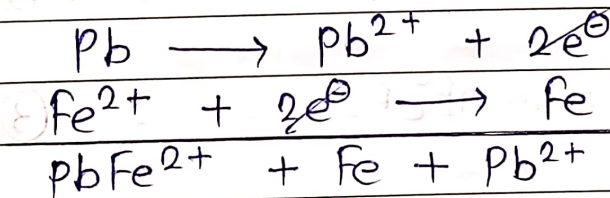
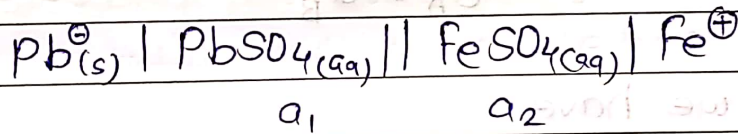
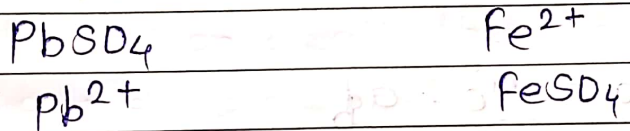
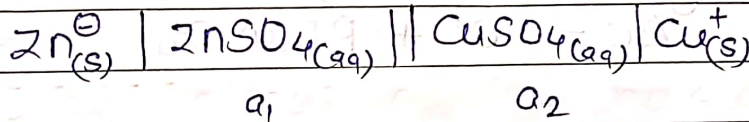
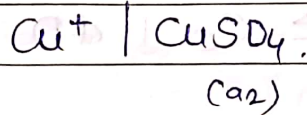
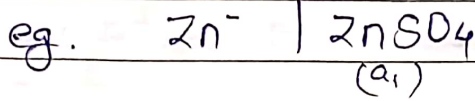


3) Double vertical line shows (||) salt bridge porous partition or liq. liq. junction.

Pure metal is 1  $E_{cell} = E_p - E_L$



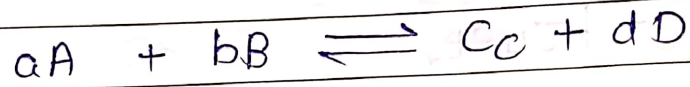
4) Activity or concentration of a solution shows at the bottom.



$\Delta G = -W_{max}$

$\Delta G = -nE_{cell}$  ①

\* 4 marks EMF of the cell and activity.  
 Consider a reversible cell for which overall reaction as follow.



According to thermodynamics.  
 $\Delta G = \Delta G^\circ + RT \ln Q_a$  ----- ①

Reaction  $Q_a$  of above reaction.

$$Q_a = \frac{a_c^c \cdot a_d^d}{a_A^a \cdot a_B^b}$$

But we have.

$$\Delta G = -nE_c F$$
 ----- ②

$$\Delta G = -nE_c^\circ F$$
 ----- ③

from eq<sup>n</sup> ① ② and ③ we have.

$$-nE_c F = -nE_c^\circ F + RT \ln Q_a$$

dividing through out by  $-nf$

$$E_c = E_c^\circ - \frac{RT}{nF} \cdot \ln Q_a$$

$$E_c = E_c^\circ - \frac{2.303 RT}{nF} \log Q_a$$
 ----- ④

At standard temp. eq<sup>n</sup> (4) becomes.

$$E_c = E_c^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96485} \log Q_a$$

$$E_c = E_c^\circ = - \frac{0.0591}{n} \log Q_a \quad (5)$$

$$E_c = E_c^\circ - \frac{0.0591}{n} \log \frac{a_c^c \cdot a_b^d}{a_A^a \cdot a_B^b} \quad (6)$$

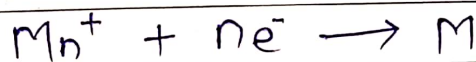
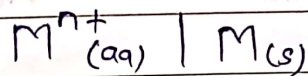
### \* Types of electrode-

#### 1) Metal-metal ion electrode-

Metal-metal ion electrode consist of pure metal M in contact with the solution it's own ion ( $M^{n+}$ )

eg. Zn in  $ZnSO_4$ , Cu in  $CuSO_4$ .

Metal metal electrode :

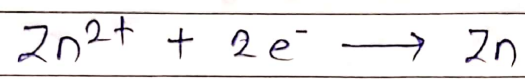
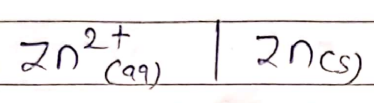


$$Q_a = \frac{a_M}{a_{M^{n+}}} = \frac{1}{a_{M^{n+}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>.

$$E_M = E_M^\circ - \frac{2.303RT}{nF} \log \frac{1}{a_{M^{n+}}}$$

eg. ① Zn - Zn ion electrode

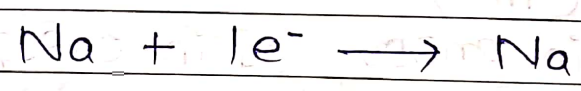


$$Q_a = \frac{1}{a_{\text{Zn}^{2+}}}$$

Nutt's eq<sup>n</sup> of above eq<sup>n</sup>.

$$E_{\text{Zn}} = E_{\text{Zn}}^{\circ} - \frac{2.303 RT}{2F} \log \frac{1}{a_{\text{Zn}^{2+}}}$$

eg. ② Na<sup>+</sup> NaCl electrode

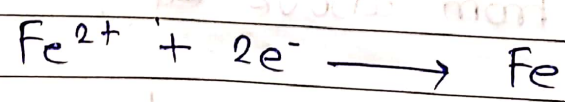


$$Q_a = \frac{a_{\text{Na}}}{a_{\text{Na}^+}} = \frac{1}{a_{\text{Na}^+}}$$

Nutt's eq<sup>n</sup> from above equation.

$$\therefore E_{\text{Na}} = E_{\text{Na}}^{\circ} - \frac{2.303 RT}{1F} \log \frac{1}{a_{\text{Na}^+}}$$

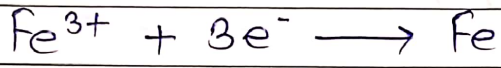
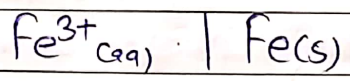
eg. ③ Fe<sup>2+</sup> Fe electrode



$$Q_a = \frac{a_{Fe}}{a_{Fe^{2+}}} = \frac{1}{a_{Fe^{2+}}}$$

Nutt's eq<sup>n</sup> of above eq<sup>n</sup>

$$\therefore E_{Fe} = E_{Fe}^{\circ} - \frac{2.303RT}{2F} \log \frac{1}{a_{Fe^{2+}}}$$



$$Q_a = \frac{a_{Fe}}{a_{Fe^{3+}}} = \frac{1}{a_{Fe^{3+}}}$$

Nutt's eq<sup>n</sup> of above eq<sup>n</sup>.

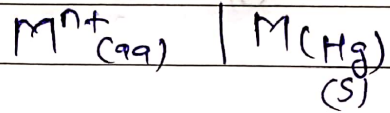
$$\therefore E_{Fe} = E_{Fe}^{\circ} - \frac{2.303RT}{3F} \log \frac{1}{a_{Fe^{3+}}}$$

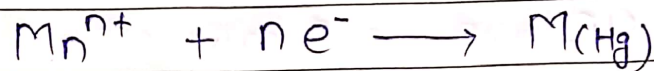
2) Metal - Amalgam

Statement :

A solution of metal in liquid mercury is an amalgam.  $M(Hg)$ . This electrode consist of an amalgam of metal M is in contact with solution containing it's own ion. i.e.  $M^{n+}$  ions.

General formula :





$$Q_a = \frac{a_{M(Hg)}}{a_{M^{n+}}}$$

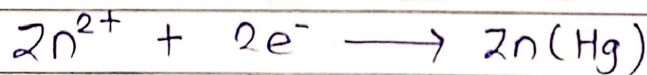
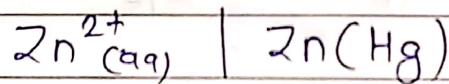
Nutt's eq<sup>n</sup> from above eq<sup>n</sup>.

$$E_{M(Hg)} = E_M^{\circ} - \frac{2.303RT}{nF} \log \frac{a_{M(Hg)}}{a_{M^{n+}}}$$

(Here  $a_{M(Hg)} \neq 1$ )

eg. ① Zn(Hg) electrode.

Where Zn(Hg) is dipped in sol<sup>n</sup> of ZnSO<sub>4</sub>

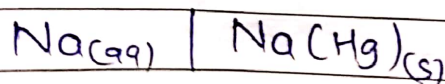


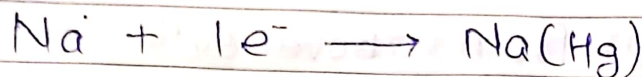
$$Q_a = \frac{a_{Zn(Hg)}}{a_{Zn^{2+}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{Zn(Hg)} = E_{Zn}^{\circ} - \frac{2.303RT}{2F} \log \frac{a_{Zn(Hg)}}{a_{Zn^{2+}}}$$

② Na(Hg) electrode is dipped in NaCl.



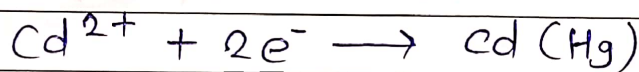
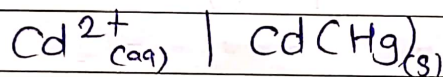


$$Q_a = \frac{a_{\text{Na(Hg)}}}{a_{\text{Na}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{\text{Na(Hg)}} = E_{\text{Na}}^{\circ} - 2.303 RT \log \frac{a_{\text{Na(Hg)}}}{a_{\text{Na}}}$$

Homework ①  $\text{Cd}^{2+} | \text{Cd(Hg)}$

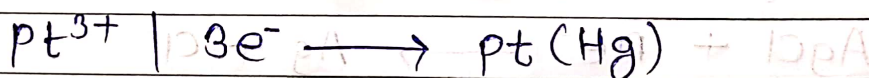


$$Q_a = \frac{a_{\text{Cd(Hg)}}}{a_{\text{Cd}^{2+}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{\text{Cd(Hg)}} = E_{\text{Cd}}^{\circ} - \frac{2.303 RT}{2F} \log \frac{a_{\text{Cd(Hg)}}}{a_{\text{Cd}^{2+}}}$$

②  $\text{Pt}^{3+} | \text{Pt(Hg)}$



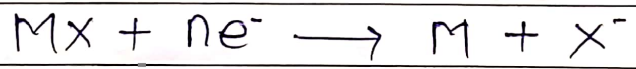
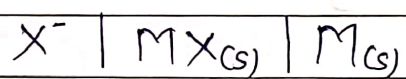
$$Q_a = \frac{a_{\text{Pt(Hg)}}}{a_{\text{Pt}^{3+}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{Pt(Hg)} = E_{Pt}^{\circ} - \frac{2.303 RT}{3F} \log \frac{a_{Pt(Hg)}}{a_{Pt}}$$

3. Metal insoluble salt electrode.

This electrode consists of metal M in contact with its sparingly soluble salt MX which in turn is in contact with solution containing X<sup>-</sup> ions. It is represented as,

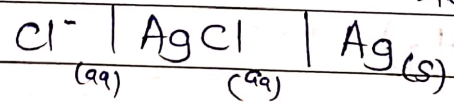


$$Q_a = \frac{a_M \cdot a_{X^{-}}}{a_{MX}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>.

$$E_c = E_c^{\circ} - \frac{2.303 RT}{F} \log a_{MX^{-}}$$

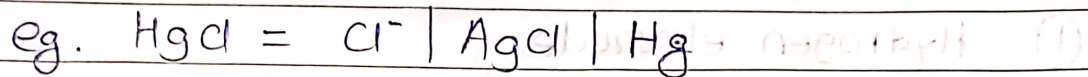
eg. ① Silver-silver chloride electrode. AgCl



$$Q_a = \frac{a_{Ag} \cdot a_{Cl^{-}}}{a_{AgCl}} = a_{Cl^{-}}$$

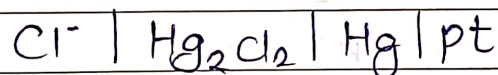
So Nutt's eq<sup>n</sup> from above eq<sup>n</sup>.

$$E_{Ag-AgCl} = E_{Ag}^{\circ} - \frac{2.303RT}{F} \log a_{Cl^{-}}$$



In this electrode pure mercury is converted by best of calomer ( $Hg + Hg_2Cl_2$ ) is in contact with in aqueous solution of KCl either it is 0.1 M, 1 M OR saturated when the saturated KCl is used then it is called saturated calomer electrode (SCE)

Here the Pt is used for make electrical current.



$$Q_a = \frac{a_{Hg}^2 \cdot a_{Cl^{-}^2}}{a_{Hg_2Cl_2}} = a_{Cl^{-}^2}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>.

$$E_{Hg-Hg_2Cl_2} = E_{Hg}^{\circ} - \frac{2.303RT}{2F} \log a_{Cl^{-}^2}$$

4) Gas electrode :

In this gas electrode gas in a contact with the solution of its own electrode in

H, Cl, O

SHE = 0.0V

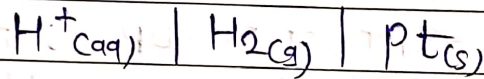


in presence of an inert metal, inert metal facilitates the rapid equilibrium gas and its ion and serves to make electric contact inert metal is usually used Pt.

① Hydrogen electrode.

VIMP

In this sol<sup>n</sup> bubbled at suitable pressure over Pt wire in the solution of HCl or H<sub>2</sub>SO<sub>4</sub> or (strong acid)



$$Q_a = \frac{a_{H_2}^{\frac{1}{2}}}{a_{H^+}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{H_2} = E_{H_2}^{\circ} - \frac{2.303 RT}{F} \log \frac{a_{H_2}^{\frac{1}{2}}}{a_{H^+}}$$

$$E_{H_2} = - \frac{2.303 RT}{F} \log \frac{1}{a_{H^+}} \left( \because E_{H_2}^{\circ} = 0.0V \right)$$

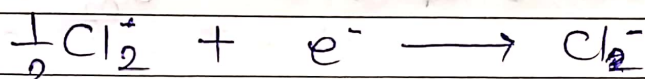
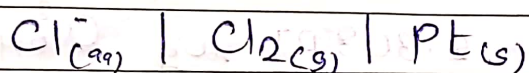
$$E_{H_2} = - \frac{2.303 RT}{F} \text{pH}$$

At 298 K and 1 bar atm. pressure above eq<sup>n</sup> is.

$$E_{H_2}^{\circ} = -0.0591 \text{ pH}$$

② Chlorine gas electrode.

Here  $\text{Cl}_2$  gas is bubbled at suitable pressure over Pt wire in immersed into solution.



$$Q_a = \frac{a_{\text{Cl}^-}}{a_{\text{Cl}_2}^{1/2}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_{\text{Cl}_2} = E_{\text{Cl}_2}^{\circ} - \frac{2.303RT}{F} \log \frac{a_{\text{Cl}^-}}{a_{\text{Cl}_2}^{1/2}}$$

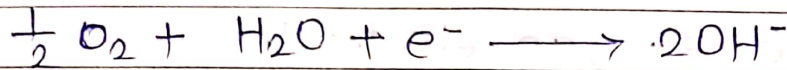
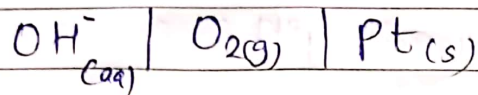
At 298 K and 1 bar atm. pressure above eq<sup>n</sup> is

$$E_{\text{Cl}_2} = E_{\text{Cl}_2}^{\circ} - 2.303RT$$

③ Oxygen gas electrode.

Here  $\text{O}_2$  gas is bubbled with suitable pressure in platinum is immersed in alkali solution.

$$\frac{1}{a_{H^+}} \cdot \frac{a_{Cl^-}}{1} \cdot \frac{a_{OH^-}^2}{1}$$



$$Q_a = \frac{a_{OH^-}^2}{a_{O_2}^{1/2} \cdot a_{H_2O}}$$

$$E_{O_2} = E_{O_2}^\circ - \frac{2.303 RT}{F} \log \frac{a_{OH^-}^2}{a_{O_2}^{1/2} \cdot a_{H_2O}}$$

activity of  $H_2O$  molecule is 1

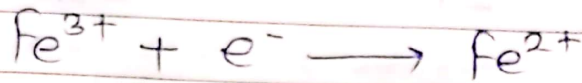
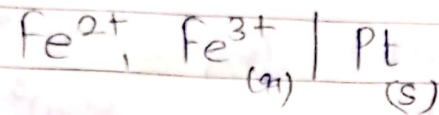
$$E_{O_2} = E_{O_2}^\circ - \frac{2.303 RT}{F} \log \frac{a_{OH^-}^2}{a_{O_2}^{1/2}} \quad (\because \text{Activity of } H_2O \text{ is } 1)$$

### 5. Redox electrode:

An inert metal like Pt dips in sol<sup>n</sup> of containing ion or the same type but in the different oxidation state.  
inert metal

EMF of electrode is arises due to the tendency of a ions to pass from state an to other and it is depends on ratio of activities of the ions.

eg. ferrous to ferric ion electrode. and Pt is imersed in a sol<sup>n</sup> containing ferrous ( $Fe_2 Fe^{2+}$ ) and ferric ( $Fe^{3+}$ )

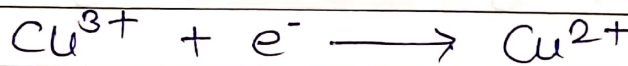
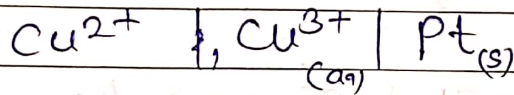


$$Q_a = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}$$

Nutt's eq<sup>n</sup> from above eq<sup>n</sup>

$$E_c = E_c^\circ - \frac{2.303RT}{f} \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}$$

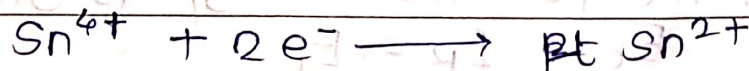
② eg. cupric to cuprous ion de. electrode and Pt is immersed



$$Q_a = \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^{3+}}}$$

$$E_c = E_c^\circ - \frac{2.303RT}{f} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^{3+}}}$$

③  $\text{Sn}^{2+}, \text{Sn}^{4+} \mid \text{Pt}$

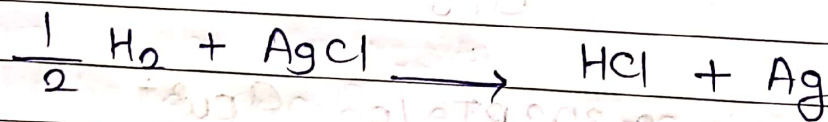
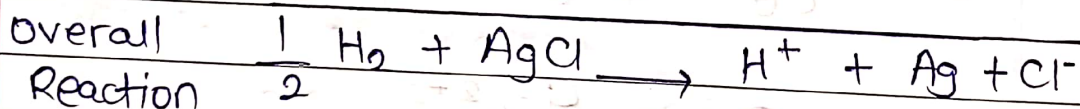
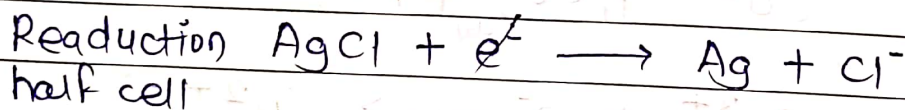
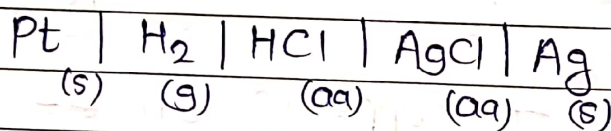


$$Q_a = \frac{a_{\text{Sn}^{2+}}}{a_{\text{Sn}^{4+}}}$$

$$E_c = E_c^\circ - \frac{2.303RT}{2F} \log \frac{a_{Sn^{2+}}}{a_{Sn^{4+}}}$$

\* Chemical cell without transference.

Chemical cell without transference can be constructed by selecting such two electrodes and electrolyte such that one of the electrode is reversible to cation and another electrode is reversible to anion, consider a cell.



$$Q_a = \frac{a_{\text{HCl}} \cdot a_{\text{Ag}}}{a_{\text{H}_2}^{1/2} \cdot a_{\text{AgCl}}}$$

So, the potential energy is given as,  
 $E_c = E_R - E_L$

$$E_c = (E_{\text{AgCl} - \text{Ag}} - E_{\text{H}_2})$$

$$E_c = \left( E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \log a_{\text{Cl}^-} \right) \quad \text{--- (2)}$$

$$E_{\text{H}_2} = E_{\text{H}_2}^{\circ} - \frac{2.303RT}{F} \log \frac{P_{\text{H}_2}^{1/2}}{a_{\text{H}^+}}$$

$$E_c = \left( E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \log a_{\text{Cl}^-} \right) -$$

$$\left( E_{\text{H}_2} = E_{\text{H}_2}^{\circ} - \frac{2.303RT}{F} \log \frac{P_{\text{H}_2}^{1/2}}{a_{\text{H}^+}} \right)$$

$$E_c = \left( E_{\text{Ag-AgCl}}^{\circ} - E_{\text{H}_2}^{\circ} \right) - \frac{2.303RT}{F} \left( \log a_{\text{Cl}^-} - \log \frac{P_{\text{H}_2}^{1/2}}{a_{\text{H}^+}} \right)$$

$$E_c = E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \left( \log a_{\text{Cl}^-} + \log \frac{a_{\text{H}^+}}{P_{\text{H}_2}^{1/2}} \right)$$

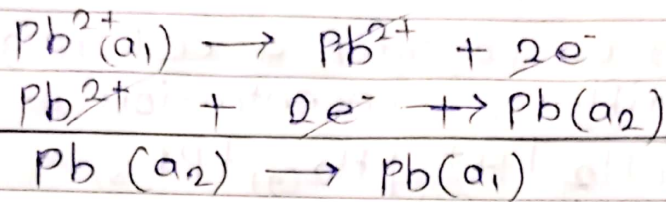
$$E_c = E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \left( \log a_{\text{Cl}^-} + \log \frac{a_{\text{H}^+}}{P_{\text{H}_2}^{1/2}} \right)$$

$$E_c = E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \log \frac{a_{\text{HCl}}}{P_{\text{H}_2}^{1/2}} \quad \text{--- (4)}$$

at 1 bar atmosphere pressure

$$E_c = E_{\text{Ag-AgCl}}^{\circ} - \frac{2.303RT}{F} \log a_{\text{HCl}} \quad \text{--- (5)}$$





The overall of the cell is given as

$$E_c = E_R - E_L$$

$$E_c = \left( E_{\text{Pb}^{2+}/\text{Pb}}^\circ - \frac{2.303RT}{2F} \log \frac{a_2}{a_{\text{Pb}^{2+}}} \right) - \left( E_{\text{Pb}^{2+}/\text{Pb}}^\circ - \frac{2.303RT}{2F} \log \frac{a_1}{a_{\text{Pb}^{2+}}} \right)$$

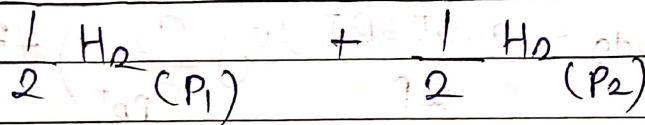
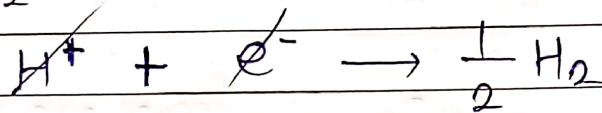
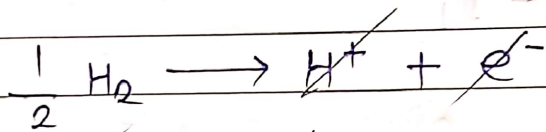
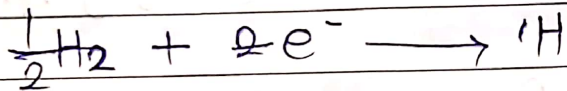
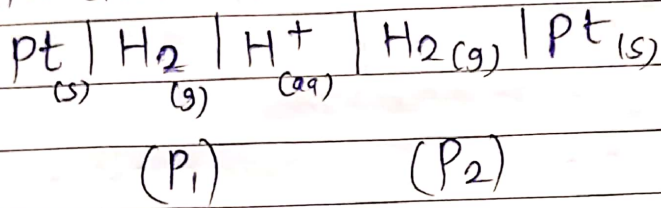
$$E_c = - \frac{2.303RT}{2F} \left( \log \frac{a_2}{a_{\text{Pb}^{2+}}} - \log \frac{a_1}{a_{\text{Pb}^{2+}}} \right)$$

$$E_c = - \frac{2.303RT}{2F} \log \frac{a_2}{a_1} \left( \frac{a_2}{a_{\text{Pb}^{2+}}} \times \frac{a_{\text{Pb}^{2+}}}{a_1} \right) \frac{a_2}{a_1}$$

$$E_c = \frac{2.303RT}{2F} \log \frac{a_1}{a_2}$$

Gas electrode reversible to cation

Let us consider a cell H<sub>2</sub> gas electrodes with different concentration or pressure



$$E_c = E_R - E_L$$

$$E_c = \left( E_{\text{H}_2}^\circ - \frac{2.303RT}{f} \log \frac{P_2^{1/2}}{a_{\text{H}^+}} \right) - \left( E_{\text{H}_2}^\circ - \frac{2.303RT}{f} \log \frac{P_1^{1/2}}{a_{\text{H}^+}} \right)$$

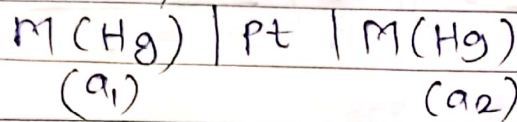
$$E_c = \frac{2.303RT}{f} \log \frac{P_2^{1/2}}{a_{\text{H}^+}} + \frac{2.303RT}{f} \log \frac{P_1^{1/2}}{a_{\text{H}^+}}$$

$$E_c = \frac{2.303RT}{f} \left( \log \frac{P_2^{1/2}}{a_{\text{H}^+}} - \log \frac{P_1^{1/2}}{a_{\text{H}^+}} \right) = \frac{2.303RT}{f} \log \frac{P_2^{1/2}}{P_1^{1/2}}$$

$$E_c = \frac{2.303RT}{f} \log \left( \frac{P_2}{P_1} \right)^{1/2} = \frac{2.303RT}{f} \left( \frac{1}{2} \right) \log \frac{P_1}{P_2}$$

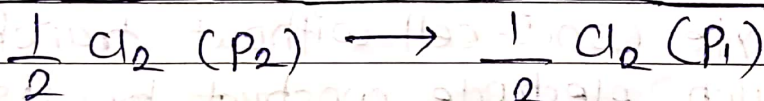
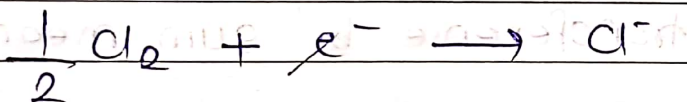
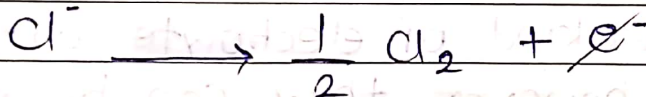
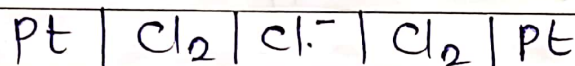
$$= \frac{2.303RT}{2F} \log \frac{P_1}{P_2}$$

In general,



b) <sup>reversible</sup> Electrode concentration cell to anion

Let us consider a cell with two chlorine gas electrode having different



$$E_c = E_R - E_L$$

$$E_c = \left( E_{\text{Cl}_2}^\circ - \frac{2.303RT}{2F} \log P_2^{1/2} \right) - \left( E_{\text{Cl}_2}^\circ - \frac{2.303RT}{2F} \log \frac{P_1^{1/2}}{P_2^{1/2}} \right)$$

$$E_c = \frac{2.303RT}{2F} \log \frac{P_2^{1/2}}{P_1^{1/2}} + \frac{2.303RT}{2F} \log \frac{P_1^{1/2}}{P_2^{1/2}}$$

$$E_c = \frac{2.303RT}{2F} \log \frac{P_2^{1/2}}{P_1^{1/2}} + \frac{2.303RT}{2F} \log \frac{P_1^{1/2}}{P_2^{1/2}}$$

$$\frac{1}{2} E_c = \frac{2.303RT}{2F} \log \left( \frac{P_2}{P_1} \right)^{1/2} = \frac{2.303RT}{2F} \left( \frac{1}{2} \right) \log \frac{P_1}{P_2}$$

$$E_c = - \frac{2.303RT}{F} \log \frac{P_1}{P_2}$$

$$E_c = \frac{2.303RT}{F} \log \frac{P_2}{P_1}$$

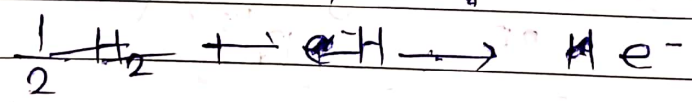
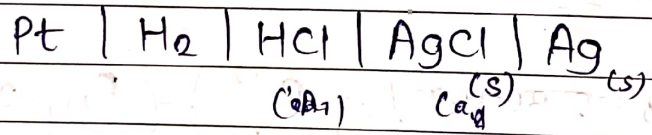
VIMP

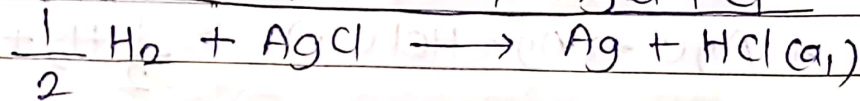
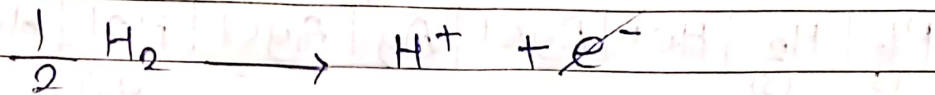
Electrolyte cocentration cell

These kind of electrolyte are with transference however they can be made without transference by sum means.

a) Electrolyte conc<sup>n</sup> cell without transference - such electrode construct by using two cell without transference

Cell I:



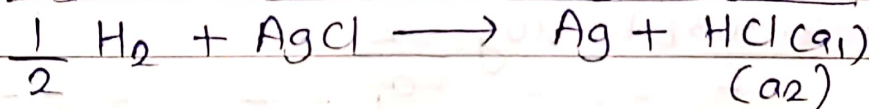
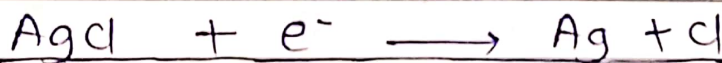
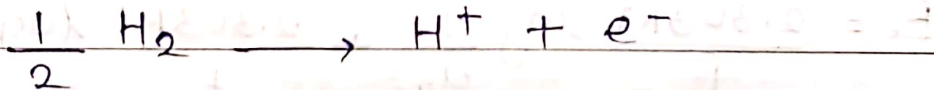


Nutt's eq<sup>n</sup> for above reaction

$$E_{c_1} = E_{c_1}^\circ - \frac{2.303RT}{F} \log a_{\text{HCl}}$$

$$E_{c_1} = E_{c_1}^\circ - \frac{2.303RT}{F} \log a_1 \quad \text{--- (1)}$$

Cell II :

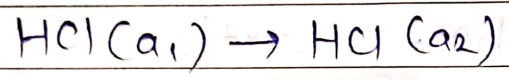
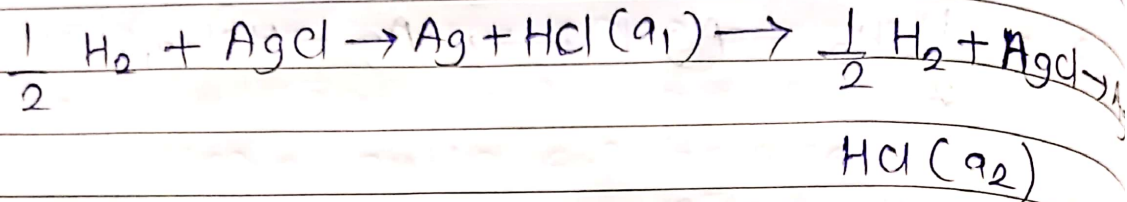
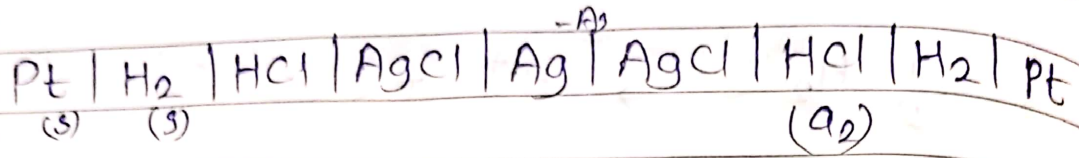


Nutt's eq<sup>n</sup> for above eq<sup>n</sup>

$$E_{c_2} = E_{c_2}^\circ - \frac{2.303RT}{F} \log a_{\text{HCl}}$$

$$E_{c_2} = E_{c_2}^\circ - \frac{2.303RT}{F} \log a_2 \quad \text{--- (2)}$$

Now join these two cell through Ag-Ag electrode then we have



$$E_c = E_{c_1} - E_{c_2} \quad \text{--- (3)}$$

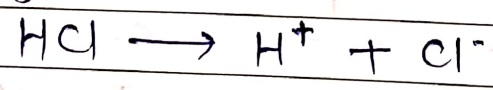
From eq<sup>n</sup> ① ② and ③

$$E_c = E_{c_1} - \frac{2.303RT}{F} \log a_1 - E_{c_2} \left( - \frac{2.303RT}{F} \log a_2 \right)$$

$$E_c = \frac{2.303RT}{F} \log \frac{1}{a_1} + \frac{2.303RT}{F} \log a_2$$

$$E_c = \frac{2.303RT}{F} \log \frac{a_2}{a_1} \quad \text{--- (4)}$$

Where  $a_1$  and  $a_2$  are nothing but activity of HCl and they can be determine as follows.



$x$  = no. of cation in the electrolyte sol<sup>n</sup>  
 $y$  = no. of anion present in the electrolyte sol<sup>n</sup>

$$a = x^x y^y \cdot m^{(x+y)} \cdot v^{(x+y)}$$

$$a = 1^1 1^1 \cdot m^{(1+1)} \cdot v^{(1+1)}$$

$$a = m^{(2)} v^{(2)}$$

$$a = (mv)^2$$

If then eq<sup>n</sup> (4) becomes

$$E_c = \frac{2.303RT}{F} \log \frac{(m_2 v_2)^2}{(m_1 v_1)^2}$$

$$E_c = \frac{2.303RT}{F} \log \left( \frac{m_2 v_2}{m_1 v_1} \right)^2$$

$$E_c = 2 \times \frac{2.303RT}{F} \log \left( \frac{m_2 v_2}{m_1 v_1} \right)$$

----- (5)

At standard condition

$$E_c = 2 \times 2.303 \cdot 0.0591 \log \frac{m_2 v_2}{m_1 v_1}$$

$$E_c = 0.1182 \log \frac{m_2 v_2}{m_1 v_1}$$

----- (6)

$$\textcircled{1} \quad \Delta G = -nFE$$

$$\textcircled{2} \quad \Delta G = -nFE$$

### \* Relation between equilibrium constant & $E_c$

When cell is at equilibrium that means free energy change  $\Delta G = 0$  and  $E_c = 0$  and we know that  $Q_a = K$ .

Hence Nernst's eq<sup>n</sup> become

$$E_c = E_c^\circ - \frac{2.303RT}{nF} \log Q_a \quad \text{--- --- --- --- --- (1)}$$

$$0 = E_c^\circ - \frac{2.303RT}{nF} \log K$$

$$E_c^\circ = \frac{2.303RT}{nF} \log K \quad \text{--- --- --- --- --- (2)}$$

At standard condition

$$E_c^\circ = \frac{0.0591}{n} \log K \quad \text{--- --- --- --- --- (3)}$$

### Method II

In this method we calculate the relation between equilibrium constant and standard cell reaction by comparing two relations which gives value of free energy change and equilibrium constant.

$$\Delta G^\circ = -RT \ln K \quad \text{--- --- --- --- --- (1)}$$

$$\Delta G^\circ = -nE_c^\circ F \quad \text{--- --- --- --- --- (2)}$$

$$t_+ = 1 - t_-$$

$$t_- = 1 + t_+$$

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D D M M Y Y Y Y

From eq<sup>n</sup> ① and ②

$$-nE_c^{\circ}F = -RT \ln k$$

Changing sign through out

$$nE_c^{\circ}F = RT \ln k$$

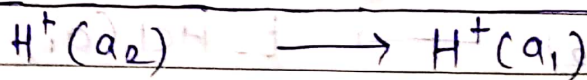
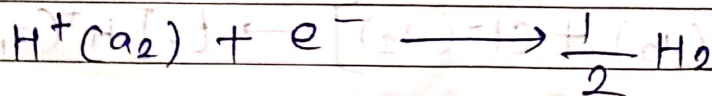
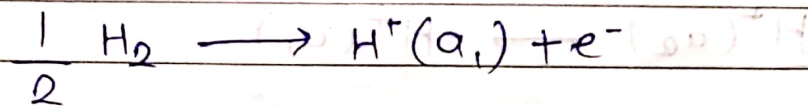
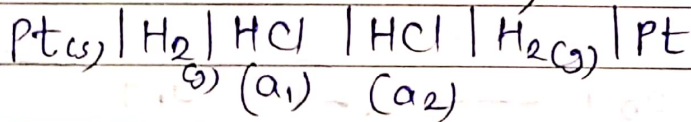
$$E_c^{\circ} = \frac{RT}{nF} \ln k \quad \text{--- (3)}$$

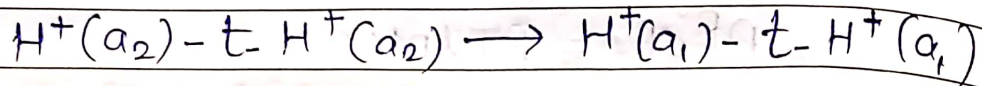
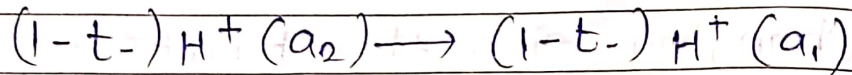
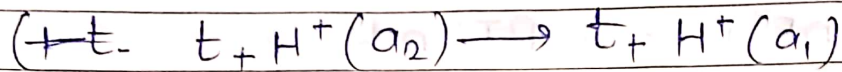
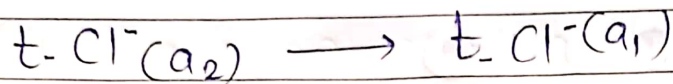
$$E_c^{\circ} = \frac{2.303RT}{nF} \log k \quad \text{--- (4)}$$

At standard condition

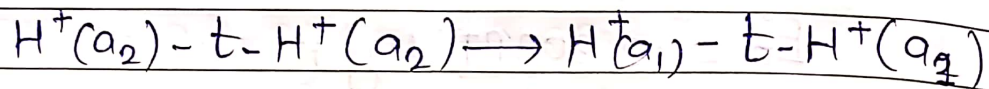
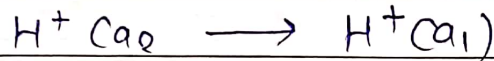
$$E_c^{\circ} = \frac{0.0591}{nF} \log k \quad \text{--- (5)}$$

Electrolyte conc<sup>n</sup> cell with transference  
(reversible to cation)



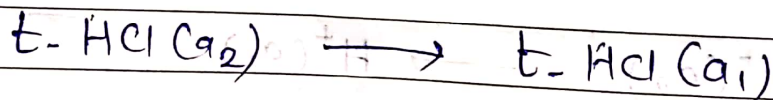
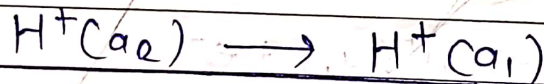
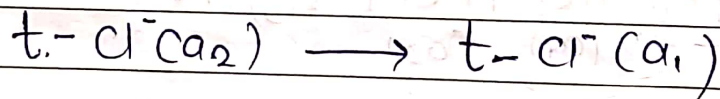
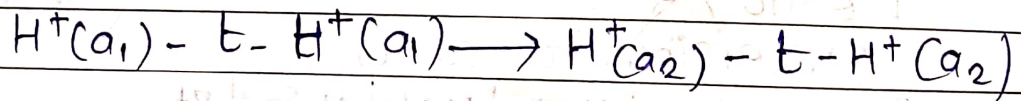
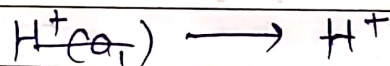


for overall reaction of the above cell



If ions are move from left to right then current is flows from right to left.

Hence above eq<sup>n</sup> becomes.



$$Q_a = \left( \frac{a_1}{a_2} \right)^t$$

The above reaction indicates that  $t$ -moles of HCl are transport from a solid of activity  $a_2$  to  $a_1$  for every faraday passing through cell.

$$(E_c)_t = - \frac{2.303RT}{f} \log \left( \frac{a_1}{a_2} \right)^t$$

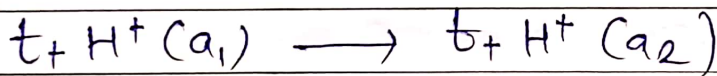
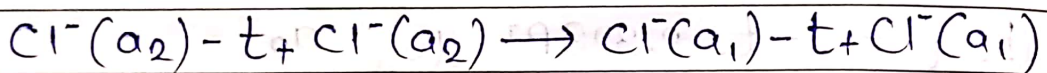
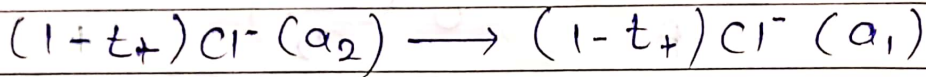
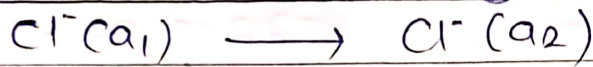
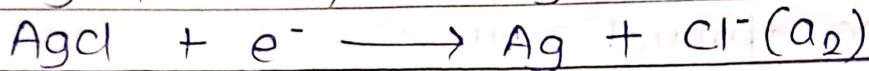
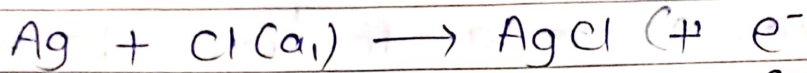
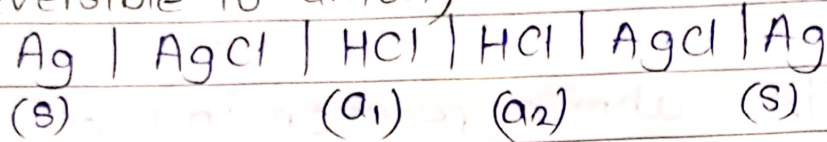
$$(E_c)_t = -t \cdot \frac{2.303RT}{f} \log \frac{a_2}{a_1}$$

$$(E_c)_t = -t \cdot \frac{2.303RT}{f} \log \left( \frac{m_2 \nu_2}{m_1 \nu_1} \right)^2$$

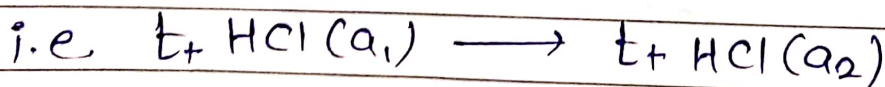
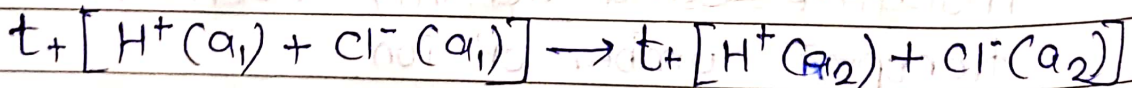
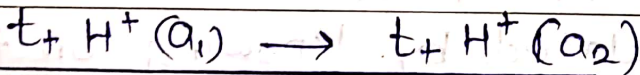
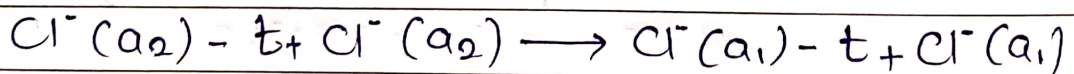
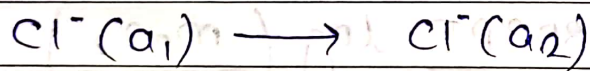
$$(E_c)_t = 2t \cdot \frac{2.303RT}{f} \log \left( \frac{m_2 \nu_2}{m_1 \nu_1} \right)$$

Hence Emf of cell with transference can be calculated by knowing on the molalities and activity coefficient with transport number of ion.

Electrolyte concentration cell with transference  
 (reversible to anion)



for overall reaction of the above cell



$$Q_a = \left( \frac{a_2}{a_1} \right)^{t_+}$$



$$0.49 \quad 0.51$$



The above reaction indicates that  $t_+$  moles HCl are transport from a solution of activity  $a_1$  to  $a_2$  for every faraday passing through cell.

$$(E_c)_t = - \frac{2.303RT}{F} \log \left( \frac{a_2}{a_1} \right)^{t_+}$$

$$(E_c)_{t_+} = + t_- \frac{2.303RT}{F} \log \frac{a_2}{a_1}$$

$$(E_c)_t = t_+ \cdot \frac{2.303RT}{F} \log \left( \frac{m_1 \nu_1}{m_2 \nu_2} \right)^2$$

$$(E_c)_t = 2t_+ \frac{2.303RT}{F} \log \frac{m_1 \nu_1}{m_2 \nu_2}$$

v.IMP

Liquid-Liquid

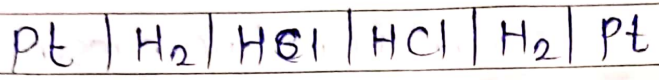
potential created due to junction between two sol<sup>n</sup> of same or different electrolytes is called liquid-liquid potential or simply junction potential.  $(E_j) \rightarrow$

Determination -

Liquid junction potential can be determined by emf of cell with transference is given by.



$$(E_c)_t = E_c + E_j \quad \text{--- (1)}$$



$$(E_c)_t = 2t - \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1} \quad \text{--- (2)}$$

$$E_c = \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1} \quad \text{--- (3)}$$

$$E_j = (E_c)_t - E_c$$

$$E_j = (2t) \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1} - \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1}$$

$$E_j = (2t - 1) \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1} \quad \text{--- (4)}$$

$$E_j = (t_- - t_+) \frac{2.303RT}{F} \log \frac{m_2 v_2}{m_1 v_1} \quad \text{--- (5)}$$

$$E_j = (t_+ - t_-) \frac{2.303RT}{F} \log \frac{m_1 v_1}{m_2 v_2}$$

VIMP

\* Determination of Thermodynamics properties  $\Delta H$ ,  $\Delta S$  &  $\Delta G$ .

The change in thermodynamic properties, like enthalpy change  $\Delta H$ , free energy change  $\Delta G$  and entropy change  $\Delta S$  can be reduced from measurement of cell emf and its temperature dependence.

kle have gives,

$$\Delta G = \Delta H + T \left( \frac{d\Delta G}{dT} \right)_p \quad \text{--- (1)}$$

$$\Delta G = \Delta H - T \left( \frac{d\Delta G}{dT} \right)_p \quad \text{--- (2)}$$

But we have equation,

$$\Delta G = -nEF \quad \text{--- (3)}$$

Differentiating above equation to respect to temperature.

$$\left( \frac{d\Delta G}{dT} \right)_p = -nEF \left( \frac{dE}{dT} \right)_p \quad \text{--- (4)}$$

The term  $\left( \frac{dE}{dT} \right)_p$  is called temp. coefficient of the cell.

Temperature coefficient is given by measuring the cell emf at different temperature of  $E_1$  and  $E_2$ , at temperature  $T_1$  and  $T_2$ .

$$\left(\frac{dE}{dT}\right)_p = \frac{E_2 - E_1}{T_2 - T_1}$$

$$-nEF - \Delta H = T \left[ -nF \left(\frac{dE}{dT}\right)_p \right]$$

i.e.  $\Delta H = nFT \left(\frac{dE}{dT}\right)_p - nEF$

$$\therefore \Delta H = nF \left[ T \left(\frac{dE}{dT}\right)_p - E \right]$$

----- (5)

for any electrochemical cell, where  $\Delta G = \Delta H$

$$\Delta G - \Delta H = -nFT \left(\frac{dE}{dT}\right)_p$$

----- (6)

It is possible only when  $\left(\frac{dE}{dT}\right)_p = 0$

so, we can write

$$\Delta G - \Delta H = -T\Delta S$$

----- (7)

from eq<sup>n</sup> (6) and (7)

$$-T\Delta S = -nFT \left(\frac{dE}{dT}\right)_p$$

$$\therefore \Delta S = nF \left(\frac{dE}{dT}\right)_p$$

----- (8)