# 5. Electromotive Force.

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

| | Oxidation | Reduction |
|---|---|---|
| Organic | $+ O_2$ | $+ H_2$ |
| Inorganic | ↑ charge | ↓ charge |
| physical | Loss of electron | Gain of electron |

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

IUPAC Rule for cell representation.

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

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

eg. ① $Zn^+ \mid ZnSO_4$
$Cu^+ \mid CuSO_4$

② $Pb \mid PbSO_4$.

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

Pure metal is ↓ $E_{cell} = E_R - E_L$

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

eg. $Zn^{-}$ | $ZnSO_4$ $(a_1)$

$Cu^{+}$ | $CuSO_4$. $(a_2)$

$Zn^{\ominus}_{(s)} | ZnSO_{4(aq)} || CuSO_{4(aq)} | Cu^{+}_{(s)}$
$a_1$ $a_2$

$PbSO_4$ $Fe^{2+}$
$Pb^{2+}$ $FeSO_4$

$Pb^{\ominus}_{(s)} | PbSO_{4(aq)} || FeSO_{4(aq)} | Fe^{\oplus}$
$a_1$ $a_2$

$Pb \longrightarrow Pb^{2+} + 2e^{\ominus}$
$Fe^{2+} + 2e^{\ominus} \longrightarrow Fe$
$PbFe^{2+} + Fe + Pb^{2+}$

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

$Fe^{\ominus} | Fe(NO_3) || Pb(NO_3) | Pb^{\oplus}$

$\Delta G = - W_{max}$

$\Delta G = - nE_cF$ . . . . . . . . ①

4 marks

* EMF of the cell and activity.

Consider a reversible cell for which overall reaction as follow.

$$aA + bB \rightleftharpoons cC + dD$$

According to thermodynamics.

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

Reaction Qa of above reaction.

$$Qa = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

But we have.

$$\Delta G = -nE_cF \quad \text{------ (2)}$$

$$\Delta G^\circ = -nE_c^\circ F \quad \text{------ (3)}$$

from eqⁿ (1) (2) and (3) we have.

$$-nE_cF = -nE_c^\circ F + RT \ln Qa$$

Dividing through out by $-nF$

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

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

At standerd temp. eq$^n$ (4) becomes.

$$E_c = E_c^o - \frac{2.303 \times 8.314 \times 298}{n \times 96485} \log Qa.$$

$$E_c = E_c^o = - \frac{0.0591}{n} \log Qa \quad \text{------ (5)}$$

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

* 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 :

$$M^{n+}_{(aq)} | M_{(s)}$$

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

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

Nutt's eq$^n$ from above eq$^n$.

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

eg. ① Zn - Zn ion electrode.

$$Zn^{2+}_{(aq)} \mid Zn_{(s)}$$

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

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

Nutt's eqn of above eqn.

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

eg. ② $Na^+_{(aq)} \mid Na_{(s)}$

$$Na + 1e^- \longrightarrow Na$$

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

Nutt's eqn from above equation.

$$\therefore E_{Na} = E^\circ_{Na} - \frac{2.303RT}{1F} \log. \frac{1}{a_{Na^+}}$$

eg. ③ $Fe^{2+}_{(aq)} \mid Fe_{(s)}$

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

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

Nutt's eqn of above eqn

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

$$Fe^{3+}_{(aq)} \mid Fe_{(s)}$$

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

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

Nutt's eqn of above eqn.

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

2) Metal - Amalgam

Statement :

A solution of metal in liquid marcury 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 :

$$M^{n+}_{(aq)} \mid M(Hg)_{(s)}$$

$$Mn^{n+} + ne^- \longrightarrow M(Hg)$$

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

Nutt's eqn from above eqn.

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

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

eg. ① Zn(Hg) electrode.
Where Zn(Hg) is dipped in soln of $ZnSO_4$

$$Zn^{2+}_{(aq)} \mid Zn(Hg)$$

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

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

Nutt's eqn from above eqn

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

② Na(Hg) electrode is dipped in NaCl.

$$Na_{(aq)} \mid Na(Hg)_{(s)}$$

$$Na^{+} + 1e^{-} \longrightarrow Na(Hg)$$

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

Nutt's eqⁿ from above eqⁿ:

$$E_{Na(Hg)} = E^{\circ}_{Na} - \frac{2.303RT}{F} \log \frac{a_{(NaHg)}}{a_{Na^{+}}}$$

Homework: ① $Cd^{2+} \mid Cd(Hg)$

$$Cd^{2+}_{(aq)} \mid Cd(Hg)_{(s)}$$

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

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

Nutt's eqⁿ from above eqⁿ

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

② $Pt^{3+} \mid Pt(Hg)$

$$Pt^{3+} \mid 3e^{-} \longrightarrow Pt(Hg)$$

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

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Nutt's eq^n from above eq^n

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

3. Metal insoluble salt electrode.

This electrode consists of metal M in contact with it's sparingly soluble salt MX which in turn is in contact with solution containing $X^-$ ions. It is represented as,

$$X^- \mid MX_{(s)} \mid M_{(s)}$$

$$MX + ne^- \longrightarrow M + X^-$$

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

Nutt's eq^n from above eq^n.

$$E_C = E^{\circ}_C - \frac{2.303RT}{F} \log a_{X^-}$$

eg. ① Silver-silver chloride electrode. AgCl

$$Cl^-_{(aq)} \mid AgCl_{(aq)} \mid Ag_{(s)}$$

$$AgCl + ne^- \longrightarrow Ag + Cl^-$$

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

so nutt's $eq^n$ from above $eq^n$.

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

eg. HgCl = $Cl^- | AgCl | Hg$

In this electrode pure mercury is convered by best of calomer ($Hg + Hg_2Cl_2$) is in contact with in aquas 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.

$$Cl^- | Hg_2Cl_2 | Hg | pt$$

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$$

$$Qa = \frac{a^2_{Hg} \cdot a^2_{Cl^-}}{a_{Hg_2Cl_2}} = a^2_{Cl^-}$$

Nutt's $eq^n$ from above $eq^n$.

$$E_{Hg-Hg_2Cl_2} = E^{o}_{Hg} - \frac{2.303RT}{2F} \log. a^2_{Cl^-}$$

4) Gas electrode :

In this gas electrode gas in a contact with the solution of it's own electrode in

SHE = 0.0V

H, Cl, O

in presence of an inert metal, inert metal facilats the rapid equiliberium gas and it's ion and surve's to make electric contact inert metal is usually used pt.

① Hydrogen electrode.

VIMP

In this soln bubbled at suitable pressure over pt wire in the solution of HCl or $H_2SO_4$ or (strong acid)

$$H^+_{(aq)} | H_{2(g)} | pt_{(s)}$$

$$H^+ + e^- \longrightarrow \frac{1}{2} H_2$$

$$Qa = \frac{a^{\frac{1}{2}}_{H_2}}{a_{H^+}}$$

Nutt's eqn from above eqn

$$E_{H_2} = E^o_{H_2} - \frac{2.303RT}{F} \log \frac{a^{\frac{1}{2}}_{H_2}}{a_{H^+}}$$

$$E_{H_2} = -\frac{2.303RT}{F} \log {}^{1}/_{a_{H^+}} \quad (\because E^o_{H_2} = 0.0V)$$

$$E^o_{H_2} = -\frac{2.303RT}{F} pH$$

At 298 K and 1 bar atm. pressure above eqn is.

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

(2) Chlorine gas electrode.

Here $Cl_2$ gas is bubbled at suitable pressure over pt wire in imersed into solution.

$$Cl^-_{(aq)} \mid Cl_{2(g)} \mid Pt_{(s)}$$

$$\frac{1}{2}Cl_2 + e^- \longrightarrow Cl^-$$

$$Qa = \frac{a_{Cl^-}}{a^{1/2}_{Cl_2}}$$

Nust's eqn from above eqn

$$E_{Cl_2} = E^{\circ}_{Cl_2} - \frac{2.303RT}{F} \log \frac{a_{Cl^-}}{a^{1/2}_{Cl_2}}$$

At 298 K and 1 bar atm. pressur above eqn is

$$E_{Cl_2} = E^{\circ}_{Cl} - 2.303RT$$

(3) Oxygen gas electrode.

Here $O_2$ gas is bubbled with suitabal pressure in platinum is imersed in alkali solution.

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

$OH^-_{(aq)} | O_{2(g)} | Pt_{(s)}$

$$\frac{1}{2} O_2 + H_2O + e^- \longrightarrow 2OH^-$$

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

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

activity of $H_2O$ moleule is is 1

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

5. Redox electrode :

An inert metal like pt dips in soln 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 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 soln containing ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$)

$Fe^{2+}, Fe^{3+}_{(aq)} | Pt_{(s)}$

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

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

Nutt's eqn from above eqn

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

(2) eg. cupric to cupperus ion ~~de~~ electrode and Pt is immersed

$Cu^{2+}, Cu^{3+}_{(aq)} | Pt_{(s)}$

$Cu^{3+} + e^- \longrightarrow Cu^{2+}$

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

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

(3) $Sn^{2+}, Sn^{4+} | Pt$

$Sn^{4+} + 2e^- \longrightarrow$ ~~Pt~~ $Sn^{2+}$

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

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

✱ Chemical cell without transference.

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

Consider a cell.

$$Pt_{(s)} | H_{2(g)} | HCl_{(aq)} | AgCl_{(aq)} | Ag_{(s)}$$

Oxidation half cell $\frac{1}{2} H_2 \longrightarrow H^+ + e^-$

Readuction half cell $AgCl + e^- \longrightarrow Ag + Cl^-$

Overall Reaction $\frac{1}{2} H_2 + AgCl \longrightarrow H^+ + Ag + Cl^-$

$$\frac{1}{2} H_2 + AgCl \longrightarrow HCl + Ag$$

$$Q_a = \frac{a_{HCl} \cdot a_{Ag}}{a^{1/2}_{H_2} \cdot a_{AgCl}}$$

So, the potential energy is given as,

$$E_c = E_R - E_L$$

$$E_c = (E_{AgCl-Ag} - E_{H_2}) \quad \text{------ (1)}$$

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

$$E_{H_2} = E^\circ_{H_2} - \frac{2.303RT}{F} \log \frac{P^{1/2}_{H_2}}{a_{H^+}}$$

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

$$\left( E_{H_2} = E^\circ_{H_2} - \frac{2.303RT}{F} \frac{P^{1/2}_{H_2}}{a_{H^+}} \right)$$

$$E_c = \left( E^\circ_{Ag-AgCl} - E^\circ_{H_2} \right) - \frac{2.303RT}{F} \left( \log a_{Cl^-} - \log \frac{P^{1/2}_{H_2}}{a_{H^+}} \right)$$

$$E_c = E^\circ_{Ag-AgCl} - \frac{2.303RT}{F} \left( \log a_{Cl^-} + \log \frac{a_{H^+}}{P^{1/2}_{H_2}} \right)$$

$$E_c = E^\circ_{Ag-AgCl} - \frac{2.303RT}{F} \left( \log \frac{a_{Cl^-} \, a_{H^+}}{P^{1/2}_{H_2}} \right)$$

$$E_c = E^\circ_{Ag-AgCl} - \frac{2.303RT}{F} \log \frac{a_{HCl}}{P^{1/2}_{H_2}} \quad \text{-----} (4)$$

at 1 bar atmosphere pressure

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

eg 1) $Pt \mid H_2 \mid H_2SO_{4(aq)} \mid HgSO_4 \mid Hg \mid Pt$.

$$H_{2(g)} + Hg_2SO_{4(s)} \longrightarrow 2Hg_{(l)} + H_2SO_{4(aq)}$$

Nutt's eqn from above eqn

$$E_c = E^{\circ}_{Hg-Hg_2SO_4} - \frac{2.303RT}{2F} \log_{10} \frac{a_{H_2SO_4}}{P_{H_2}}$$

2) $Cd \mid CdSO_{4(aq)} \mid HgSO_4 \mid Hg \mid Pt$

$$Cd + HgSO_4 \longrightarrow 2Hg + CdSO_4$$

Nutt's eqn from above eqn

$$E_c = E^{\circ}_{Hg-HgSO_4} - \frac{2.303RT}{F} \log a_{CdSO_4}$$

Electrode concn cell

Here EMF is due to difference in concn of electrode. eg. gas electrode and amalagam electrode.

A) Electrode concn cell reversible to cations

Let us consider a cell constructed using two amalgam with different concn of same metal.

$$Pb(Hg)_{(s)} \mid Pb^{2+} \mid Pb(Hg)$$
$$(a_1) \qquad\qquad (a_2)$$

$$Pb^{2+}(a_1) \longrightarrow Pb^{2+} + 2e^-$$
$$Pb^{2+} + 2e^- \rightarrow Pb(a_2)$$
$$Pb(a_2) \longrightarrow Pb(a_1)$$

The overall of the cell is given as

$$E_c = E_R - E_L$$

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

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

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

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

## Gas electrode reversible to cation

Let us consider a cell H gas electrodes with different concentration ~~of~~ pressure

$$Pt_{(s)} | H_{2(g)} | H^+_{(aq)} | H_{2(g)} | Pt_{(s)}$$

$$(P_1) \qquad (P_2)$$

$$\frac{1}{2}H_2 + 2e^- \longrightarrow {}^1H$$

$$\frac{1}{2}H_2 \longrightarrow H^+ + e^-$$

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$$\frac{1}{2}H_2 (P_1) + \frac{1}{2}H_2 (P_2)$$

$$E_c = E_R - E_L$$

$$E_c = \left(E^\circ_{H_2} - \frac{2.303RT}{F}\log\frac{P_2^{1/2}}{a_{H^+}}\right) - \left(E^\circ_{H_2} - \frac{2.303RT}{F}\log\frac{P_1^{1/2}}{a_{H^+}}\right)$$

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

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

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

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

In general,

$$\underset{(a_1)}{M(Hg)} \mid Pt \mid \underset{(a_2)}{M(Hg)}$$

b) Electrode concentration cell reversible to anion

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

$$Pt \mid Cl_2 \mid Cl^- \mid Cl_2 \mid Pt$$

$$Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$$

$$\frac{1}{2} Cl_2 + e^- \longrightarrow Cl^-$$

$$\frac{1}{2} Cl_2 \, (P_2) \longrightarrow \frac{1}{2} Cl_2 \, (P_1)$$

$$E_C = E_R - E_L$$

$$E_C = \left(E^\circ_{Cl_2} - \frac{2.303RT}{2F} \log \frac{P_2^{1/2}}{P_1^{1/2}}\right) - \left(E^\circ_{Cl_2} - \frac{2.303RT}{2F} \log \frac{P_1^{1/2}}{P_2^{1/2}}\right)$$

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

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

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

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

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

VIMP **Electrolyte cocentration cell**

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

a) **Electrolyte conc^n cell without transference** -

such electrode construct by using two cell without transference.

Cell I :

$Pt \mid H_2 \mid HCl_{(a_1)} \mid AgCl_{(s)} \mid Ag_{(s)}$

$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$

$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$

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

$\frac{1}{2} H_2 + AgCl \longrightarrow Ag + HCl (a_1)$

Nutt's eqⁿ for above reaction

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

$$E_{cl} = E^\circ_{cl} - \frac{2.303RT}{F} \log a_1 \quad \text{------} (1)$$

Cell II :

$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$

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

$\frac{1}{2} H_2 + AgCl \longrightarrow Ag + HCl (a_1)$ $(a_2)$

Nutt's eqⁿ for above eqⁿ

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

$$E_{c2} = E^\circ_{c2} - \frac{2.303RT}{F} \log a_2 \quad \text{------} (2)$$

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

$Pt_{(s)} | H_{2(g)} | HCl | AgCl | Ag | AgCl | HCl (a_2) | H_2 | Pt$

$\frac{1}{2} H_2 + AgCl \rightarrow Ag + HCl(a_1) \longrightarrow \frac{1}{2} H_2 + AgCl \rightarrow HCl(a_2)$

$HCl(a_1) \rightarrow HCl(a_2)$

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

from eq^n (1) (2) and (3)

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

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

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

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

$HCl \longrightarrow H^+ + Cl^-$

$x$ = no. of cation in the electrolyte sol^n

$y$ = no. of ~~cation~~ anion present in the electrolyte sol^n

$$a = x^x y^y . m^{(x+y)} . \nu^{(x+y)}$$

$$a = 1^1 y^1 . m^{(1+1)} . \nu^{(1+1)}$$

$$a = m^{(2)} \nu^{(2)}$$

$$a = (m\nu)^2$$

If then eq$^n$ (4) becomes

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

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

$$E_c = 2 \times \frac{2.303RT}{F} \log \left(\frac{m_2\nu_2}{m_1\nu_1}\right) \quad \text{-------- (5)}$$

At standerd condition

$$E_c = 2 \times \cancel{2.303}\, 0.0591 \log \frac{m_2\nu_2}{m_1\nu_1}$$

$$E_c = 0.1182 \cancel{\log} \log \frac{m_2\nu_2}{m_1\nu_1} \quad \text{-------- (6)}$$

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* Relation between equilliberium constant & Em

When cell it as equiliberium that means free energy change $\Delta G = 0$ and $E_c = 0$ and we know that $Q_a = K$.

Hence nutt's eq^n become

$$E_c = E_c^{\circ} - \frac{2.03RT}{nF} \log Q_a \quad \text{- - - - - - (1)}$$

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

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

At standerd conditon

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

Method II In this method we calculate the relation between equillliberium constant and standerd cell reation by comparing two relations which gives value of free energy change and equillliberium 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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From eq^n ① and ②

$$-nE_c^\circ f = -RT\ln K$$

Changing sign though 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 standerd condition

$$E_c^\circ = \frac{0.0591}{n}\log K \quad \text{--- ⑤}$$

Electrolyte con^n cell with transferace (reversible to cation)

$$Pt_{(s)} | H_{2(g)} | \underset{(a_1)}{HCl} | \underset{(a_2)}{HCl} | H_{2(g)} | Pt$$

$$\frac{1}{2}H_2 \longrightarrow H^+(a_1) + e^-$$

$$H^+(a_2) + e^- \longrightarrow \frac{1}{2}H_2$$

$$H^+(a_2) \longrightarrow H^+(a_1)$$

$t_- Cl^-(a_2) \longrightarrow t_- Cl^-(a_1)$

(~~+t_-~~ $t_+ H^+(a_2) \longrightarrow t_+ H^+(a_1)$

$(1-t_-) H^+(a_2) \longrightarrow (1-t_-) H^+(a_1)$

$H^+(a_2) - t_- H^+(a_2) \longrightarrow H^+(a_1) - t_- H^+(a_1)$

for overall reaction of the above cell

$H^+ (a_2 \longrightarrow H^+(a_1)$

$H^+(a_2) - t_- H^+(a_2) \longrightarrow H^+(a_1) - t_- H^+(a_1)$

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

Hence above eqn becomes.

$H^+$~~$(a_1)$~~ $\longrightarrow H^+$

$H^+(a_1) - t_- H^+(a_1) \longrightarrow H^+(a_2) - t_- H^+(a_2)$

$t_- Cl^-(a_2) \longrightarrow t_- Cl^-(a_1)$

$H^+(a_2) \longrightarrow H^+(a_1)$

$t_-[H^+(a_2) + Cl^-(a_2)] \longrightarrow t_-[H^+(a_1) + Cl^-(a_1)]$

$t_- HCl(a_2) \longrightarrow t_- HCl(a_1)$

$$Qa = \left(\frac{a_1}{a_2}\right)^{t_-}$$

The above reaction indicates that $t_-$ moles of HCl are transport from a sol^n of activity $a_2$ to $a_1$ for every Faraday passing through cell.

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

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

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

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

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)

$$Ag_{(s)} | AgCl | HCl_{(a_1)} | HCl_{(a_2)} | AgCl | Ag_{(s)}$$

$$Ag + Cl(a_1) \longrightarrow AgCl (+ e^-$$
$$AgCl + e^- \longrightarrow Ag + Cl^-(a_2)$$
$$Cl^-(a_1) \longrightarrow Cl^-(a_2)$$

$$(1-t_+)Cl^-(a_2) \longrightarrow (1-t_+)Cl^-(a_1)$$

$$Cl^-(a_2) - t_+Cl^-(a_2) \longrightarrow Cl^-(a_1) - t_+Cl^-(a_1)$$

$$t_+ H^+(a_1) \longrightarrow t_+ H^+(a_2)$$

for overall reaction of the above cell

$$Cl^-(a_1) \longrightarrow Cl^-(a_2)$$

$$Cl^-(a_2) - t_+ Cl^-(a_2) \longrightarrow Cl^-(a_1) - t_+ Cl^-(a_1)$$

$$t_+ H^+(a_1) \longrightarrow t_+ H^+(a_2)$$

$$t_+[H^+(a_1) + Cl^-(a_1)] \longrightarrow t_+[H^+(a_2) + Cl^-(a_2)]$$

i.e. $t_+ HCl(a_1) \longrightarrow t_+ HCl(a_2)$

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

$KCl = K^+ \quad Cl^-$

0.49   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.

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

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

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

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

V.IMP

## Liquid- Liquid

potential created due to junction between two soln of same or different electrolytes is called liquid- liquid potential or simply junction potential. ($E_j$) ω.

Determination -

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

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

$Pt \mid H_2 \mid HCl \mid HCl \mid H_2 \mid Pt$

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

$$E_c = \frac{2.303RT}{F} \log \frac{m_2 \nu_2}{m_1 \nu_1} \text{ ---- } (3)$$

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

$$E_j = (2t_-) \frac{2.303RT}{F} \log \frac{m_2 \nu_2}{m_1 \nu_1} - \frac{2.303RT}{F} \log \frac{m_2 \nu_2}{m_1 \nu_1}$$

$$E_j = (2t_- - 1) \frac{2.303RT}{F} \log \frac{m_2 \nu_2}{m_1 \nu_1} \text{ ------ } (4)$$

$$E_j = (t_- - t_+) \frac{2.303RT}{F} \log \frac{m_2 \nu_2}{m_1 \nu_1} \text{ ---- } (5)$$

$$E_j = (t_+ - t_-) \frac{2.303RT}{F} \log \frac{m_1 \nu_1}{m_2 \nu_2}$$

14/08/2025

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 entrophy change $\Delta S$ can be reduced from measurement of cell emf and it's temperature dependence.

We 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.

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

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

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

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

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

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

$$\therefore \Delta H = nF\left[T\left(\frac{dE}{dT}\right)_p - E\right] \quad \text{--------- (5)}$$

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

$$\Delta G - \Delta H = -nFT\left(\frac{dE}{dT}\right)_p \quad \text{--------- (6)}$$

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

so, we can write

$$\Delta G - \Delta H = -T\Delta S \quad \text{--------- (7)}$$

From eqn (6) and (7)

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

$$\therefore \Delta S = nF\left(\frac{dE}{dT}\right)_p \quad \text{--------- (8)}$$