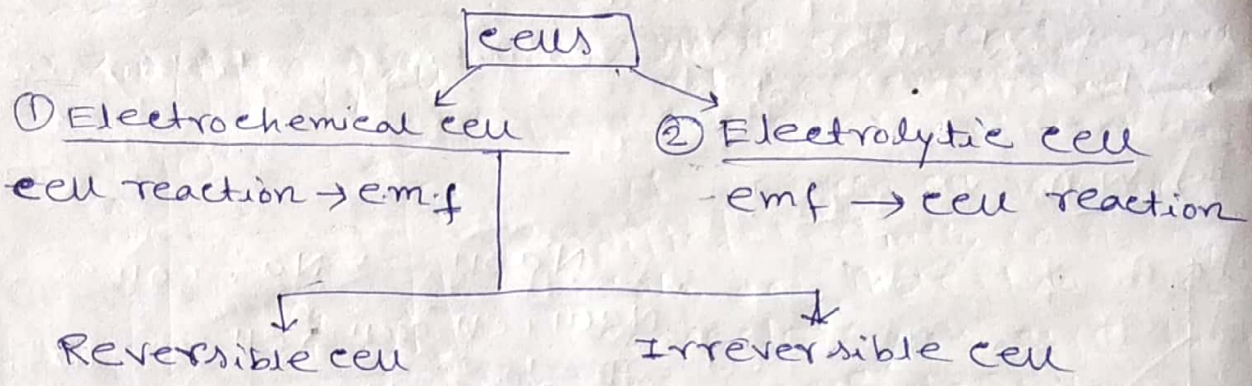
In galvanic cell (Electrochemical cell) emf. is obtained from chemical reaction or cell reaction.

For spontaneous reaction, $\Delta G_r < 0$

$$-\Delta G_r = nFE$$

$$E = -\Delta G_r / nF$$

But in case of electrolytic cell where external emf performs the cell reaction.

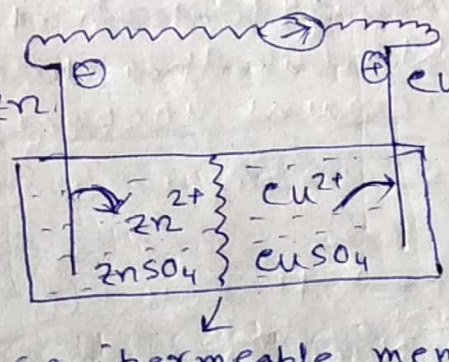


Reversible cell:-

Ex:- $Zn \mid ZnSO_4 \;\|\; CuSO_4 \mid Cu$

Reversible cells are those where cell reaction will be reversed in presence of external emf.

Let a Zn rod and a Cu rod are partially dipped in $ZnSO_4$ soln. and $CuSO_4$ soln. respectively. So two electrodes are formed. If two electrodes are connected by a wire, then Zn goes into soln. as Zn^{2+} and Cu^{2+} comes out from soln. as Cu at Cu electrode. So Zn electrode will be -ve, called anode, and Cu electrode will be +ve, called cathod.



At Zn electrode:- $Zn \longrightarrow Zn^{2+} + 2e^-$

At Cu electrode:- $Cu^{2+} + 2e^- \longrightarrow Cu$

Cell reaction:- $Zn + Cu^{2+} + 2e^- \rightarrow Zn^{2+} + 2e^- + Cu$

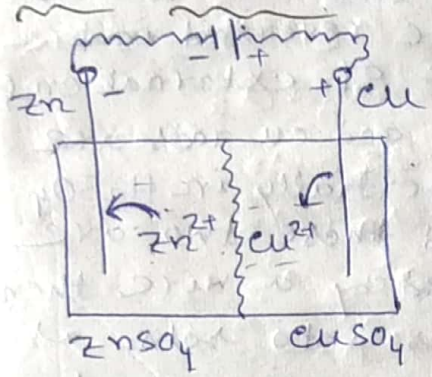
$$\boxed{Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu}$$

Now if we use an external emf, whose -ve end is connected with Zn and +ve end is connected with Cu, then electrode processes are as follows:

At Zn electrode (-ve): $Zn^{2+} + 2e^- \rightarrow Zn$

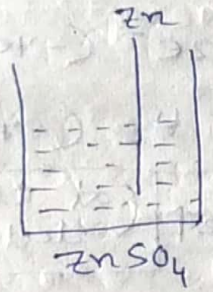
At Cu " (+ve): $Cu \rightarrow Cu^{2+} + 2e^-$

Cell reaction:- $\boxed{Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}}$

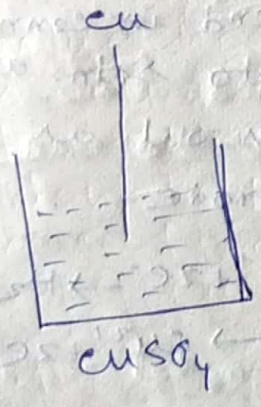


So the cell reaction is totally reversed.

**Note:-



Oxidn: $Zn \rightarrow Zn^{2+} + 2e^-$ (or) Redn: $Zn^{2+} + 2e^- \rightarrow Zn$



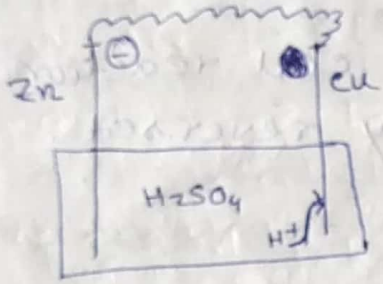
$Cu \rightarrow Cu^{2+} + 2e^-$ (or) $Cu^{2+} + 2e^- \rightarrow Cu$

Let Zn/$ZnSO_4$ and Cu/$CuSO_4$, two electrodes are taken respectively. Now Zn, Cu -- are metals and metal are electropositive. so both want to release e^-s to form cations. therefore they will prefer oxidn process, ie, both want to be a -ve electrode. But if these two electrodes are connected now, then Zn and Cu both want to go to the soln as Zn^{2+}

and Cu^{2+} by release of e^-s respectively. Actually Zn can go to soln. as Zn^{2+} and Cu can not. Here Zn is more electropositive than Cu. (ie, Zn wants to quickly go as Zn^{2+}) on that time Cu^{2+} takes e's, which are given from Zn and follows reduction process and it will be +ve electrode.

Irreversible cell:- These are the cells where cell reaction will not be reversed in presence of external emf.

$Zn/H_2SO_4/Cu$



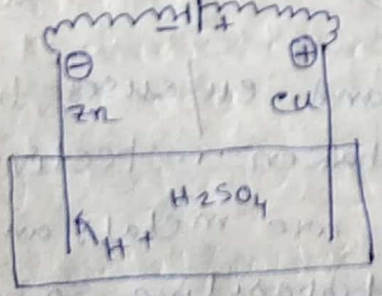
If Zn and Cu rods are dipped partially in H_2SO_4 soln, and these two are connected by a wire then Zn goes into soln. as Zn^{2+} and H^+ comes out from soln. as H_2 at Cu-electrode.

At Zn-electrode:- $Zn \longrightarrow Zn^{2+} + 2e^-$ (-ve)

At Cu " :- $2H^+ + 2e^- \longrightarrow H_2$ (+ve)

cell reaction: $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2\uparrow$ (at Cu-electrode)

If we use an external emf, whose -ve end is connected with Zn and +ve end is connected with Cu, then Cu goes into soln. as Cu^{2+} and H^+ comes out as H_2 at Zn-electrode.



At Zn electrode: $2H^+ + 2e^- \longrightarrow H_2$

At Cu " : $Cu \longrightarrow Cu^{2+} + 2e^-$

cell reaction:- $2H^+ + Cu \longrightarrow Cu^{2+} + H_2\uparrow$ (Zn-electrode)

So cell reaction is not reversed. Therefore given cell is irreversible.

Reversible electrochemical cell $\xrightarrow{\text{e.m.f}}$ Electrolytic cell

strength ?

$-nFE = \Delta G_r$

$\boxed{E = -\Delta G_r/nF}$

So applied external emf should be $\geq -\frac{\Delta G_r}{nF}$

ΔG_r is the free energy change for cell reaction of electrochemical cell.

Spontaneous cell reaction :- $\Delta G_r < 0$, $E > 0$

convention :-

	Electrochemical cell	Electrolytic cell
(1)	-ve electrode (anode)	-ve electrode (cathod)
	+ve " (cathod)	+ve " (anode)

(2) Oxidⁿ always occurs at anode.
redⁿ " " " cathod.

(3) If you are supplied electrode potential of the electrodes without mentioning electrode process as oxidⁿ or redⁿ, you should take it as redⁿ potential.

Free energy and e.m.f :-

For reversible cell, $-\Delta G_r = nFE$

at standard state, $-\Delta G^\circ = nFE^\circ$

$n \rightarrow$ no. of e^-s involved in redox process

$E^\circ \rightarrow$ emf of cell at standard state.

NOW, $\Delta G_r = \Delta H - T\Delta S$

$= \Delta H + T\left\{\frac{\partial(\Delta G_r)}{\partial T}\right\}_P$

$\therefore \Delta S = -\left\{\frac{\partial(\Delta G_r)}{\partial T}\right\}_P = -\left\{\frac{\partial}{\partial T}(-nFE)\right\}_P$

$\left(\frac{\partial E}{\partial T}\right)_P \rightarrow$ Tempr. gradient of emf of cell.

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

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

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

$\boxed{E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P}$

Nernst's equation:- Let us consider a cell reaction,

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

From reaction isotherm,

$$\Delta G_R = \Delta G_R^\circ + RT \sum \nu \ln a$$

$$\Delta G_R^\circ = -nFE^\circ = -RT \ln K_a$$

$$\therefore \boxed{E^\circ = \frac{RT}{nF} \ln K_a}$$

At only equilⁿ

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

↳ equⁿ const.

$$\Delta G_R = \Delta G_R^\circ + RT \sum \nu \ln a$$

$$\text{or, } \Delta G_R = -RT \ln K_a + RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

$$\text{or, } -nFE = -RT \ln K_a + RT \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

$$\therefore E = \frac{RT}{nF} \ln K_a - \frac{RT}{nF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

$$\therefore \boxed{E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}}$$ This is Nernst's Equⁿ.

If cell reaction, $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

$n = 2$

$a_{Zn} = 1$, $a_{Cu} = 1$

Electrodes/Types of electrodes:-

A cell is developed by connecting two electrodes. These electrodes are also called half cell.

① Electrodes of 1st kind:-

ⓐ metal/metal ion electrode:- A metal rod is placed partially in the soln. containing same metal ion. Here an equilm process is running between metal and metal ion.

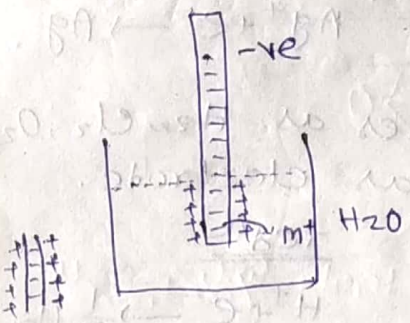
Ex: (i) $Zn/ZnSO_4$

$Pt / Sn^{2+}, Sn^{4+}$ $\quad Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-$

$Pt / Fe^{2+}, Fe^{3+}$ $\quad Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$

Electrode potential :-

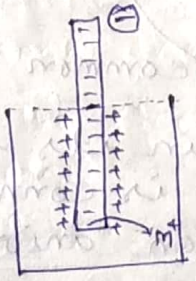
(i) When a metal is placed in water due to electrolytic soln. tension metal comes into solution as metal ion by releasing of e⁻s. So, here metal rod acts as -ve electrode. Now soln. phase is +ve and +ve metal ion make a positive layer at the vicinity of metal surface. So an electrical double layer is developed. The potential difference between these two oppositely charged electrical double layer is the electrode potential.



(ii) When a metal is placed pertially in the soln. containing some metal ion / other metal ions.

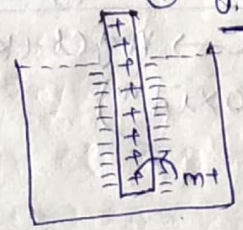
Two cases may arise :-

(a) O.P < S.P



When O.P < S.P, then metal comes into soln. as metal ion. Then metal rod becomes -ve and soln. phase becomes +ve. So, at the vicinity of metal rod an electrical double layer is developed. The potential diff. between these two electrical double layer is called electrode potential.

(b) O.P > S.P



(***) $\Pi = P^0 - P = CRT$

O.P ↙ S.P ↙

when C is low
O.P is less
S.P is high
} O.P < S.P

when C is more
O.P is high
S.P is less
} O.P > S.P

So, O.P and S.P depends on the concentration of the solution.

Using Nernst's equation we can get magnitude of electrode potential:-

Ex:- (i) $Zn/ZnSO_4$

If the process is oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

$$E_{Zn/Zn^{2+}} = E^\circ_{Zn/Zn^{2+}} - \frac{RT}{2F} \ln \frac{a_{Zn^{2+}}}{a_{Zn}}$$

$E_{Zn/Zn^{2+}}$ → oxidation potential of Zn/Zn^{2+} electrode

$E^\circ_{Zn/Zn^{2+}}$ → standard oxidation potential of Zn/Zn^{2+} "

when $a_{Zn^{2+}} = 1$

then $E_{Zn/Zn^{2+}} = E^\circ_{Zn/Zn^{2+}}$ Electrode $Zn/ZnSO_4 (a=1)$

If process is reduction:- $Zn^{2+} + 2e^- \rightarrow Zn$

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{RT}{2F} \ln \frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$= E^\circ_{Zn^{2+}/Zn} + \frac{RT}{2F} \ln a_{Zn^{2+}}$$

↳ standard red^n pot^n of electrode

reduction potential of Zn^{2+}/Zn electrode

(ii) $Cu/CuSO_4$

Process

$Cu \rightarrow Cu^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu$

Nernst's equation

$$E_{Cu/Cu^{2+}} = E^\circ_{Cu/Cu^{2+}} - \frac{RT}{2F} \ln a_{Cu^{2+}}$$

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} + \frac{RT}{2F} \ln a_{Cu^{2+}}$$

(iii) $Ag/AgCl - KCl$

Process (oxidation)

$Ag + KCl \rightarrow AgCl + K^+ + e$

$$E_{Ag-AgCl} = E^\circ_{Ag-AgCl} - \frac{RT}{F} \ln \frac{a_{AgCl} \cdot a_{K^+}}{a_{Ag} \cdot a_{KCl}}$$

$$= E^\circ_{Ag-AgCl} - \frac{RT}{F} \ln \frac{a_{K^+}}{a_{KCl}}$$

Reduction:- $AgCl + K^+ + e \rightarrow Ag + KCl$

$$E = E^\circ + \frac{RT}{F} \ln \frac{a_{K^+}}{a_{KCl}}$$

☒ Oxidation potential of an electrode is same but opposite in sign with reduction potential.

$$E^{oxid^n} = -E^{red^n}$$

Let the electrode is Zn/Zn^{2+}

$$E^{oxid^n}_{Zn/Zn^{2+}} = E^{o\,(oxid^n)}_{Zn/Zn^{2+}} - \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Zn}}$$

$$E^{red^n}_{Zn^{2+}/Zn} = E^{o\,(red^n)}_{Zn^{2+}/Zn} + \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Zn}}$$

$$= -E^{o\,(oxid^n)}_{Zn/Zn^{2+}} + \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Zn}}$$

$$= -\left\{E^{o\,(oxid^n)}_{Zn/Zn^{2+}} - \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Zn}}\right\}$$

$$= -E^{oxid^n}_{Zn/Zn^{2+}}$$

$$\therefore E^{oxid^n} = -E^{red^n}$$

$$E^{o\,(red)}_{Zn^{2+}/Zn} = -E^{o\,(oxid)}_{Zn/Zn^{2+}}$$

we know that $E^\circ = \frac{RT}{nF}\ln Ka$

when the electrode is Zn^{2+}/Zn :- $Zn^{2+} + 2e^- \rightarrow Zn$

$$E^{o\,(red)}_{Zn^{2+}/Zn} = \frac{RT}{2F}\ln\frac{a_{Zn}}{a_{Zn^{2+}}}$$

when the electrode is Zn/Zn^{2+} :- $Zn \rightarrow Zn^{2+} + 2e^-$

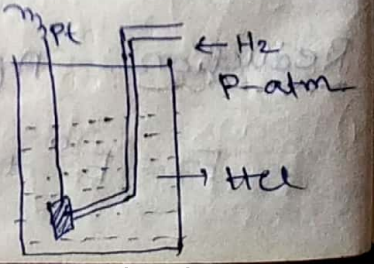
$$E^{o\,(oxid)}_{Zn/Zn^{2+}} = \frac{RT}{2F}\ln\frac{a_{Zn^{2+}}}{a_{Zn}}$$

$$= -\frac{RT}{2F}\ln\frac{a_{Zn}}{a_{Zn^{2+}}}$$

$$= -E^{o\,(red)}_{Zn^{2+}/Zn}$$

$$\therefore E^{o\,(red)}_{Zn^{2+}/Zn} = -E^{o\,(oxid)}_{Zn/Zn^{2+}}$$

H_2 electrode :- $Pt(H_2)\,|\,HCl\,(a)$
(P-atm)



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

$$E^{oxid}_{H_2} = E^{o(oxid)}_{H_2} - \frac{RT}{F}\ln\frac{a_{H^+}}{a_{H_2}^{1/2}}$$

$$E^{oxid}_{H_2} = E^{o\,(oxid)}_{H_2} - \frac{RT}{F} \ln \frac{a_{H^+}}{p^{1/2}_{H_2}}$$

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

$$E^{red}_{H_2} = E^{o\,(red)}_{H_2} + \frac{RT}{F} \ln \frac{a_{H^+}}{p^{1/2}_{H_2}}$$

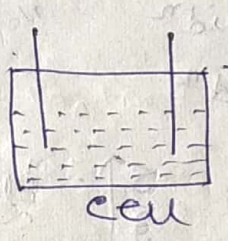
If $a_{H^+} = 1$, $P_{H_2} = 1$ then $E^{oxid}_{H_2} = E^{o\,(oxid)}_{H_2}$

or $E^{red}_{H_2} = E^{o\,(red)}_{H_2}$

$E^{o}_{H_2}$ (oxidⁿ or redⁿ) are taken universally as zero, i.e, $E^{o}_{H_2} = 0$ (Standard Hydrogen electrode potⁿ)

Std. H_2-electrode:- $Pt\,(H_2) \;|\; HCl$; $P_{H_2} = 1$ atm, $a = 1$

Convention:- EMF of cell



$$E_{cell} = E^{oxid}_{-ve} + E^{red}_{+ve} = E^{oxid}_{left} + E^{red}_{right}$$

$$= E^{oxid}_{-ve} - E^{oxid}_{+ve} = E^{oxid}_{left} - E^{oxid}_{right}$$

$$= E^{red}_{+ve} - E^{red}_{-ve} = E^{red}_{right} - E^{red}_{left}$$

Determination of electrode potential:-

The electrode potential can be determined by coupling it with a standard H_2-electrode to form a cell.

Determination of Zn/Zn^{2+} electrode potential:-

when it is coupling with standard H_2-electrode, the following cell is developed.

cell: $\ominus\; Zn \;|\; Zn^{2+} \;\|\; HCl \;|\; Pt(H_2) \;\oplus$; $a = 1$, 1 atm

$$E_{cell} = E^{oxid^n}_{-ve} + E^{red}_{+ve}$$

$$= E^{oxid^n}_{Zn/Zn^{2+}} + E^{o}_{H_2}$$

$$= E^{oxid^n}_{Zn/Zn^{2+}} = x \text{ (say)}$$

$$= -E^{red^n}_{Zn/Zn^{2+}} = -x$$

or, E_{cell}

$$= -E^{red^n}_{Zn^{2+}/Zn} = -x.$$

Determination of Cu/Cu^{2+} electrode potential:-

cell:- $Pt(H_2) \mid HCl \,\vdots\, Cu^{2+} / Cu$

$1\ atm$ $\quad a=1$ $\quad$ (⊖ at $Pt(H_2)$, ⊕ at Cu)

$$E_{cell} = E^{o\,(oxid)}_{H_2} + E^{red}_{Cu/Cu^{2+}}$$

$$= 0 + Y \text{ (say)}$$

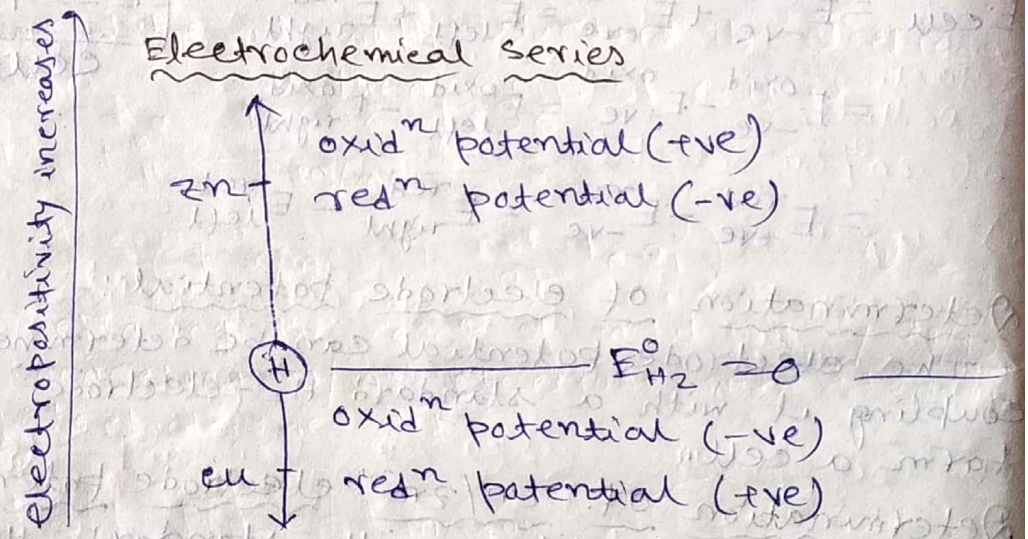
$$\therefore E^{red}_{Cu/Cu^{2+}} = Y \text{ say}$$

$$E^{oxid}_{Cu/Cu^{2+}} = -Y$$

$E^{oxid}_{Cu/Cu^{2+}} = -Y$

Oxidⁿ potential of Zn/Zn^{2+} electrode is +ve
redⁿ " " Zn^{2+}/Zn " " -ve
oxidⁿ " " Cu/Cu^{2+} " " -ve
redⁿ " " Cu^{2+}/Cu " " +ve

Electrochemical series



EMF of cell, cell reaction, Equilibrium constant:-

(i) Electrode having higher oxidation potential will be -ve
" " lower reduction " will be -ve

(ii) oxidation always occur at -ve electrode
Reduction " " " +ve "

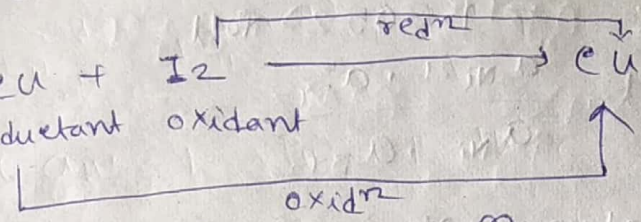
Ex(a) Oxidation Potential of Cu/Cu^{2+} and I_2/I^- are -0.337 and -0.535 volt at standard state.

$E^{o\,(oxid)}_{Cu/Cu^{2+}} = -0.337$ volt

$E^{o\,(oxid)}_{I_2/I^-} = -0.535$ volt

Cell reaction:- convention:-

(i) The oxident of the electrode having lower oxidⁿ potⁿ will oxidise the reductant of the electrode having higher oxidation potential



$E^\circ_{cell} = E^{\circ(oxid)}_{-ve} - E^{\circ(oxid)}_{+ve}$

$= -0.337 + 0.535$

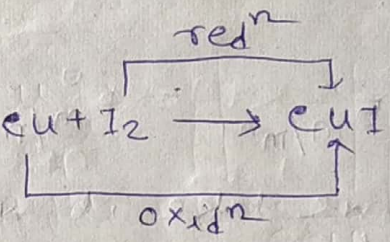
$= 0.198$ volt

Cell: $Cu/Cu^{2+} \,\|\, I^-/I_2$ (⊖ | ⊕)

(ii) The reductant of the electrode having lower reduction potential will reduce the oxidant of the electrode having higher reduction potential.

$E^{\circ(red)}_{Cu/Cu^{2+}} = 0.337$ volt

$E^{\circ(red)}_{I_2/I^-} = 0.535$ volt



$E^\circ_{cell} = E^{\circ(red)}_{+ve} - E^{\circ(red)}_{-ve}$

$= 0.535 - 0.337$

$= 0.198$ volt

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

$= -2 \times 96500 \times 0.198$ joule

$= -38214$ joule

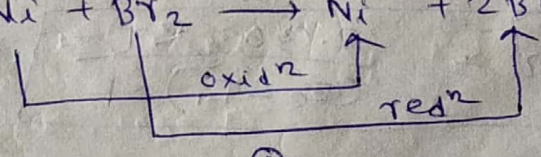
$\Delta G^\circ = -RT\ln K = -2 \times 96500 \times 0.198$

$\ln K = \dfrac{2 \times 96500 \times 0.198}{8.314 \times 298}$ $(T = 25^\circ C)$

$\therefore K = \exp\left(\dfrac{2 \times 96500 \times 0.198}{8.314 \times 298}\right)$

Calculate the e.m.f of cell containing two electrodes Ni/Ni^{2+} and Br_2/Br^- having electrode potentials $E^\circ_{Ni/Ni^{2+}} = -0.24$ volt and $E^\circ_{Br_2/Br^-} = 1.0652$ volt.

Cell reaction:- $Ni + Br_2 \longrightarrow Ni^{2+} + 2Br^-$



Cell:- $Ni \,|\, Ni^{+2} \,\|\, Br^- \,|\, Br_2$ (⊖ | ⊕)

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F} \ln \frac{a_{Ni^{2+}} \cdot a^2_{Br^-}}{a_{Ni} \cdot a_{Br_2}}$$

$$E^{\circ}_{cell} = E^{\circ}_{+ve} - E^{\circ}_{-ve} = 1.0652 + 0.24$$
$$= 1.3052 \text{ volt}$$

$$E = 1.3052 - \frac{RT}{2F} \ln \frac{a_{Ni^{2+}} \cdot a^2_{Br^-}}{a_{Ni} \cdot a_{Br_2}}$$

Determination of valency of ion:-

Let an electrode is M/M^{n+}. So the valency of metal ion is n.

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

This electrode having different electrode potential under different conen of reversible ion.

$$\therefore E_{M/M^{n+}} = E^{\circ}_{M/M^{n+}} + \frac{RT}{nF} \ln a_1$$

If we take it with standard H_2-electrode to form a cell, then emf. of cell is —

$$E_1 = E^{\circ}_{H_2} - E_{M/M^{n+}}$$
$$= -\left(E^{\circ}_{M/M^{n+}} + \frac{RT}{nF} \ln a_1\right) \quad \text{---} (1)$$

Now replacing the conen of metal ion by $a_1/10$ and connecting M/M^{n+} electrode with standard H_2-electrode we get,

$$\therefore E_2 = E^{\circ}_{H_2} - E_{M/M^{n+}}$$
$$= -\left(E^{\circ}_{M/M^{n+}} + \frac{RT}{nF} \ln a_1/10\right)$$

$$\therefore E_1 - E_2 = \frac{RT}{nF} \ln \frac{a_1}{10} \cdot \frac{1}{a_1}$$
$$= -\frac{RT}{nF} \ln 10 = -\frac{2.303\,RT}{nF}$$

$$\therefore E_2 - E_1 = \frac{2.303\,RT}{nF}$$

$$\therefore \boxed{n = \frac{2.303\,RT}{(E_2 - E_1) \times F}}$$

Here M/M^{n+} electrode acting as -ve, but in note it is taken as +ve w.r.to H_2-electrode.

EMF measurement at 25°c for the cell,

$Pt(H_2) / HCl(m) / AgCl-Ag$

1 atm

molality of HCl	0.0032	0.1238
EMF of cell	0.5205	0.3420

Find E° of $Ag-AgCl, Cl^-$ and calculate the mean activity coefficient ($\gamma_\pm$) for HCl soln.

cell reaction:

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

oxidn ↑ ; redn ↑

$$E = E^\circ - \frac{RT}{F}\ln a_{H^+}.a_{Cl^-} \qquad a_{H_2} = 1 \ (\text{as } P_{H_2} = 1)$$

$$= E^\circ - \frac{RT}{F}\ln a_\pm^2 \qquad a_{Ag} = 1,\ a_{AgCl} = 1$$

$$E = E^\circ - \frac{2RT}{F}\ln m - \frac{2RT}{F}\ln\gamma_\pm \qquad a_\pm = m.\gamma_\pm$$

(1)

Now, $\boxed{E = E^\circ - 0.118\log m - 0.118\log\gamma_\pm}$

$$\log\gamma_\pm = 0.059\,|z_+|\,|z_-|\sqrt{i}$$
$$= 0.059\sqrt{m}$$

For HCl

$i = m$

$i = \frac{1}{2}m1^2 + \frac{1}{2}m1^2$

$= m$

$$E = E^\circ - 0.118\log m - 0.118\times 0.059\sqrt{m}$$

Now, $E_1 = E_1^\circ - 0.118\log m_1 - 0.118\times 0.059\sqrt{m_1}$

$E_1^\circ = ?$

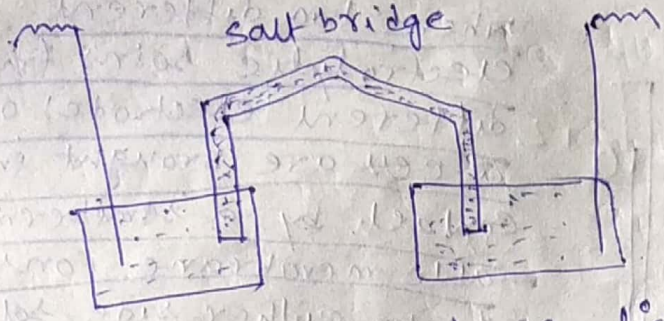
$E_1^\circ(cell) = E^\circ_{AgCl-Ag} - E^\circ_{H_2} = E^\circ_{AgCl-Ag} = ?$

$$\log(\gamma_\pm)_1 = \frac{E_1 - E_1^\circ + 0.118\log m_1}{0.118} \quad \text{i.e. } (\gamma_\pm)_1 = ?$$

$$\log(\gamma_\pm)_2 = \frac{E_2 - E_2^\circ + 0.118\log m_2}{0.118} \quad \text{i.e. } (\gamma_\pm)_2 = ?$$

In this way we can determine the mean activity coefficient ($\gamma_\pm$) for HCl solution.

Q: How LJP can be eliminated?



By using salt bridge LJP can be eliminated. In salt bridge, such types of salts are used where $l_e^0 \simeq l_a^0$ or $t_+ \simeq t_-$

Ex: NH_4NO_3 (Explosive) → now it is not used.
KCl → is used as salt bridge.

Here potential difference between 1st electrode and salt bridge is same and opposite to the potential difference between salt bridge and 2nd electrode.
Thus LJP is eliminated.

cells
- cells with transport / LJP present
- cells without transport / LJP absent.

Concentration cells: Concentration cells are those where emf is obtained from the transfer of matter from one electrode to another electrode.

Types: i) Electrode conc^n cells:-

Ex: $Cd(Hg)_{a_1} \,|\, CdCl_2 \,|\, Cd(Hg)_{a_2}$

$Pt(H_2) \,|\, HCl \,|\, Pt(H_2)$
$a_1 = P_1 \qquad a_2 = P_2$

Here two electrodes are same but differing in their activities of metal rod or of gases use in gas electrode.

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2} \qquad a_1 > a_2$$

At LHE (oxidn): $E_1 = E^0_{Cd} - \frac{RT}{2F} \ln \frac{a_{Cd^{2+}}}{a_{Cd}}$

$Cd(a_1) \rightarrow Cd^{2+} + 2e^-$

$= E^0_{Cd} - \frac{RT}{2F} \ln \frac{a_{Cd^{2+}}}{a_1}$

At R.H.E (redn):-

$Cd^{2+} + 2e^- \longrightarrow Cd(a_2)$ $\quad E_2 = E^\circ_{Cd} + \frac{RT}{2F} \ln \frac{a_{Cd^{2+}}}{a_2}$

$Cd(a_1) \longrightarrow Cd(a_2)$

$E = E_1 + E_2 = \frac{RT}{2F} \ln \frac{a_1}{a_2}$

These types of cells are the group of cell without transport.

ii) Electrolytic conc^n cells:-

Ex: $Cd(Hg)/CdCl_2 \underset{a_1}{;} \underset{a_2}{CdCl_2}/Cd(Hg)$

$Pt(H_2)/HCl \underset{a_1}{;} \underset{a_2}{HCl}/Pt(H_2)$

Here two electrodes are same but differing in the activities of soln. w.r. to reversible ion.

$E = \frac{RT}{nF} \ln \frac{a_2}{a_1}$ $\quad a_2 > a_1$ considering LJP is eliminated.

$Cd(Hg)/\underset{a_1}{CdCl_2} ; \underset{a_2}{CdCl_2}/Cd(Hg)$

Let LJP is absent

At LHE (oxidn):- $Cd \longrightarrow Cd^{2+}(a_1) + 2e^-$

At R.H.E (redn):- $Cd^{2+}(a_2) + 2e^- \longrightarrow Cd$

$\therefore Cd^{2+}(a_2) \longrightarrow Cd^{2+}(a_1)$

$E = \frac{RT}{2F} \ln \frac{a_2}{a_1}$

cell with transport; LJP and transport no.:

Let us consider a cell

$Pt(H_2)/\underset{a_1}{HCl} ; \underset{a_2}{HCl}/Pt(H_2)$

Let LJP is assumed to eliminated.

At L.H.E: $\frac{1}{2} H_2 \longrightarrow H^+(a_1) + e^-$

$E_1 = E^\circ_{H_2} - \frac{RT}{F} \ln a_{H^+}(a_1)$

At R.H.E; $H^+(a_2) + e^- \longrightarrow \frac{1}{2} H_2$

$$E_2 = E^\circ_{H_2} + \frac{RT}{F} \ln a_{H^+(a_2)}$$

$$E = E_1 + E_2 = \frac{RT}{F} \ln \frac{a_{H^+(a_2)}}{a_{H^+(a_1)}}$$

$$= \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2}$$

$$= \frac{RT}{2F} \ln \frac{a_2}{a_1}$$

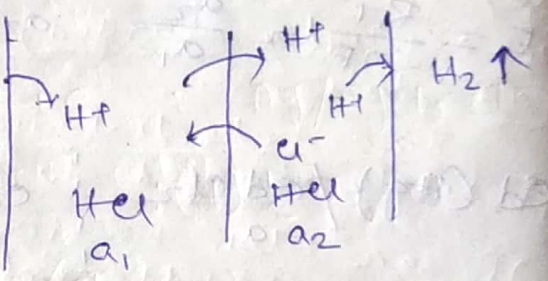
$a_{H^+} = a_\pm$

For HCl, $a_\pm^2 = a$

Electrode process transfer of matter at electrode :- $H^+(a_2) \longrightarrow H^+(a_1)$

When LJP is not eliminated:

At the junction, H^+ from left soln. goes to right side and Cl^- from right side comes to left side



If 1 faraday of electricity is passed,

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

Net transfer of matter,

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

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

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

or, $t_- \cdot HCl(a_2) \longrightarrow t_- HCl(a_1)$

$\Delta G_R = \Delta G_{H^+} + \Delta G_{Cl^-}$ | $\mu = \mu^\circ + RT \ln a$

$\Delta G = \int_2^1 t_- \cdot d\mu_{H^+} + \int_2^1 t_- \cdot d\mu_{Cl^-}$ | $d\mu = RT\, d\ln a$

$\Delta G = t_- \int_2^1 RT\, d\ln a_{H^+} + t_- \int_2^1 RT\, d\ln a_{Cl^-}$

$\Delta G = t_- RT \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} + t_- RT \ln \frac{(a_{Cl^-})_1}{(a_{Cl^-})_2}$

$\Delta G = t_- \cdot RT \ln \frac{(a_\pm)_1}{(a_\pm)_2} + t_- \cdot RT \ln \frac{(a_\pm)_1}{(a_\pm)_2}$

$\Delta G = 2t_- \cdot RT \ln \frac{(a_\pm)_1}{(a_\pm)_2}$

Now $-nFE_{total} = 2t_- \cdot RT \ln \frac{(a_\pm)_1}{(a_\pm)_2}$

$E_{Total} = 2t_- \cdot \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}$

$= 2t_- \cdot \frac{RT}{2F} \ln \frac{a_2}{a_1}$

$E_{Total} = E + E_j = (E_1 + E_2) + E_j$

E_{mf} of cell without LJP.

$E_j = E_{Total} - E$

$= 2t_- \cdot \frac{RT}{2F} \ln \frac{a_2}{a_1} - \frac{RT}{2F} \ln \frac{a_2}{a_1}$

$= (2t_- - 1) \frac{RT}{2F} \ln \frac{a_2}{a_1}$

$$\boxed{E_j = (t_- - t_+) \frac{RT}{2F} \ln \frac{a_2}{a_1}} \quad [t_+ + t_- = 1]$$

If $t_- = t_+$ then, $E_j = 0$

Construct a cell with transport but do not have LJP:-

$Pt(Cl_2) | KCl_{a_1} || KCl_{a_2} | Pt(Cl_2)$

Construct the cell for the following cell reac

a) $\overset{+4}{PbO_2} + \overset{0}{Pb} + 2H_2SO_4 \rightarrow \overset{+2}{2PbSO_4} + 2H_2O$

oxid

red

L·H·E : $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$: $Pb/PbSO_4 - H_2SO_4$

R·H·E : $PbO_2 + 2H_2SO_4 + 2e^- \rightarrow PbSO_4 + 2H_2O + SO_4^{2-}$

cell :- $Pb/PbSO_4 - H_2SO_4 / PbSO_4 / PbO_2 (Pb)$

↳ $Pb / H_2SO_4 / PbO_2 (Pb)$

b) $\frac{1}{2}Cl_2 + Ag \rightarrow AgCl$

oxid

red

L·H·E :- $Ag + Cl^- \rightarrow AgCl + e^-$: $Ag/AgCl, Cl^-$

R·H·E :- $\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$: $(Pt)\ \frac{1}{2}Cl_2/Cl^-$

cell :- $Ag/AgCl - Cl^-/Cl^-/Cl_2 (Pt)$

↳ $Ag/AgCl - Cl^- / Cl_2 (Pt)$

↖ KCl or HCl

c) $AgCl + \frac{1}{2}H_2 \rightarrow Ag + H^+ + Cl^-$

oxid

red

L·H·E :- $\frac{1}{2}H_2 \rightarrow H^+ + e^-$: $H_2(Pt)/H^+$

R·H·E :- $AgCl + e^- \rightarrow Ag + Cl^-$: $Ag/AgCl - Cl^-$

cell : $Pt(H_2)/Cl^- - AgCl/Ag$

↳ $Pt(H_2)/HCl - AgCl/Ag$

d) $Ag^+ + I^- \longrightarrow AgI$

red, oxid

L.H.E : $I^- \longrightarrow \frac{1}{2} I_2 + e^-$: I_2/I^-

R.H.E : $Ag^+ + \frac{1}{2} I_2 + e^- \longrightarrow AgI$: $Ag/AgI-I^-$

cell :- $I_2/I^- \| AgI/Ag$

e) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

red, oxid

In note :- cell :-

(Pt) $H_2/HO^-/O_2$ (Pt)

L.H.E : $H_2 \longrightarrow 2H^+ + 2e^-$: $Pt(H_2)/H^+$

R.H.E :- $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$: $Pt(O_2)/H^+$

cell :- $Pt(H_2)/H^+ \| O_2(Pt)$

f) $H^+ + OH^- \longrightarrow H_2O$ or $HCl + NaOH \rightarrow H_2O + NaCl$

red, oxid

L.H.E :- $2OH^- \longrightarrow H_2O + \frac{1}{2} O_2 + 2e^-$: $Pt(O_2)/OH^-$

R.H.E :- $2H^+ + \frac{1}{2} O_2 + 2e^- \longrightarrow H_2O$: $Pt(H_2)/H^+$

cell :- $Pt(O_2)/OH^- \| H^+/H_2(Pt)$

cell :- $Pt(O_2)/NaOH \| HCl/H_2(Pt)$

g) $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

red, oxid

L.H.E :- $5H_2O_2 \longrightarrow 5O_2 + 10H^+ + 10e^-$: $O_2/H_2O_2-H^+$

R.H.E :- $2MnO_4^- + 16H^+ + 10e^- \longrightarrow 8H_2O + 2Mn^{2+}$

(Pt)/MnO_4^-, Mn^{2+}, H^+

cell :- $Pt(O_2)/H_2O_2-H^+ \| H^+, Mn^{2+}, MnO_4^-/Pt$