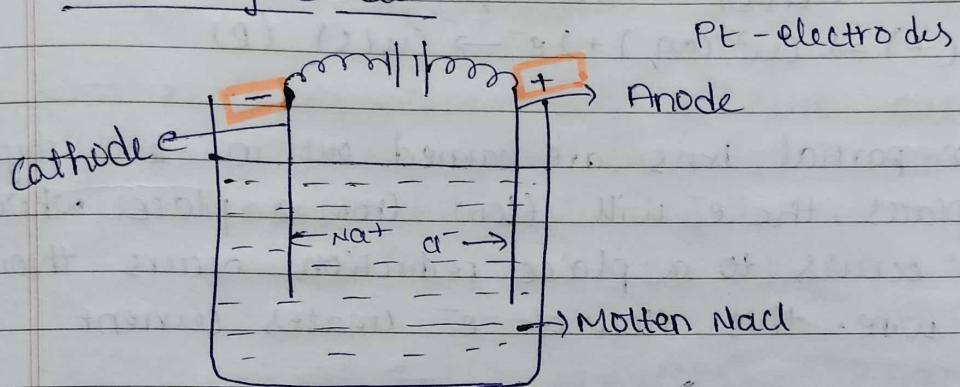


8) ELECTROCHEMICAL CELLS

→ 2 TYPES of electrochemical cells :- spontaneous ($\Delta G < 0$)

- 1) Electrolytic cells (Electrical Energy to chemical energy)
- 2) Galvanic cells (Chemical " " Electrical ")

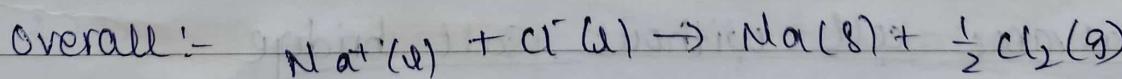
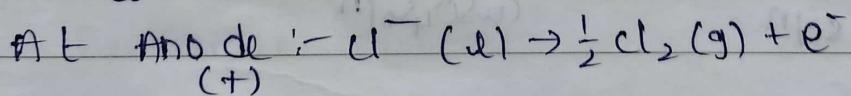
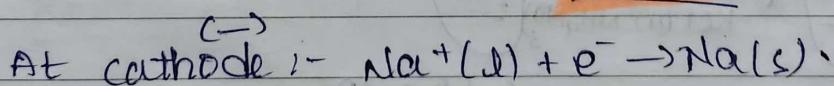
Electrolytic cell



→ within solⁿ electricity is carried by the movement of electrons ions.

cell rxns

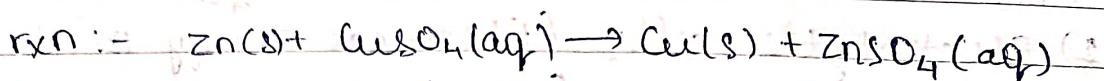
AAO/CCR



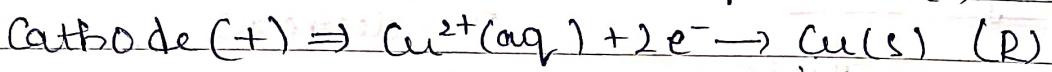
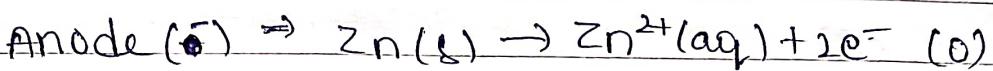
Galvanic cell

→ current is generated as a result of some spontaneous chemical rxns that takes place in cell.

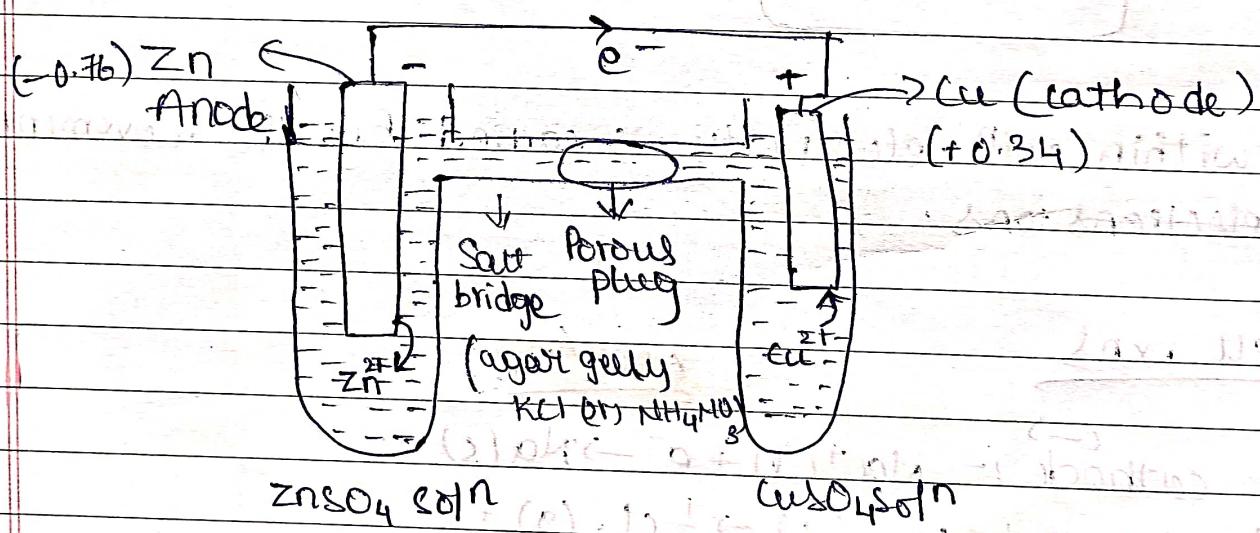
Working of Daniel cell



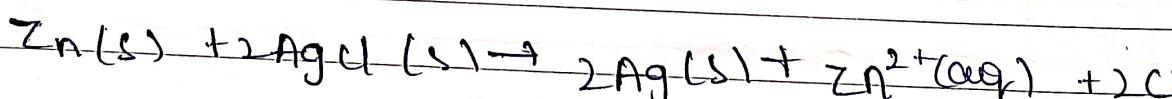
very fast →



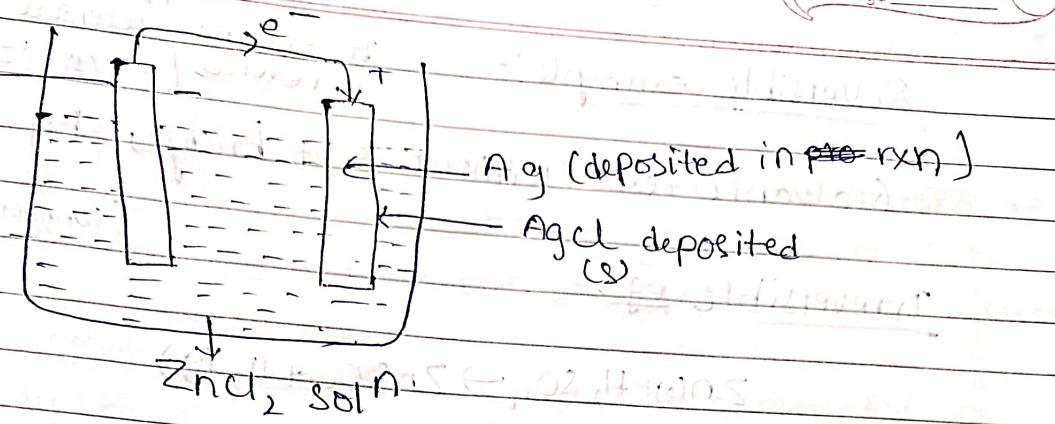
→ If the '2' partial rxns are carried out in two phys. separate places, the e^- will flow from a place where oxidation occurs to a place reduction occurs through external wire. This flow of e^- creates current.



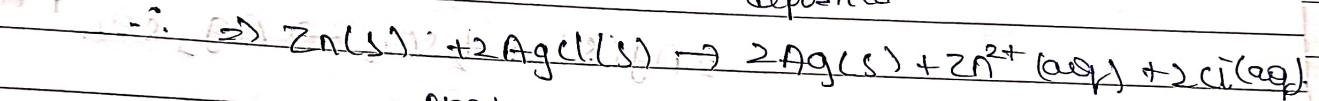
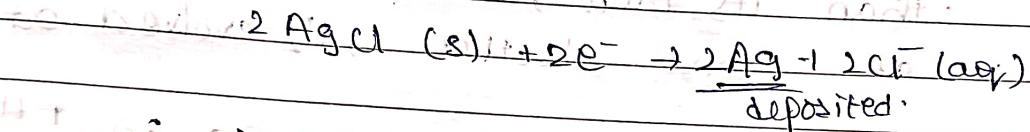
Galvanic cell without salt bridge



→ If Zn(s) & AgCl(s) are brought together the rxn takes place very slowly.



→ the e^- left behind on zinc can travel through the external wire to the silver-silver chloride electrode where:



Anode Cathode
Galvanic : - (-) Oxidation (+) Red
Electrolytic : - (+) Oxidation (-) Red

Reversible & Irreversible cells

Reversible conditions:-

— Laminar rotating fluid = ... Immeasurably (or) Inextricably

1) Driving & opposing forces be infinitesimally different from each other.

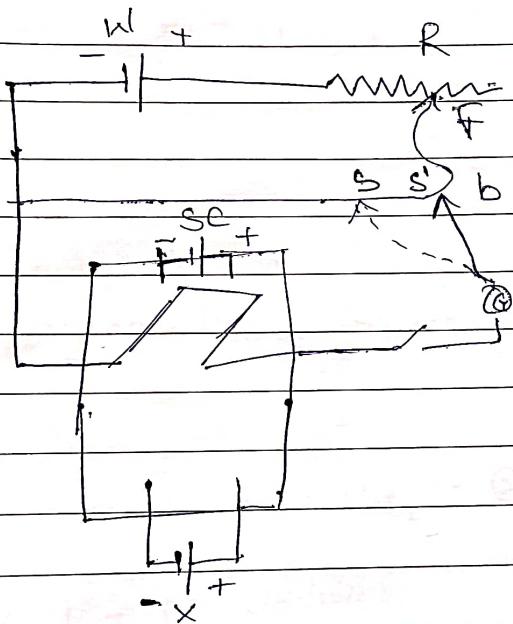
2) It should be possible to reverse any change taking place by applying a force infinitesimally greater than the acting one.

→ If the cell doesn't satisfy any of above, it's ~~not~~ irreversible:

Measurement of e.m.f

- Accurate measurement is not possible with the direct use of voltmeter, which will change the emf due to the changes in concentration of species due to electrode rxns.
- With appreciable current flow part of emf will have to be utilized to overcome IResistance. ∴ Voltmeter measurement is inaccurate

→



Standard cell

- Potential should be reproducible, const with time, reversible.
- should not suffer permanent damage due to passage of current & should have low temperature coefficient of emf.
- Weston, unsaturated & standard cells

Single Electrode Potential & its sign

Tendency to lose or gain electron

$$\Delta G_{1f} = -nFE_{cell}$$

↳ spontaneity.

Gibb's free energy at constant pressure

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

Derivation

Initial :- Temp $\rightarrow T$



Final :- Temp $\rightarrow T + dT$

$$G_2 \rightarrow G_2 + dG_2 \quad \text{--- (1)}$$

$$dS = \frac{dQ}{T} \quad \text{--- (2)}$$

$$G_1 = H - TS$$

$$G_1 = U + PV - TS$$

$$dG_1 = (dU + (Pdv) + vdp) + vdp - dS - SdT$$

$$dG_1 = \underbrace{dQ}_{\text{(at const P)}} + \underbrace{vdp}_{T/dS - SdT} - SdT \quad \text{from (1)}$$

$$dG_1 = -SdT$$

(from (1) & (2))

$$dG_2 - dG_1 = -S_2 dT + S_1 dT$$

$$d(G_2 - G_1) = \frac{1}{T} (S_1 - S_2) - \frac{H}{T}$$

$$\Delta G_f = -dT (\Delta S)$$

$$\left(\frac{\partial(\Delta G_1)}{\partial T} \right)_P = -\Delta S$$

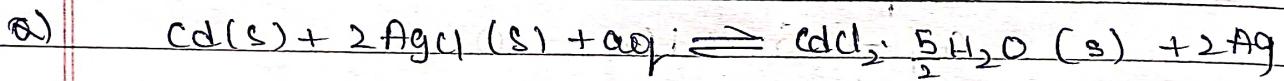
$$\Delta G_1 = \Delta H - T \Delta S$$

$$\boxed{\Delta G_1 = \Delta H + T \left(\frac{\partial(\Delta G_1)}{\partial T} \right)_P}$$

$$\Delta G_1 = -nFE_{cell}$$

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

ΔH depends on magnitude & sign of $\left(\frac{\partial E_{cell}}{\partial T} \right)_P$



$$\text{EMF} = 0.6753 \text{ at } 25^\circ\text{C} \quad \text{at } 0^\circ\text{C}$$

$$\Delta G_1 = ? \quad \Delta H = ? \quad \Delta S = ?$$

solt:-

$$\begin{aligned} \Delta G_1 &= -nFE_{cell} \text{ at } 25^\circ\text{C} \\ &= -(2)(96500)(0.6753) \end{aligned}$$

$$\boxed{\Delta G_1 = -130,332.9}$$

$$\times \left\{ \begin{array}{l} \Delta G_1 = \Delta H + T \left(\frac{\partial(\Delta G_1)}{\partial T} \right)_P \\ 130,332.9 = \Delta H + \cancel{298} \left(\frac{\partial(\Delta G_1)}{\partial T} \right)_P \end{array} \right\} \quad 0.0162$$

$$\frac{\Delta H}{nF} = T \left(\frac{\partial E_{cell}}{\partial T} \right)_P - E_{cell} \quad 0.6753$$

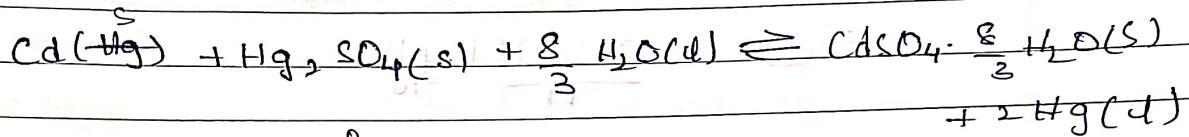
$$\frac{\Delta H}{2 \times 96500} = -298 \left(\frac{0.0162}{25} \right) - 0.6753 \quad \frac{2.5}{298} \quad 0.0162$$

$$\Delta H = -167.601 \text{ kJ}$$

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

$$\Delta S = \frac{\Delta H - \Delta G_f}{T}$$

(Q) Emf of cell involving



is 1.0185 V at 25°C.

calculate ΔG_f° , ΔH° , ΔS° for the cell reaction at 25°C.

If $\left(\frac{\partial E}{\partial T}\right)_P$ for the cell is $5.0 \times 10^{-5} \text{ V K}^{-1}$

& $F = 95485 \text{ C mol}^{-1}$

$$[\text{Ans: } \Delta G_f^\circ = -196.501 \text{ kJ}, \Delta H^\circ = -193.6 \text{ kJ}, \Delta S^\circ = 9.65 \text{ J K}^{-1}]$$

$$\text{Sol: } \Delta G_f^\circ = -nF E_{\text{cell}}$$

$$= -2(95485)(1.0185)$$

$$> -194.502 \text{ kJ}$$

$$\frac{\Delta H}{nF} = +\left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_P - E_{\text{cell}}$$

$$\Delta H = 2 \times 95485 \left(\frac{298 \times 5 \times 10^{-5}}{1} - 1.0185 \right)$$

$$= -191.657 \text{ kJ}$$

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

$$\Delta S = \frac{(\Delta H - \Delta G_f)}{T} = 9.54 \text{ J K}^{-1}$$

commercial cells - types & eq

→ Primary cells

→ Secondary "

→ Fuel "

corrosion.

Nernst Equation

For a reaction $pA + qB \rightleftharpoons rC + sD$

Gibbs free energy change is given as

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

where Q is the rxn quotient, given as

$$Q = \frac{a_c^r a_s}{a_A^p a_B^q}$$

at Eq $\Rightarrow Q = k_{eq} \& \Delta G_f^\circ = 0$

Nernst eq is obtained by using the relations

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

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \frac{a_c^r a_s}{a_A^p a_B^q}$$

At 298 K,

$$E_{cell} = E_{cell}^\circ = 0.0591 \log \frac{a_c^r a_s}{a_A^p a_B^q}$$

The electrode potential of a metal M in contact with M^{n+} ions, involving the electrode reaction



$$E_{el} = E_{el}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

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

In general, if both reactant & product have ions, say
 v_o Oxidised state + $n e^- \Rightarrow v_R$ Reduced state

The above eqn becomes:-

$$E_{el} = E_{el}^{\circ} - \frac{0.0591}{n} \log \frac{[Reduced\ state]}{[Oxidised\ state]}$$

Problems

- Q) * Write down the expression for electrode potential a Calomel electrode, which involves the following electrode rxn

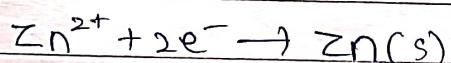


Sol:

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Cl^-]^2}{[Hg]^2}$$

- Q) A Zn rod is placed in 0.1M soln of $ZnSO_4$ at $25^\circ C$. Assuming that the salt is dissociated to the extent of 95% at its dilution, calculate the potential of the electrode at this temperature. $E_{Zn^{2+}/Zn}^{\circ} = -0.76$

Sol:

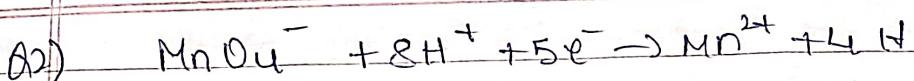


$$[Zn^{2+}] = 0.1 \times 95$$

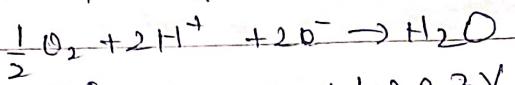
$$= 0.095$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

$$E_{cell} = -0.76 + \frac{0.0591}{2} \log$$



$$\text{E}^\circ_{\text{Mn}^{2+}/\text{MnO}_4^-} = -1.510 \text{ V}$$



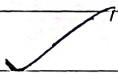
$$\text{E}^\circ_{\text{O}_2/\text{H}_2\text{O}} = +1.233 \text{ V}$$



$$E_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 1.510 - 1.233 = 0.287 \text{ (+ve) } \Delta G_f \text{ since rxn occurs spontaneously}$$

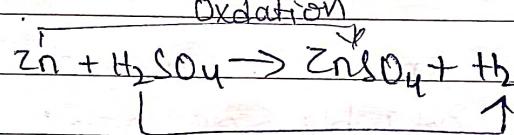
(Q3)



(Q4)

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.761 \text{ V}$$

Oxidation



Ag X

$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.76 \text{ V}$$

$$E^\circ_{\text{H}^+/\text{H}_2} = 0$$

Reduction

Calculation of S.P of an unknown half-cell rxn

If $\text{HCR}_1 = \text{HCR}_2 + \text{HCR}_3 + \text{HCR}_4 + \dots$ then

$$\Delta G_f^\circ_1 = \Delta G_f^\circ_2 + \Delta G_f^\circ_3 + \dots$$

$$n_1 F E_{\text{cell}}^\circ_1 = n_2 F E_{\text{cell}}^\circ_2 + n_3 F E_{\text{cell}}^\circ_3 + \dots$$

Ex:- find E_{cell}° for $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ ①if E_{cell}° for :-

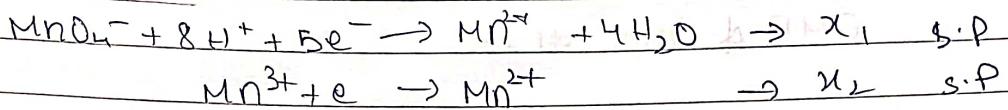
$$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}, \quad E_{\text{cell}}^\circ = -0.036 \text{ V} \quad (2)$$

$$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}, \quad E_{\text{cell}}^\circ = -0.440 \text{ V} \quad (3)$$

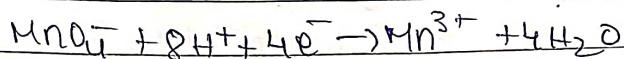
half cell ① $\text{E}^\circ = (2) - (3)$

$$-1 \text{ (F)} E_{\text{cell},1}^\circ = -3 F E_{\text{cell}(2)}^\circ + 2 F \times E_{\text{cell}(3)}^\circ \\ \Rightarrow E_{\text{cell},1}^\circ = -0.772 \text{ V}$$

Practice Problem



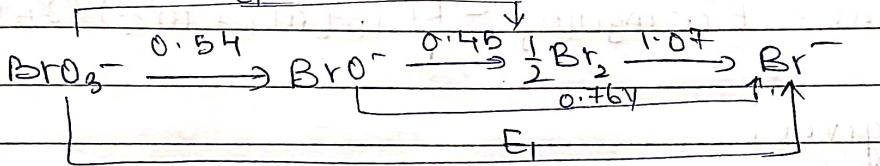
Then for rxn 1 + rxn 3 (adding)



$$-4 E_{\text{cell}} = -(5)x_1 + x_2$$

$$E_{\text{cell}} = \frac{5x_1 - x_2}{4}$$

Q1 Find E_1° and E_2°



$$\therefore (5) E_1^\circ = 4(0.54) + (1)(0.45)$$

$$E_1^\circ = \frac{2.16 + 0.45}{5} = \frac{2.61}{5} = 0.522$$

$$6 \cdot E_2^\circ = 4(0.54) + (2)(0.76)$$

$$E_2^\circ = \frac{2.16 + 1.52}{6} = \frac{3.68}{6} = 0.6133$$

(c_i = conc. of i -th ion, z_i = charge on ion): the plot is extrapolated to $\mu=0$, when all the x 's become 1.

Step 3:- From the value of LHS at $\mu=0$, $-\ln K_a^\circ$ & hence K_a° is evaluated.

14/08/23 Lecture-4

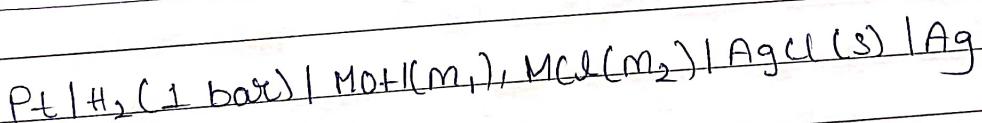
Topics

- some more applications of O.M.F
- calculation of standard potential for an unknown half cell rxn
- Accurate value of acid dissociation const
- Accurate value of ionic pdt of water.
- Commercial cells types & eg.
- primary cells
- Secondary cells
- Full cells.

→ Corrosion

Accurate value of ionic product of water

Use the following cell



EMF of this cell is

$$E_{\text{cell}} = E_{\text{Cr}^{\circ}/\text{AgCl}/\text{Ag}} - E_{\text{H}^+/|\text{H}_2/\text{Pt}}$$

$$E_{\text{cell}} = E_{\text{Cr}^{\circ}/\text{AgCl}/\text{Ag}} - \frac{RT}{F} \ln a_{\text{Cr}^{\circ}} + \frac{RT}{F} \ln \frac{1}{a_{\text{H}^+}}$$

$$E_{cell} = E_{\text{Cl}^-/\text{AgCl}/\text{Ag}} - \frac{RT}{F} \ln (a_{\text{H}^+} \times a_{\text{Cl}^-})$$

Ionic product of water is given as: $[K_w^\circ = a_{\text{H}^+} \times a_{\text{OH}^-}]$

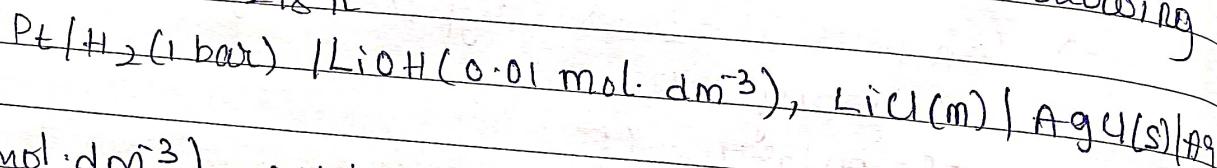
$$\Rightarrow E_{cell} = E_{\text{Cl}^-/\text{AgCl}/\text{Ag}} - \frac{RT}{F} \ln K_w^\circ - \frac{RT}{F} \ln \frac{a_{\text{Cl}^-}}{a_{\text{OH}^-}}$$

using relation b/w activity, molality, activity coefficient, we get

$$\rightarrow \frac{F}{RT} (E_{cell} - E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}) + \ln \frac{m'_{\text{Cl}^-}}{m'_{\text{OH}^-}} = -\ln \frac{\gamma_{\text{Cl}^-}}{\gamma_{\text{OH}^-}} - \ln$$

same procedure is used as we did previously in

* Eg :- The following EMFs refer to the following cell at 298 K



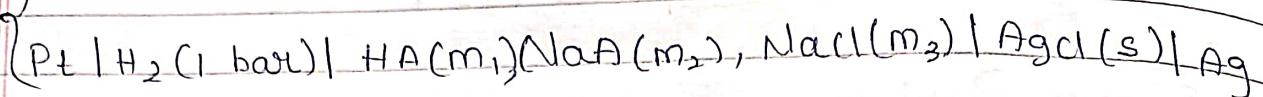
$m(\text{mol dm}^{-3})$	0.01	0.02	0.05	0.10	0.20
$E_{cell} (\text{V})$	1.0495	1.0315	1.0073	0.9885	0.9694

The standard potential of silver-silver chloride half cell is 0.2225 V. Determine the ionic pdt of

sofr

Accurate value of dissociation const of w.a

use the following cell



EMF of this cell is

$$E_{\text{cell}} = E_{\text{Cl}^- | \text{AgCl} | \text{Ag}} - E_{\text{H}^+ | \text{H}_2 | \text{Pt}}$$

$$E_{\text{cell}} = E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ - \frac{RT}{F} \ln a_{\text{Cl}^-} + \frac{RT}{F} \ln \frac{1}{a_{\text{H}^+}}$$

$$E_{\text{cell}} = E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ - \frac{RT}{F} \ln (a_{\text{H}^+} \times a_{\text{Cl}^-})$$

$\therefore a = \text{molality (m)} \times \text{activity coefficient (\gamma)}$

$$E_{\text{cell}} = E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ - \frac{RT}{F} \ln (m'_{\text{H}^+} m'_{\text{Cl}^-}) (\gamma_{\text{H}^+} \gamma_{\text{Cl}^-})$$

This gives,

$$\frac{F}{RT} (E_{\text{cell}} - E_{\text{Cl}^- | \text{AgCl} | \text{Ag}}^\circ) + \ln \frac{m'_{\text{HA}} m'_{\text{Cl}^-}}{m'_{\text{A}^-}} = - \ln \frac{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}}{\gamma_{\text{A}^-}}$$

where $K_a^\circ = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}}$

Procedure

Step 1:- E_{cell} is measured for diff values of m'_{HA} , m'_{A^-}

Step 2:- LHS is evaluated and plotted as a function ionic-strength μ , which is given as $\mu = \frac{1}{2} \sum_i c_i z_i^2$

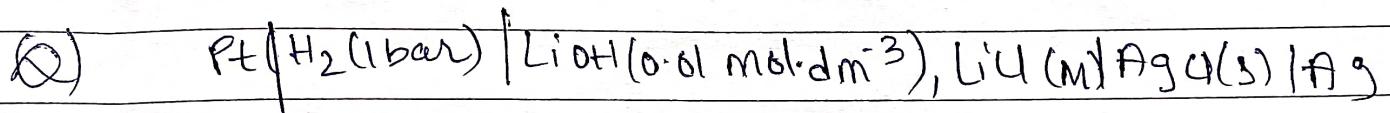
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$m(\text{mol} \cdot \text{dm}^{-3})$	0.01	0.02
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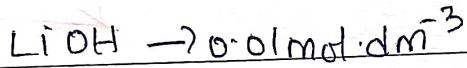
$E_{\text{cell}}(\text{V})$	1.0495	1.6315
-----------------------------	--------	--------

standard potential of silver-silver chloride half cell
 $\rightarrow 0.2225 \text{ V}$ determine ionic pdt of H_2O
from these data at 298 K

Solution :-

$$\frac{F}{RT} (\epsilon_{\text{HCl}} - \epsilon_{\text{LiOH}}^{\circ}) + \ln \frac{m_{\text{Li}^+}}{m_{\text{OH}^-}} = \gamma - \ln K_w^{\circ}$$

LiCl -----



$$\mu = \frac{1}{2} \sum c_i z_i^2$$

at $m = 0.01 \text{ mol dm}^{-3}$ (LiCl)

$$\mu = \frac{1}{2} [0.01 \times 1^2 + 0.01 \times 1^2 + 0.01 \times 1^2 - 0.01 \times 1^2]$$

$$\mu = 0.02$$

$$\text{L.H.S} = \frac{F}{RT} [1.0495 - 0.2225] + \ln \frac{0.01}{0.01}$$

$$= \frac{96500}{8.314 \times 298} \times 0.827$$

$$= 32.211$$

$$\mu = 0.02, \text{ L.H.S} = 32.211$$

For $m = 0.02 \text{ mol dm}^{-3}$

$$\mu = \frac{1}{2} [0.01 \times 1^2 + 0.01 \times 1^2 + 0.02 \times 1^2 + 0.62]$$

$$= 0.03$$

$$E_{cell} = -0.76 + 0.0295 \log(0.095) \\ = -0.790$$

P*

Significance of reduction potential list aka electrochemical series

→ On connecting with SHE,

+ if reduction occurs at the connected half cell - standard potential of the half-cell would be the.

* if oxidation occurs at the connected half cell - standard potential of the half cell would be positive - ve.

→ A half-cell with lower s.p and reduced half-cell with higher s.p

Q) Answer whether under standard conditions the following reactions are possible or not

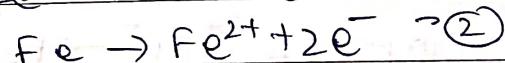
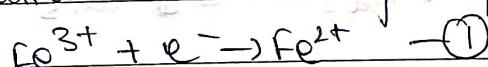
(i) will Fe reduce Fe^{3+} to Fe^{2+} ?

(ii) will the MnO_4^- liberate O_2 from water in the trace of an acid?

(iii) will O_2 oxidize gold to $\text{Au}(\text{CN})_2^-$ in the trace of CN^- & OH^- ions?

(iv) from the values of diff electrode potential find out whether Zn and Ag would react with dil H_2SO_4 or not.

Sol: (i) This requires the following half-cell rxns:-

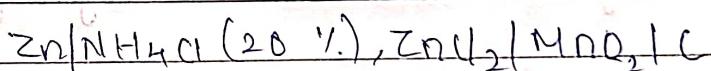


(i) has r.p. 0.771V & (2) has 0.44 . therefore, E_{cell} becomes $0.771 + 0.44 = 1.211\text{V}$ (positive). therefore, ΔG_f is -ve ($-\text{NF}_{cell}$)
∴ rxn is spontaneous.

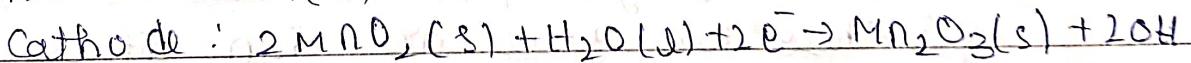
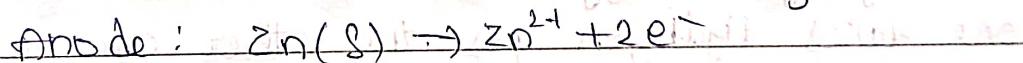
Commercial cell

→ Primary cells: These can be used only till the active materials are ~~nt~~. These cannot be recharged and hence ~~the~~ has to be discarded once the active materials are consumed.

Eg:- Example of primary cells: Leclanche (or) Dry cell.



• Reactions involved in this dry cell are:

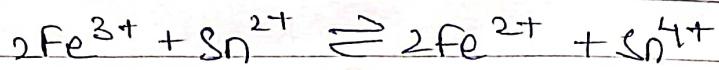


→ Secondary cells: These are rechargeable cells

Eg: Lead storage cell.

• Here Lead acts as anode and Lead impregnated with lead oxide acts as cathode. 20% H_2SO_4 with a specific

Q) Determine the standard eq. const of the following rxn at 298 K



Given: $E^\circ(\text{Fe}^{3+}, \text{Fe}^{2+}) = 0.771 \text{ V}$; $E^\circ(\text{Sn}^{4+}, \text{Sn}^{2+}) = 0.150 \text{ V}$
 (Ans) :- $K_{\text{eq}} = 1.0 \times 10^{21}$

$$\text{So! } \Delta G_f^\circ = -RT \ln K$$

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

$$0.771 \text{ V} - 0.150 \text{ V} = \frac{0.0591}{2} \log K$$

$$0.621 \text{ V} = \frac{0.0591}{2} \log K$$

$$K = 10^{21}$$

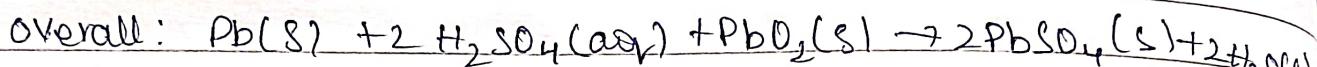
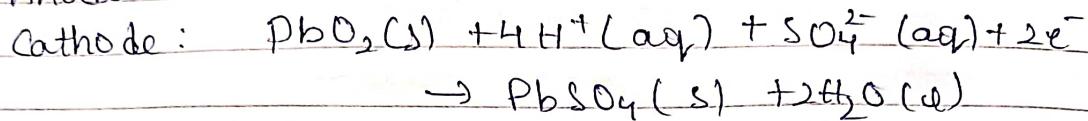
Lecture - 2

Topics :-

- * Nernst equation
- * significance of reduction potential list aka electrochemical series
- * Some more applications of EMF
 - calculation of standard potential for an unknown half reaction.
 - Accurate value of ionic product of water.

gravity of about 1.15 at room temperature is used as electrolytic soln

- Reactions involved in this cell are



- The EMF of this cell depends upon the activity of H_2SO_4 soln.

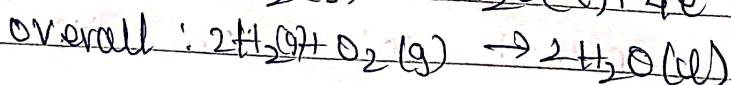
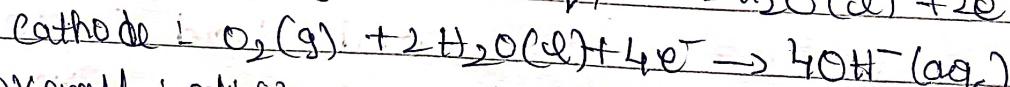
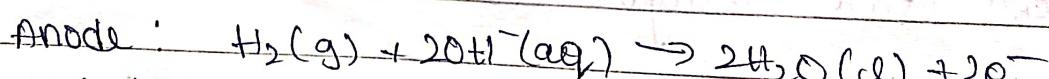
→ Fuel cells

Another means of chemical energy to electrical energy conversion.

- Cathode and anode constituents are continually supplied → energy can be withdrawn as long as the outside supply of the fuel is maintained.
- Eg of fuel cell is hydrogen-oxygen fuel cell.

In hydrogen-oxygen fuel cell, there are 3 compartments. One takes Hydrogen gas, the other one takes oxygen gas. These two gases are then diffuse slowly through the electrodes & react with an electrolyte (aq soln of a base) in the central compartment.

- The rxns are:



Effect of corrosion

- Economical loss
 - Damage of costly structures, equipment, etc.
- Health issue
 - Corrosion may lead to toxic materials.
- Environmental hazard
 - Corroded materials mix into environment & cause pollution.
 - May lead to contamination.

Corrosion control

→ choice of metals

- Use of noble metals - corrosion resistant metals
- Use of corrosion resistant alloys
 - stainless steel containing chromium - to prevent oxide formation.
 - cupro-nickel alloys are used in condenser tubes
 - Nimonic alloys (Ni-Cr-Mo) - highly resistant to hot gases.

→ Proper Designing

- Designs having less angles, edges, corners, crevices (gaps or cracks) less corroded.
- Avoid contact of dissimilar metals.
- Bolts & rivets should be replaced by proper ones.
- Metals washers should be replaced by rubber ones.

→ Protective coating - covering the metal surface with some chemical coating.

- Inorganic coatings.

- Metallic coating - galvanizing, electroplating, etc.

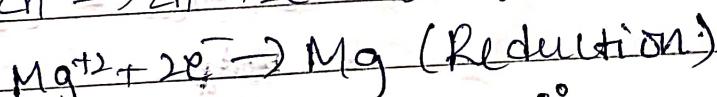
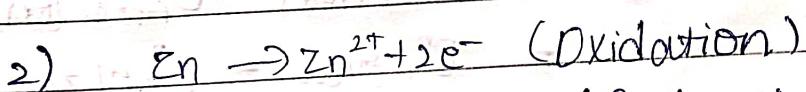
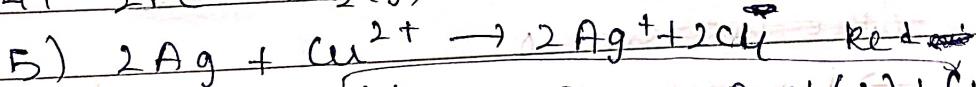
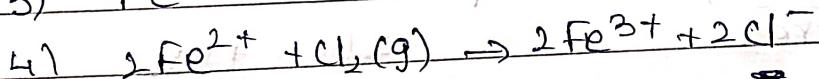
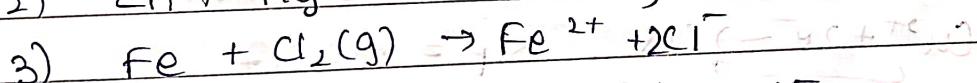
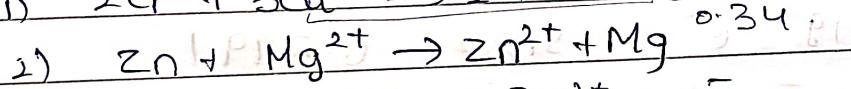
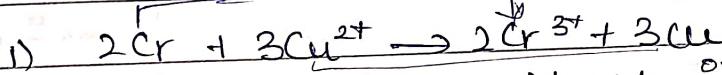
- Non-Metallic coating - chromate, phosphate, oxid-coating / porcelain coating, etc.

→ Organic coatings

- Paints, Varnishes, etc.

Practice problems

Q) Ascertain, with a little calculation, whether or not each of the following rxns will proceed to the forward or backward direction at 25°C when all the concentrations & pressures are unity.



$$\text{E}_{\text{Zn}/\text{Zn}}^\circ \rightarrow$$

$$\text{S.R.P} = 0.763$$

$$\text{E}_{\text{cell}}^\circ = \text{E}_{\text{red}}^\circ - \text{E}_{\text{oxi}}^\circ$$

$$= -\text{ve} = -2.37 - 0.763$$

$\Delta G^\circ = +\text{ve}$ \therefore The reaction proceeded backward.

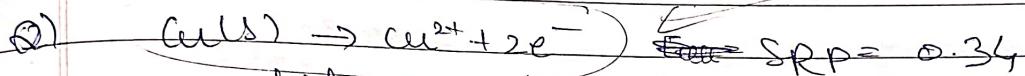
(6) $E_{\text{cell}}^{\circ} = -0.7991 + 0.337$

-ve

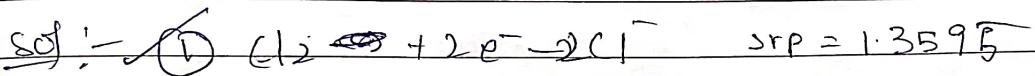
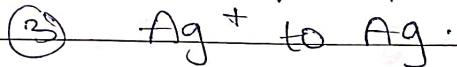
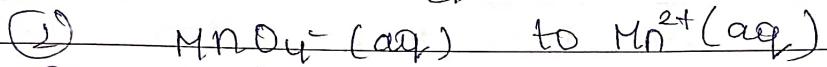
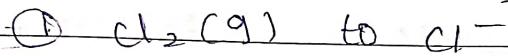
$\Delta G_r = +\text{ve}$ [Backward]

(1) $E_{\text{cell}}^{\circ} = +\text{ve}$

$\Delta G_r = -\text{ve}$ [Forward]

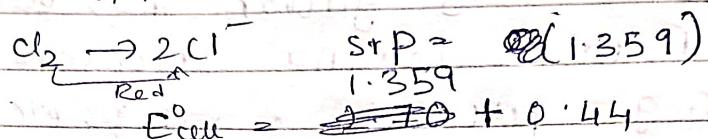
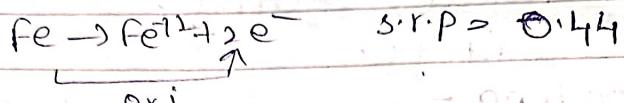
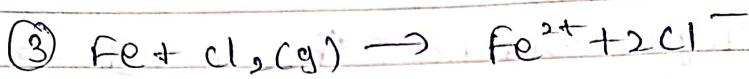


which of the following will oxidise under standard conditions



(2)

(3)

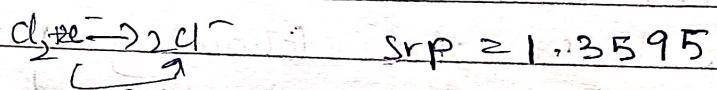
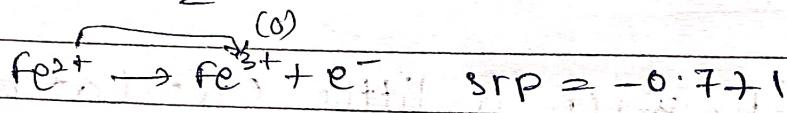
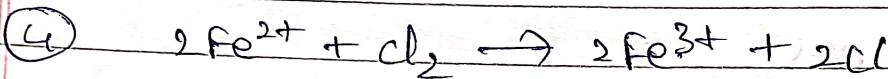
Doubts

$$E_{\text{cell}}^{\circ} = \cancel{-0.44} + 0.44$$

$\Rightarrow +\text{ve}$

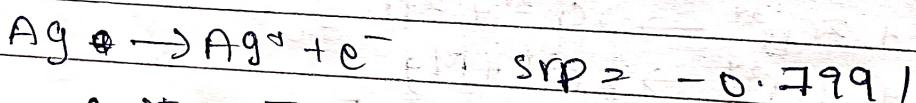
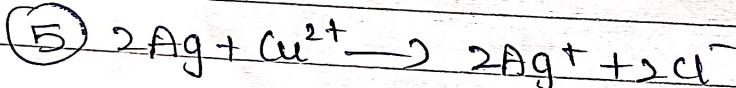
$$\Delta G_c = -\text{ve}$$

\Rightarrow Reaction proceeds forward.



$$\Delta G_c = -\text{ve}$$

\rightarrow Forward rxn.



$$\Delta G_c = +\text{ve}$$

\rightarrow forward rxn \rightarrow Backward rxn.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode(red)}}^{\circ} - E_{\text{anode(ox)}}^{\circ}$$

$$= E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= R \cdot P_{\text{cat}} - f \cdot P_{\text{Anode}}$$

$$= R \cdot P_{\text{cat}} + O \cdot P_{\text{Anode}}$$

$$- 0.3 + 0.7$$

Corrosion

- * corrosion of metal is the spontaneous destruction of metals during their chemical, electrochemical or biochemical interactions with the environment.
- * Eg:- Rusting of iron (A layer of reddish scale & powder of oxide (Fe_2O_3) is formed on the surface of iron metal.)
- * A green film of basic carbonate ($CuCO_3 + Cu(OH)_2$) is formed on the surface of copper, when it is exposed to moist-air containing carbon dioxide.

Types of corrosion

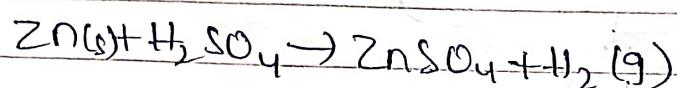
- Dry or chemical corrosion
 - occurs in dry condition
 - Due to direct attack of chemical on the metal surface
 - Both homogeneous & heterogeneous surfaces get corroded.
 - Eg:- Rusting of iron in absence of moisture.
- Wet or electrochemical corrosion
 - occurs in presence of moisture or an electrolyte
 - Due to the formation of anodic & cathodic areas
 - Only heterogeneous surfaces get corroded.
 - Eg:- Rusting of iron in presence of moisture.

Reversible example:-

If external potential is greater than
(opposing)
it reverses $[Ag(s) + \frac{1}{2}Zn^{2+}(aq) + Cl^-(aq)] \rightarrow$

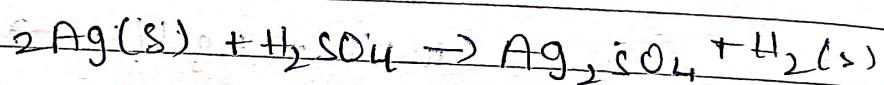
D \rightarrow Galvanic cell (without salt bridge) by connecting electrodes

Irreversible eg :-



However

\rightarrow when the cell is connected with an external source of potential slightly greater than its own, silver dissociates at one electron, H_2 evolved at other.



Thus, 1st condition of reversibility satisfied
as 2nd (didn't)

EM.F

Zn atom more easily oxidised to Zn^{2+} than Cu \rightarrow Cu²⁺

$E_{cell} = \text{Higher oxidation Potential} - \text{Lower}$

$$E_{cell} = -(H.O.P) + (L.O.P)$$

$$= -L.R.P + H.R.P$$

Measurement:- Potentiometric method